Highly Versatile Methods for the Synthesis of Quinonylporphyrins via Benzannulation of Fischer Carbene Complexes and Palladium-Catalyzed Cross-Coupling Reactions

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Covalently-linked porphyrin mono- and tetraquinones with well-defined distances and orientations were synthesized on the basis of two synthetic approaches. (1) The benzannulation of Fischer carbene complexes with *meso*-(alkynylphenyl)-substituted porphyrins, followed by oxidation, produced quinone-linked porphyrins, with both electron-donating and -withdrawing substituents on the quinone moieties. (2) The palladium-catalyzed Suzuki cross-coupling reactions of (2,5-dimethoxyphenyl)boronic acid with porphyrin *meso*-aryl triflates and aryl bromides, followed by subsequent demethylation and oxidation, gave *meso*-(benzoquinonylphenyl)-substituted porphyrins.

Introduction

The biological importance of porphyrin-like compounds such as hemin and chlorophyll, coupled with their unusual and striking physical and chemical properties, makes them both interesting and important objects of research.[1] Single-crystal studies on the photosynthetic reaction center reveal that porphyrins and quinones are in close proximity.[2] Indeed, the chlorophyll (electron donors) and quinone (electron acceptors) groups in the photosynthetic reaction centers are positioned at precise distance and orientation to promote an efficient photo-induced charge separation and to impede charge recombination.[2] Porphyrins possessing covalent linkages to quinones have thus received much attention as models of the reaction center to study the primary electron transfer reaction in photosynthesis.[3] A number of attempts have been made to assemble such biomimetic systems including models of the primary electron donor and intermediate electron acceptor being held together intramolecularly.[3]

The earliest and simplest quinone-linked porphyrins were synthesized by the following groups. Kong and Loach[4] prepared covalently linked porphyrin–quinone molecules with diester linkage. Quinone-substituted porphyrins with flexible *n*-methylene bridges with diamide links were synthesized by Bolton and co-workers.[5] A *meso*-substituted porphyrin–quinone was prepared by Dalton and co-workers.[6] Lindsey and Mauzerall[7] reported the synthesis of cofacial quinone-capped porphyrins via entropically favored macro-polycyclization. Recent work for the synthesis of quinonylporphyrin compounds includes that by Staab and Weiser,[8] Wasielewski,[9] and Sessler.[10] Some of the above-mentioned porphyrins possess conformationlly nonrigid linkages between porphyrins and quinones. This nonrigid structure may lead to serious problems in interpreting the results of the orientation-dependent photochemistry;[11] some models with a hydrolytically unstable linkage (such as an ester or amide) between the porphyrin and the quinone may also hinder the photochemical studies on these models.[8] Studies of model systems possessing well-defined donor–acceptor distances and geometries and hydrolytically stable linkages are necessary to fully understand the critical role of these parameters in the photochemistry of porphyrins.

Apart from serving as chemical models for the photosynthetic reaction center, the quinone-linked porphyrins may be utilized as catalysts for small molecule redox processes. In these reduction processes, rapid multiple electron/proton transfer steps are often involved.[12] Multiple electron/proton transfer steps require the concerted activity of coupled redox centers that operate at electrochemical potentials capable of effecting reduction with minimum overpotential.[13] Hence, the quinone-linked porphyrin systems may possibly be used as electrocatalysts, where the reducible quinones can serve as electron reservoirs to facilitate the multi-electron transfer reactions.

Consequently, we explored a highly versatile methodology for the synthesis of quinone-linked porphyrins with

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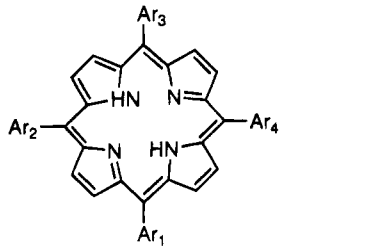
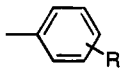
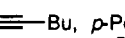
Scheme 1

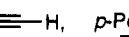


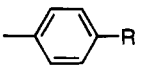
$Ar_1 = Ar_2 = Ar_3 =$ tol $Ar_4 =$ 

R = OTf, *p*-PorOTf **1a**
m-PorOTf **1b**

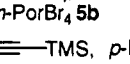
R =  TMS, *p*-PorCCTMS, **2a**
m-PorCCTMS, **2b**

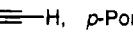
R =  Bu, *p*-PorCCBu, **3a**
m-PorCCBu, **3b**

R =  H, *p*-PorCCH, **4a**
m-PorCCH, **4b**

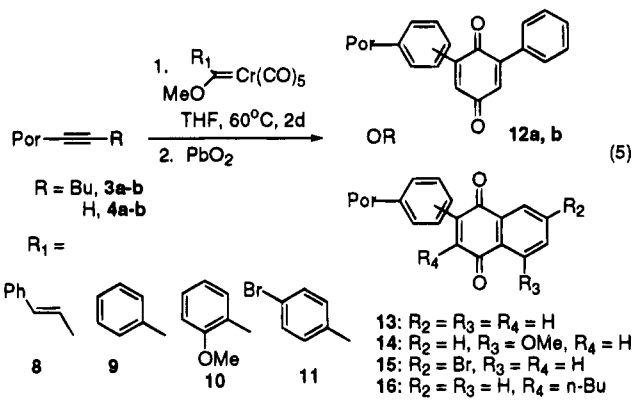
$Ar_1 = Ar_2 = Ar_3 = Ar_4 =$ 

R = Br, *p*-PorBr$_4$, **5a**
m-PorBr$_4$ **5b**

R =  TMS, *p*-Por(CCTMS)$_4$, **6a**

R =  H, *p*-Por(CCH)$_4$, **7a**

Scheme 2

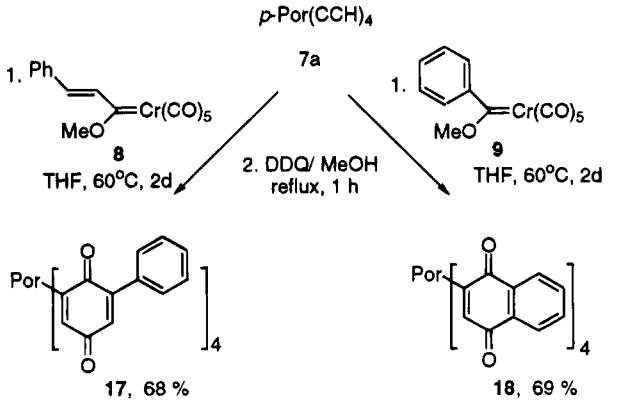


a rigid and hydrolytically stable linkage such as the phenylene group to allow fixed geometry and orientation. We now report our full results[14] on the synthesis of mono- and tetraquinonylporphyrins via benzannulation of Fischer carbene complexes with unsymmetrical (alkynylphenyl)porphyrins, and palladium-catalyzed cross-coupling reactions of (2,5-dimethoxyphenyl)boronic acid with unsymmetrical porphyrin aryl triflates, followed by oxidative treatment.

Results and Discussion

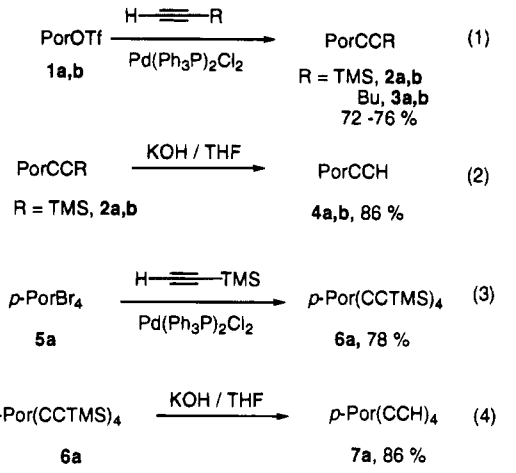
A. Benzannulation of Fischer Carbene Complexes. The preparation of a series of quinone-substituted porphyrins takes advantages of high chemical yields, ease of operation, and a short synthetic sequence of the benzannulation of Fischer carbene complexes with

Scheme 3



(alkynylphenyl)porphyrins (Scheme 1). This highly regioselective synthesis of quinones is a well-known process discovered by Dötz[15a] and developed by Wulff.[15b]

The mono(alkynylphenyl)porphyrins **2a,b**, **3a,b**, and **4a,b**[16] were prepared as previously reported *via* the palladium-catalyzed alkynylation of porphyrin triflates (eqs 1 and 2). In a similiar manner, the tetrakis-(alkynylphenyl)porphyrins **6a** and **7a** were also synthesized smoothly (eqs 3 and 4).



All the (alkynylphenyl)porphyrins **3a,b** and **4a,b** underwent smooth benzannulation with chromium carbene complexes **8**–**11**[15] in THF at 60 °C for 2 d (Scheme 2). After oxidative workup with PbO_2 or DDQ, porphyrin–monoquinones **12**–**16** and porphyrin–tetraquinones **17** and **18** were obtained respectively in good overall yields (Scheme 3). Only one regioisomer was observed as the reaction is highly regioselective.[15] Both alkenyl and aryl carbene complexes were effective in producing porphyrin–benzoquinones and porphyrin–naphthoquinones which have different redox potentials.[14]

The oxidants for obtaining quinones were crucial to achieve optimum yields without overoxidation of porphyin rings. For the benzannulation of chromium carbene complexes with the mono(alkynylphenyl)porphyrins **3a,b**, **4a,b** (Scheme 2),[14] lead(IV) oxide and DDQ were used as the best oxidants for the oxidative treatment of the benzannulated products to give the corresponding

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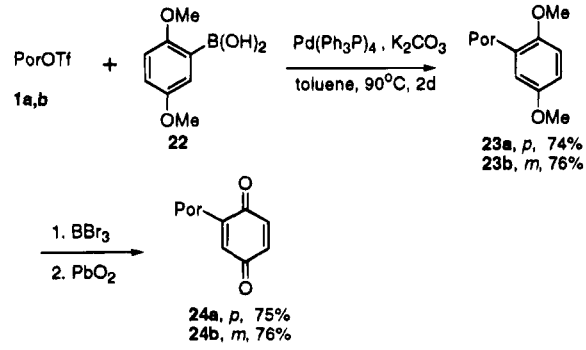
Table 1. Synthesis of Monoquinone Porphyrins from the Benzannulation

porphyrin	complex	product	% yield
4a	**8**	**12a**	73
4a	**9**	**13a**	72
4a	**10**	**14a**	75
4a	**11**	**15a**	76
3a	**9**	**16a**	75
4b	**8**	**12b**	71
4b	**9**	**13b**	74
4b	**10**	**14b**	74
3b	**9**	**16b**	73

Scheme 4



mono- and tetraquinone-substituted porphyrins **12–18**, respectively (Schemes 2 and 3, Table 1). Potassium ferricyanide, ferric sulfate, and ferric chloride were found to be less satisfactory. For the synthesis of tetraquinone, excess *p*-chloranil and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in methylene chloride were both acceptable. On the basis of chromatographic characteristics, DDQ was chosen because of better chromatographic separation with the desired tetraquinone-substituted porphyrins **17** and **18**.

All the quinone-linked phenylporphyrins have characteristic IR absorptions for the carbonyl groups (1660–1680 cm^{-1}) of the quinone moieties. The proton NMR spectra of the benzoquinone-linked phenylporphyrins clearly indicate the additional benzoquinonic protons at δ 6.93–7.04 and 7.18–7.27 while those of the naphthoquinone-linked phenylporphyrins show the additional naphthoquinonic protons at δ 7.29–7.43.

B. Palladium-Catalyzed Cross-Coupling Reactions of (2,5-Dimethoxyphenyl)boronic Acid. The palladium-catalyzed Suzuki cross-coupling reactions[17] of (2,5-dimethoxyphenyl)boronic acid (**22**) with porphyrin aryl triflates **1a,b** or aryl bromide substituted porphyrins **5a,b**, followed by subsequent demethylation and oxidation, gave (benzoquinonylphenyl)porphyrins **24a,b** and **26a,b**.

For the preparation of (*p*-benzoquinonylphenyl)-tritolylporphyrin **23a** and (*m*-benzoquinonylphenyl)tritolylporphyrin **23b**,[16] the unsymmetrical porphyrin aryl triflates **1a** and **1b** were thus cross-coupled with (2,5-dimethoxyphenyl)boronic acid (**22**) using a catalytic amount of $Pd(Ph_3P)_4$ (15 mol % yield) and anhydrous potassium carbonate (2 equiv) in toluene at 90 °C for 2 days under N_2 (Scheme 4).[17] The desired mono((dimethoxyphenyl)phenyl)tritolylporphyrins **23a,b** were isolated in 74 and 76% yields, respectively.

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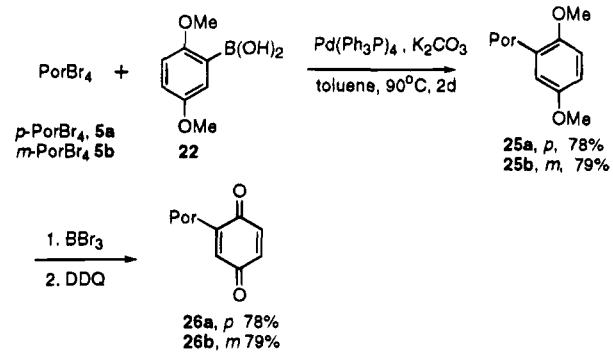
Scheme 5



The above mono((dimethoxyphenyl)phenyl)tritolylporphyrins **23a,b** were thus converted to their corresponding hydroquinone-substituted porphyrins by treatment with boron tribromide at low temperature, and subsequent oxidation of the hydroquinone-substituted porphyrins with lead(IV) oxide in methylene chloride gave the mono((benzoquinonylphenyl)tritolylporphyrins **24a,b** (Scheme 4).[14] The overall yields of the syntheses of the mono(benzoquinonylphenyl)tritolylporphyrins **24a,b** from the unsymmetrical porphyrin aryl triflates **1a,b** were about 57%.

For the preparation of tetrakis(benzoquinonylphenyl)-porphyrins, the tetrakis(bromophenyl)porphyrins **5a,b** were thus cross coupled with (2,5-dimethoxyphenyl)-boronic acid (**22**) using a catalytic amount of $Pd(Ph_3P)_4$ (20 mol % yield) and anhydrous potassium carbonate (8 equiv) in toluene at 90 °C for 2 d under N_2. The desired tetrakis((dimethoxyphenyl)phenyl)porphyrin **25a,b** (para and meta) were isolated in 78 and 79% yields, respectively (Scheme 5). The tetrakis((dimethoxyphenyl)phenylporphyrins **25a,b** with additional methoxy protons appear as singlets at δ 3.80–3.95 in their proton spectra.

The above tetrakis((dimethoxyphenyl)phenyl)porphyrins **25a,b** were thus converted to their corresponding hydroquinone-substituted porphyrins by treatment with boron tribromide at low temperature, followed by oxidation.[4] For the oxidative step, the tetrahydroquinone-substituted porphyrins were oxidized by DDQ in refluxing methanol for 1 h. The tetrakis(benzoquinonylphenyl)porphyrins **26a,b** (para and meta) were thus obtained in 78 and 79% yields, respectively (Scheme 5). They were purified by simply washing with methanol and air-drying to give the tetrakis(benzoquinonyl)phenyl)-porphyrins **26a,b** as purple solids which were then recrystallized from CH_2Cl_2/MeOH. The overall yields of the synthesis of the tetrakis(benzoquinonylphenyl)-porphyrins **26a,b** from the tetrakis(bromophenyl)porphyrins **5a,b** were about 57%.

Conclusion

A variety of mono- and tetraquinone-linked porphyrins with tuned redox potentials have been efficiently prepared by the two synthetic methods. (1) The benzannulation of Fischer carbene complexes with *meso*-(alkynylphenyl)-substituted porphyrins, followed by oxidation, produced quinone-linked porphyrins, with both electron-donating and -withdrawing substituents on the quinone moieties. (2) The palladium-catalyzed Suzuki cross-coupling reaction of (2,5-dimethoxyphenyl)boronic acid with porphyrin *meso*-aryl triflate and aryl bromide, followed by subsequent demethylation and oxidation,

gave *meso*-(benzoquinonylphenyl)-substituted porphyrins. The advantages of these approaches include high chemical yields, ease of operation, readily accessible starting materials, and a short synthetic sequence.

Experimental Section

Melting points are uncorrected. All ^{1}H NMR spectra were recorded at 250 MHz, using the residue $CHCl_3$ at δ 7.24 in $CDCl_3$ or Me_4Si (TMS) at δ 0.00 as the internal reference unless otherwise stated. IR spectra were recorded on a FT spectrometer. UV–vis spectra were recorded with in CH_2Cl_2. FABMS were recorded using *m*-nitrobenzyl alcohol (NBA) as the matrix in National Tsing Hua University in Taiwan. Elemental analyses were carried out either at the Shanghai Institute of Organic Chemistry, Academic Sinica, China, MEDAC Ltd., Department of Chemistry, Brunel University, United Kingdom, or Department of Chemistry, National Taiwan University. All reactions were monitored by thin layer chromatography (TLC). Flash chromatography was carried out on columns of silica gel (230–400 mesh or 70–230 mesh). All solvents were reagent grade. Pyridine was distilled from anhydrous barium oxide and stored in the presence of potassium hydroxide pellets. THF was freshly distilled from Na/benzophenone ketyl under nitrogen. Anhydrous CH_2Cl_2 was prepared by distillation over anhydrous P_2O_5 and stored over 4-Å molecular sieves. DMF was distilled over anhydrous CaH_2 under reduced pressure and stored over 3-Å molecular sieves under nitrogen. Anhydrous Et_3N was prepared by distilling Et_3N from anhydrous CaH_2.

Monoalkynyl porphyrins[16] **2a,b**, **3a,b**, and **4a,b** and chromium carbene complexes **8**,[18] **9**,[19] **10**,[19] and **11**[20] were prepared according to literature procedures. 1-Bromo-2,5-dimethoxybenzene (**21**)[21] (2,5-dimethoxyphenyl)boronic acid (**22**)[22] were prepared as reported.

***meso*-Tetrakis[((trimethylsilyl)ethynyl)phenyl]-porphyrin (6a).** *meso*-Tetrakis-(*p*-(bromophenyl))porphyrin (**5a**) (61 mg, 0.07 mmol), $Pd(Ph_3P)_2Cl_2$ (7 mg, 9 μmol), and ethynyltrimethylsilane (27 mg, 0.27 mmol) in dry triethylamine (10 mL) were added into a 25 mL Telfon-stoppered flask. The purple suspension was degassed by the freeze–pump–thaw method (3 cycles) and was then heated at 90 °C under N_2 for 2 d. The reaction mixture was evaporated to dryness and the residue was purified by column chromatography on silica gel using a solvent mixture of methylene chloride:hexane (1:1) as the eluent. The purple band was collected and evaporated to dryness to give purple solids which were further recrystallized from chloroform/methanol to give pure purple solids of *meso*-tetrakis[(((trimethylsilyl)ethynyl))phenyl]-porphyrin (**6a**) in 78% yield: R_f = 0.67 (CH_2Cl_2 /hexane = 1/1); ^{1}H NMR δ 8.42 (s, 8 H), 7.77 (d, 8 H, J = 8.0 Hz), 7.45 (d, 8 H, J = 8.0 Hz), 0.00 (s, 36 H), −2.54 (s, 2 H); UV/vis (λ_{max}, nm, CH_2Cl_2, $\times 10^4$ cm^{-1} M^{-1}) 422.0 (5.65), 517.5 (4.33), 553.0 (3.94), 591.0 (3.86); FABMS m/z 999 (M + 1)$^+$, 998 (M$^+$). Repeated microanalysis did not give satisfactory results.

***meso*-Tetrakis(ethynylphenyl)porphyrin (7a).** *meso*-Tetrakis[((trimethylsilyl)ethynyl)phenyl]porphyrin (**6a**) (65 mg, 0.07 mmol) was dissolved in THF (15 mL), and an aqueous solution (15 mL) of potassium hydroxide (0.26 g, 6.50 mmol) was then added. After stirring at room temperature for 12 h, the reaction mixture was washed with water and satd NaCl; then the organic layer was dried ($MgSO_4$) and evaporated to dryness. Upon column chromatography on silica gel using a solvent mixture of methylene chloride/hexane (1:1) as the eluent, the purple band was collected and evaporated to dryness to give purple solids which were recrystallized from chloroform–methanol to yield pure purple solids of *meso*-tetrakis(ethynylphenyl)porphyrin (**7a**) in 86% yield: R_f = 0.67 (CH_2Cl_2:hexane = 1:1); ^{1}H NMR (250 MHz) δ 8.42 (s, 8 H), 7.77 (d, 8 H, J = 8.0 Hz), 7.45 (d, 8 H, J = 8.0 Hz), 3.30 (s, 4 H), −2.80 (s, 2 H); UV/vis (λ_{max}, nm, CH_2Cl_2, $\times 10^4$ cm^{-1} M^{-1}) 422.0 (5.87), 515.5 (4.32), 552.0 (4.25), 591.0 (2.70); FABMS m/z 711 (M + 1)$^+$, 710 (M$^+$). Repeated microanalysis did not give satisfactory results.

General Procedure for the Preparation of Mono-(quinonylphenyl)tritolylporphyrins from the Benzannulation of Chromium Carbene Complexes with the Mono(alkynylphenyl)tritolylporphyrins. The mono(alkynylphenyl)tritolylporphyrin (for example, **4a**) (0.08 mmol), chromium aryl carbene complex (for example, **8**) (0.10 mmol), and anhydrous THF (10 mL) were added into a 25 mL Telfon-stoppered flask, and the purple red solution was degassed by the freeze–pump–thaw method (3 cycles) and was then heated at 60 °C under N_2 for 2 days. After the reaction mixture was evaporated to dryness, the residue was redissolved in CH_2Cl_2 (20 mL) and PbO_2 (0.5 g, 2.10 mmol) was added as the oxidant. After the solution was stirred at rt for 30 min, the suspension was filtered and concentrated and the residue was purified by column chromatography on silica gel using a solvent mixture of CH_2Cl_2/hexane (3:1) as the eluent. The purple band was collected and evaporated to dryness to give purple solids which were further recrystallized from $CHCl_3$/MeOH to give the pure purple solids of mono(quinonylphenyl)tritolylporphyrins (for example, **12a**).

5-[4-(3-Phenyl-2,5-benzoquinonyl)-phenyl]-10,15,20-tritolylporphyrin (12a) (73% yield): R_f = 0.41 (CH_2Cl_2:hexane = 3:1); ^{1}H NMR δ 8.87 (m, 8 H), 8.31 (d, 2 H, J = 8.0 Hz), 8.09 (d, 6 H, J = 7.8 Hz), 7.92 (d, 2 H, J = 8.1 Hz), 7.61–7.50 (m, 11 H), 7.27 (d, 1 H, J = 2.6 Hz), 7.04 (d, 1 H, J = 2.7 Hz), 2.69 (s, 9 H), −2.79 (s, 2 H); IR (neat) 1662, 1678 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 $\times 10^4$ cm^{-1} M^{-1}) 248.5 (4.93), 418.5 (27.16), 516.0 (2.08), 553.0 (1.15), 591.0 (0.70); FABMS m/z 839 (M + 1)$^+$, 838 (M$^+$). Anal. Calcd for $C_{59}H_{42}N_4O_2$: C, 84.28; H, 5.00; N, 6.66. Found: C, 83.68; H, 5.32; N, 6.81.

5-[3-(3-Phenyl-2,5-benzoquinonyl)-phenyl]-10,15,20-tritolylporphyrin (12b) (71% yield): R_f = 0.43 (CH_2Cl_2:hexane = 3:1); ^{1}H NMR δ 8.87 (m, 8 H), 8.37 (s, 1 H), 8.31 (d, 1 H, J = 6.9 Hz), 8.09 (d, 6 H, J = 7.8 Hz), 7.92–7.81 (m, 2 H), 7.54 (d, 6 H, J = 7.8 Hz), 7.50–7.40 (m, 5 H), 7.18 (d, 1 H, J = 2.6 Hz), 6.93 (d, 1 H, J = 2.6 Hz), 2.69 (s, 9 H), −2.80 (s, 2 H); IR (neat) 1668, 1680 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 $\times 10^4$ cm^{-1} M^{-1}) 248.5 (5.21), 420.0 (29.41), 515.5 (2.43), 551.5 (1.18), 591.0 (0.68); FABMS m/z 839 (M + 1)$^+$, 838 (M$^+$). Anal. Calcd for $C_{59}H_{42}N_4O_2$: C, 84.28; H, 5.00; N, 6.66. Found: C, 83.79; H, 4.97; N, 7.08.

5-{4-[2-(1, 4-Naphthoquinonyl)]phenyl}-10,15,20-tritolylporphyrin (13a) (72% yield): R_f = 0.34 (CH_2Cl_2: hexane = 3:1); ^{1}H NMR δ 8.86 (m, 8 H), 8.33 (d, 2 H, J = 8.0 Hz), 8.29 (s, 1 H), 8.18 (m, 1 H), 8.09 (d, 6 H, J = 7.9 Hz), 7.98 (d, 2 H, J = 8.0 Hz), 7.84 (m, 2 H), 7.55 (d, 6 H, J = 7.9 Hz), 7.43 (s, 1 H), 2.69 (s, 9 H), −2.76 (s, 2 H); IR (neat) 1662, 1668 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 $\times 10^4$ cm^{-1} M^{-1}) 248.0 (5.34), 421.0 (26.69), 516.0 (2.18), 553.0 (1.22), 591.0 (0.68); FABMS m/z 813 (M + 1)$^+$, 812 (M$^+$). Anal. Calcd for $C_{57}H_{40}N_4O_2$: C, 84.23; H, 4.93; N, 6.90. Found: C, 83.93; H, 5.18; N, 6.93.

5-{3-[2-(1,4-Naphthoquinonyl)]phenyl}-10,15,20-tritolylporphyrin (13b) (74% yield): R_f = 0.36 (CH_2Cl_2:hexane = 3:1); ^{1}H NMR δ 8.90 (s, 4 H), 8.85 (s, 4 H), 8.44 (s, 1 H), 8.32 (d, 1 H, J = 6.9 Hz), 8.18 (m, 1 H), 8.09 (d ,6 H, J = 7.9 Hz), 7.99–7.85 (m, 3 H), 7.76–7.72 (m, 2 H), 7.55 (d, 6 H, J = 7.8 Hz), 7.34 (s, 1 H), 2.69 (s, 9 H), −2.79 (s, 2 H); IR (neat) 1668, 1678 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 $\times 10^4$ cm^{-1} M^{-1}) 249.5 (4.36), 419.0 (28.31), 516.0 (2.16), 551.5 (1.08), 591.0 (0.62); FABMS m/z 813 (M + 1)$^+$, 812 (M$^+$). Anal. Calcd for $C_{57}H_{40}N_4O_2$: C, 84.23; H, 4.93; N, 6.90. Found: C, 84.11; H, 4.90; N, 6.78.

5-{4-[2-(5-Methoxy-1,4-naphthoquinonyl)]phenyl}-10,-15,20-tritolylporphyrin (14a) (75% yield): R_f = 0.32 CH_2Cl_2:hexane = 3:1); ^{1}H NMR δ 8.86 (m, 8 H), 8.30 (d, J = 8.3 Hz, 2 H), 8.08 (d, 6 H, J = 7.8 Hz), 7.97 (m, 2 H), 7.78 (t, 1 H,

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J = 8.2 Hz), 7.53 (d, 6 H, J = 7.7 Hz), 7.41–7.33 (m, 3 H), 4.09 (s, 3 H), 2.69 (s, 9 H), −2.79 (s, 2 H); IR (neat) 1667, 1680 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 $\times 10^4$ cm^{-1} M^{-1}) 249.0 (4.80), 419.5 (30.46), 516.5 (1.93), 553.0 (1.15), 592.0 (0.65); FABMS m/z 843 $(M + 1)^+$, 842 (M^+). Anal. Calcd for $C_{58}H_{42}N_4O_3$: C, 82.66; H, 4.99; N, 6.65. Found: C, 82.91; H, 4.90; N, 6.78.

5-{3-[2-(5-Methoxy-1,4-naphthoquinonyl)]phenyl}-10,-15,20-tritolylporphyrin (14b) (74% yield): R_f = 0.34 (CH_2Cl_2:hexane = 3:1); ^1H NMR δ 8.87 (m, 8 H), 8.44 (s, 1 H), 8.30 (d, 1 H, , J = 6.9 Hz), 8.09 (d, 6 H, J = 7.7 Hz), 7.98 (d, 1 H, J = 7.8 Hz), 7.85 (d, 2 H, J = 7.7 Hz), 7.67 (d, 2 H, J = 8.2 Hz), 7.54 (d, 6 H, J = 7.8 Hz), 7.29 (d, 1 H, J = 8.2 Hz), 3.99 (s, 3 H), 2.69 (s, 9 H), −2.79 (s, 2 H); IR (neat) 1670, 1678 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 $\times 10^4$ cm^{-1} M^{-1}) 248.5 (5.33), 419.5 (29.24), 516.5 (1.50), 552.0 (0.80), 592.5 (0.50); FABMS m/z 843 $(M + 1)^+$, 842 (M^+). Anal. Calcd for $C_{58}H_{42}N_4O_3$: C, 82.66; H, 4.99; N, 6.65. Found: C, 82.99; H, 4.87; N, 6.75.

5-{4-[2-(7-Bromo-1,4-naphthoquinonyl)]phenyl}-10,15,-20-tritolylporphyrin (15a) (76% yield): R_f = 0.42 (CH_2Cl_2: hexane = 3:1); ^1H NMR δ 8.87 (m, 8 H), 8.42 (d, 1 H, J = 1.9 Hz), 8.33 (d, 2 H, J = 8.0 Hz), 8.09 (d, 6 H, J = 7.8 Hz), 8.06 (d, 1 H, J = 8.2 Hz), 7.99 (s, 1 H), 7.97 (d, 2 H, J = 8.0 Hz), 7.55 (d, 6 H, J = 7.8 Hz), 7.43 (s, 1 H), 2.69 (s, 9 H), −2.79 (s, 2 H); IR (neat) 1665, 1679 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 $\times 10^4$ cm^{-1} M^{-1}) 249.0 (5.12), 418.5 (26.23), 516.0 (2.14), 553.5 (1.28), 590.5 (0.79); FABMS m/z 892 $(M + 1)^+$, 891 (M^+). Anal. Calcd for $C_{57}H_{39}BrN_4O_2$: C, 76.76; H, 4.38; N, 6.28. Found: C, 76.74; H, 4.61; N, 5.93.

5-{4-[2-(3-Butyl-1,4-naphthoquinonyl)]phenyl}-10,15,-20-tritolylporphyrin (16a) (75% yield): R_f = 0.39 (CH_2Cl_2: hexane = 3:1); ^1H NMR δ 8.89 (m, 8 H), 8.30 (d, 2 H, J = 8.0 Hz), 8.23 (d, 2 H, J = 2.5 Hz), 8.09 (d, 6 H, J = 7.9 Hz), 7.81 (m, 2 H), 7.60 (d, 6 H, J = 8.1 Hz), 7.55 (d, 6 H, J = 7.9 Hz), 2.80 (t, 2 H, J = 7.2 Hz), 2.70 (s, 9 H), 1.64–1.41 (m, 4 H), 0.96 (t, 3 H, J = 7.2 Hz), −2.78 (s, 2 H); IR (neat) 1668, 1676 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 $\times 10^4$ cm^{-1} M^{-1}) 249.5 (5.17), 418.5 (29.47), 515.5 (2.10), 551.5 (1.25), 590.5 (0.68); FABMS m/z 869 $(M + 1)^+$, 868 (M^+). Anal. Calcd for $C_{61}H_{48}N_4O_2$: C, 84.33; H, 5.53; N, 6.45. Found: C, 84.01; H, 5.94; N, 6.27.

5-{3-[2-(3-Butyl-1,4-naphthoquinonyl)]phenyl}-10,15,-20-tritolylporphyrin (16b) (73% yield): R_f = 0.43 (CH_2Cl_2: hexane = 3:1); ^1H NMR δ 8.89 (m, 8 H), 8.30 (d, 1 H, J = 7.6 Hz), 8.18–8.07 (m, 9 H), 7.84 (t, 1 H, J = 7.9 Hz), 7.74–7.70 (m, 2 H), 7.62 (d, 1 H, J = 7.8 Hz), 7.54 (d, 6 H, J = 7.5 Hz), 2.78 (t, 2 H, J = 7.3 Hz), 2.69 (s, 9 H), 1.63–1.36 (m, 4 H), 0.83 (t, 3 H, J = 7.1 Hz), −2.80 (s, 2 H); IR (neat) 1664, 1681 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 $\times 10^4$ cm^{-1} M^{-1}) 248.5 (4.93), 420.5 (29.35), 515.5 (2.07), 551.5 (1.01), 590.5 (0.59); FABMS m/z 869 $(M + 1)^+$, 868 (M^+). Anal. Calcd for $C_{61}H_{48}N_4O_2$: C, 84.33; H, 5.53; N, 6.45. Found: C, 84.40; H, 5.72; N, 6.34.

General Procedure for the Preparation of tetrakis-(quinonylphenyl)porphyrins from the Benzannulation of Chromium Aryl Carbene Complexes Porphyrin 7a. The tetrakis(alkynylphenyl)porphyrin **7a** (0.08 mmol), chromium aryl carbene complex **8** or **9** (0.40 mmol), and dry THF (10 mL) were added into a 25 mL Telfon-stoppered flask, the purple red solution was degassed by the freeze–pump–thaw method (3 cycles), and then the solution was heated at 60 °C under N_2 for 2 d. The reaction mixture was evaporated to dryness; then the residue was redissolved in MeOH (20 mL). DDQ (0.5 g, 2.20 mmol) was added as the oxidant, and the mixture was refluxed for 1 h. After filteration, the residue was purified by column chromatography using a solvent mixture of CH_2Cl_2/hexane (3:1) as the eluent. The purple band was collected and evaporated to dryness to give purple solids which were further recrystallized from $CHCl_3$/MeOH to give the pure purple solids of tetrakis(quinonylphenyl)porphyrin **17** or **18**.

***meso*-Tetrakis-[4-(3-phenyl-2,5-benzoquinonyl)phenyl]-porphyrin (17)** (68% yield): R_f = 0.41 (CH_2Cl_2:hexane = 3:1); ^1H NMR δ 8.91 (s, 8 H), 8.31 (d, 8 H, J = 8.3 Hz), 7.92 (d, 8 H, J = 8.3 Hz), 7.65–7.50 (m, 20 H), 7.27 (d, 4 H, J = 2.6 Hz), 7.04 (d, 4 H, J = 2.7 Hz), −2.76 (s, 2 H); IR (neat) 1662, 1678 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 $\times 10^4$ cm^{-1} M^{-1}) 354.5 (2.38), 418.5 (24.16), 516.0 (1.38), 555.0 (0.92), 591.0 (0.62). Compound was insufficiently stable to obtain satisfactory analytical results.

***meso*-Tetrakis{4-[2-(1,4-naphthoquinonyl)]phenyl}-porphyrin (18)** (69% yield): R_f = 0.34 (CH_2Cl_2:hexane = 3:1); ^1H NMR δ 8.93 (m, 8 H), 8.32 (d, 8 H, J = 8.0 Hz), 8.09 (m, 8 H), 7.98 (d, 8 H, J = 8.0 Hz), 7.69 (m, 8 H), 7.43 (s, 4 H), −2.79 (s, 2 H); IR (neat) 1663, 1680 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 $\times 10^4$ cm^{-1} M^{-1}) 419.5 (26.69), 517.0 (1.99), 554.0 (1.33), 593.0 (0.84). Compound was insufficiently stable to obtain satisfactory analytical results.

General Procedure for the Palladium-Catalyzed Cross-Coupling of Porphyrin Aryl Triflates 1a,b with Boronic Acid 22. Unsymmetrical porphyrin aryl triflate **1a** or **1b** (0.07 g, 0.09 mmol), (2,5-dimethoxyphenyl)boronic acid **(22)** (0.33 g, 0.18 mmol), anhydrous potassium carbonate (15 mg, 0.14 mmol), $Pd(Ph_3P)_4$ (12 mg, 0.01 mmol), and anhydrous toluene (10 mL) were added into a 25 mL Telfon-stoppered flask. After degassing by the freeze–pump–thaw method (3 cycles), the purple suspension was heated at 90 °C under N_2 for 2 d. The reaction mixture was then diluted with CH_2Cl_2 (25 mL), washed with satd $NaHCO_3$ (20 mL), water (2 × 20 mL), and satd NaCl (20 mL), and dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography over silica gel using a solvent mixture of CH_2Cl_2/hexane (3:1) as the eluent. The purple band was collected and evaporated to dryness to give purple solids which were further recrystallized from $CHCl_3$/MeOH to give purple solids of mono(2,5-dimethoxyphenyl)aryl-substituted porphyrin **23a** or **23b**.

5-[4-(2,5-Dimethoxyphenyl)phenyl]-10,15,20-tritolylporphyrin (23a) (74% yield): R_f = 0.34 (CH_2Cl_2:hexane = 3:1); ^1H NMR δ 8.96 (d, 2 H, J = 4 Hz), 8.87 (m, 6 H), 8.25 (d, 2 H, J = 8.2 Hz), 8.10 (d, 6 H, J = 7.9 Hz), 7.94 (d, 2 H, J = 8.2 Hz), 7.54 (d, 6 H, J = 7.9 Hz), 7.26 (d, 1 H, J = 3.0 Hz), 7.06 (d, 1 H, J = 8.8 Hz), 6.96 (m, 1 H), 3.94 (s, 3 H), 3.92 (s, 3 H), 2.69 (s, 9 H), −2.76 (s, 2 H); UV/vis (λ_{max}, nm, CH_2Cl_2 $\times 10^4$ cm^{-1} M^{-1}) 419.0 (31.53), 516.5 (1.87), 552.5 (1.07), 592.0 (0.57). Anal. Calcd for $C_{55}H_{44}N_4O_2$: C, 83.23; H, 5.55; N, 7.06. Found: C, 83.62; H, 5.33; N, 6.98.

5-[3-(2,5-Dimethoxyphenyl)phenyl]-10,15,20-tritolylporphyrin (23b) (76% yield): R_f = 0.37 (CH_2Cl_2:hexane = 3:1); ^1H NMR δ 9.00 (d, 2 H, J = 4.8 Hz), 8.85 (m, 6 H), 8.46 (d, 1 H, J = 1.6 Hz), 8.16 (d, 1 H, J = 6.3 Hz), 8.09 (d, 6 H, J = 7.7 Hz), 7.93 (d, 1 H, J = 7.9 Hz), 7.78 (t, 1 H, J = 7.7 Hz), 7.54 (d, 6 H, J = 7.7 Hz), 7.18 (d, 1 H, J = 3.0 Hz), 6.96 (d, 1 H, J = 8.9 Hz), 6.87 (m, 1 H), 3.85 (s, 3 H), 3.80 (s, 3 H), 2.69 (s, 9 H), −2.78 (s, 2 H); UV/vis (λ_{max}, nm, CH_2Cl_2 $\times 10^4$ cm^{-1} M^{-1}) 421.0 (28.77), 516.0 (2.15), 552.0 (1.15), 591.0 (0.65). Anal. Calcd for $C_{55}H_{44}N_4O_2$: C, 83.23; H, 5.55; N, 7.06. Found: C, 83.08; H, 5.40; N, 6.85.

General Procedure for the Preparation of mono-(benzoquinonylphenyltritolylporphyrins 24a,b from 23a,b. All glasswares were dried before use and CH_2Cl_2 was freshly distilled from anhydrous K_2CO_3. (2,5-Dimethoxyphenyl)arylmono-substituted porphyrin **23a** or **23b** (0.09 g, 0.12 mmol) dissolved in the minimum volume of CH_2Cl_2 was dropped from a pressure-equalizing funnel into BBr_3 (0.03 mL, 0.25 mmol) in CH_2Cl_2 (20 mL) at −78 °C under N_2. After stirring at −78 °C for an hour, the mixture warmed slowly to rt and stirred overnight. The mixture was cooled to 0 °C, and water was added slowly to hydrolyze excess BBr_3. The mixture was washed with triethylamine to neutralize the green porphyrin dication in the aqueous phase until the purple porphyrin partitioned in the organic layer. Then the organic layer was separated, dried ($MgSO_4$), and evaporated to dryness. The residue was redissolved in CH_2Cl_2 (20 mL), and PbO_2 (0.50 g, 2.10 mmol) was added. The suspension was stirred for 30 min and filtered. The CH_2Cl_2 filtrate was concentrated, and the residue was purified by column chromatography on silica gel using a solvent mixture of CH_2Cl_2/hexane (3:1) as the eluent. The purple band was collected and evaporated to dryness to give purple solids which were further recrystallized from $CHCl_3$/MeOH to give the pure purple solids of monobenzoquinonyl porphyrin **24a** or **24b**.

5-[4-(2,5-Benzoquinonyl)phenyl]-10,15,20-tritolylporphyrin (24a) (75% yield): R_f = 0.35 (CH_2Cl_2:hexane = 3:1);

^{1}H NMR δ 8.88 (m, 8 H), 8.29 (d, 2 H, J = 8.2 Hz), 8.08 (d, 6 H, J = 7.9 Hz), 7.88 (d, 2 H, J = 8.2 Hz), 7.54 (d, 6 H, J = 7.9 Hz), 7.20 (d, 1 H, J = 2.3 Hz), 7.00 (d, 1 H, J = 9.9 Hz), 6.97 (m, 1 H), 2.69 (s, 9 H), −2.79 (s, 2 H); IR (neat) 1662, 1678 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 ×10^4 cm^{-1} M^{-1}) 249.0 (4.31), 418.5 (29.94), 515.5 (2.04), 552.5 (1.14), 591.5 (0.70); FABMS m/z 763 (M + 1)$^+$, 762 (M$^+$). Anal. Calcd for $C_{53}H_{38}N_4O_2$: C, 83.46; H, 4.99; N, 7.35. Found: C, 83.28; H, 5.17; N, 7.49.

5-[3-(2,5-Benzoquinonyl)phenyl]-10,15,20-tritolylporphyrin (24b) (76% yield): R_f = 0.37 (CH_2Cl_2:hexane = 3:1); ^{1}H NMR δ 8.90 (m, 8 H), 8.32 (m, 2 H), 8.09 (d, 6 H, J = 7.7 Hz), 7.90−7.82 (m, 2 H), 7.54 (d, 6 H, J = 7.8 Hz), 7.11 (d, 1 H, J = 2.3 Hz), 6.90 (d, 1 H, J = 9.9 Hz), 6.82 (m, 1 H), 2.69 (s, 9 H), −2.80 (s, 2 H); IR (neat): 1660, 1677 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 ×10^4 cm^{-1} M^{-1}) 248.5 (5.33), 420.5 (29.16), 516.0 (2.16), 552.5 (1.10), 591.0 (0.67); FABMS m/z 763 (M + 1)$^+$, 762 (M$^+$). Anal. Calcd for $C_{53}H_{38}N_4O_2$: C, 83.46; H, 4.99; N, 7.35. Found: C, 83.26; H, 5.13; N, 7.39.

General Procedure for the Palladium-Catalyzed Cross-Coupling of *meso*-Tetrakis(bromophenyl)porphyrins 5a and 5b with Boronic Acid 22. *meso*-Tetrakis(bromophenyl)-porphyrin **5a** or **5b** (0.08 g, 0.09 mmol), (2,5-dimethoxyphenyl)-boronic acid **(22)** (0.99 g, 0.54 mmol), anhydrous potassium carbonate (76 mg, 0.72 mmol), $Pd(Ph_3P)_4$ (12 mg, 0.01 mmol), and anhydrous toluene (10 mL) were added into a 25 mL Teflon-stoppered flask. The purple suspension was degassed by the freeze−pump−thaw method (3 cycles) and then heated at 90 °C under N_2 for 2 d. The reaction mixture was diluted with CH_2Cl_2 (25 mL) and washed sequentially with satd $NaHCO_3$ (20 mL), water (2 × 20 mL), and satd NaCl (20 mL). The organic phase was dried ($MgSO_4$) and concentrated, and the residue was purified by column chromatography (silica gel) using a solvent mixture of CH_2Cl_2/hexane (3:1) as the eluent. The purple band was collected and evaporated to dryness to give purple solids which were recrystallized from $CHCl_3$/MeOH to give pure purple solids of *meso*-tetrakis[(2,5-dimethoxyphenyl)phenyl]porphyrin **25a** or **25b**.

***meso*-Tetrakis[4-(2,5-dimethoxyphenyl)phenyl]porphyrin (25a)** (78% yield): R_f = 0.64 (CH_2Cl_2:hexane = 3:1); ^{1}H NMR δ 9.01 (s, 8 H), 8.29 (d, 8 H, J = 8.0 Hz), 7.96 (d, 8 H, J = 8.0 Hz), 7.27 (d, 4 H, J = 3.0 Hz), 7.06 (d, 4 H, J = 8.9 Hz), 6.95 (m, 4 H), 3.95 (s, 12 H), 3.92 (s, 12 H), −2.76 (s, 2 H); UV/vis (λ_{max}, nm, CH_2Cl_2 ×10^4 cm^{-1} M^{-1}) 423.0 (28.67), 518.0 (1.54), 553.5 (1.07), 592.5 (0.49). Anal. Calcd for $C_{76}H_{62}N_4O_8$: C, 78.58; H, 5.35; N, 4.84. Found: C, 78.30; H, 5.33; N, 4.75.

***meso*-Tetrakis[3-(2,5-dimethoxyphenyl)phenyl]porphyrin (25b)** (79% yield): R_f = 0.65 (CH_2Cl_2:hexane = 3:1); ^{1}H NMR δ 9.11 (s, 8 H), 8.55 (br, s, 4 H), 8.25 (br, s, 4 H), 7.99 (d, 4 H, J = 7.8 Hz), 7.84 (t, 4 H, J = 7.7 Hz), 7.26 (d, J = 2.8 Hz, 4 H), 6.96 (d, J = 7.8 Hz, 4 H), 6.87 (m, 4 H), 3.88 (s, 12 H), 3.80 (s, 12 H), −2.63 (s, 2 H); UV/vis (λ_{max}, nm, CH_2Cl_2 ×10^4 cm^{-1} M^{-1}) 423.0 (26.69), 517.0 (1.68), 553.0 (1.22), 592.0 (0.58). Anal. Calcd for $C_{76}H_{62}N_4O_8$: C, 78.58; H, 5.35; N, 4.84. Found: C, 78.18; H, 5.33; N, 4.77.

General Procedure for the Preparation of *meso*-Tetrakis[(benzoquinonyl)phenyl]porphyrins 26a and 26b from Porphyrins 25a and 25b. All glasswares were dried before use and CH_2Cl_2 was freshly distilled from anhydrous K_2CO_3. *meso*-Tetrakis[(2,5-dimethoxyphenyl)phenyl]porphyrin **25a** or **25b** (0.14 g, 0.12 mmol) dissolved in the minimum volume of CH_2Cl_2 was dropped from a pressure-equalizing funnel into BBr_3 (0.12 mL, 0.96 mmol) in CH_2Cl_2 (20 mL) at −78 °C under N_2. After stirring at −78 °C for an hour, the mixture was warmed slowly to room temperature and stirred overnight. The mixture was cooled to 0 °C and water was added slowly to hydrolyze excess BBr_3. The mixture was washed with triethylamine to neutralize the green porphyrin dication in the aqueous phase until the purple porphyrin partitioned in the organic layer. Then the organic layer was separated and dried ($MgSO_4$) and evaporated to dryness. The residue was redissolved in MeOH (20 mL) and DDQ (0.50 g, 2.20 mmol) was added. The mixture was refluxed for 30 min and filtered. The residue was redissolved in CH_2Cl_2 and purified by column chromatography on silica gel using CH_2Cl_2 as the eluent. The purple band was collected and evaporated to dryness to give purple solids which were further recrystallized from $CHCl_3$/MeOH to give pure purple solids of *meso*-tetrakis[(benzoquinonyl)phenyl]porphyrin **26a** or **26b**.

***meso*-Tetrakis[4-(2,5-benzoquinonyl)phenyl]porphyrin (26a)** (78% yield): R_f = 0.35 (CH_2Cl_2); ^{1}H NMR δ 8.89 (s, 8H), 8.30 (d, 8H, J = 8.1 Hz), 7.90 (d, 8H, J = 8.1 Hz), 7.20 (s, 4H), 6.98 (d, 4H, J = 9.9 Hz), 6.91 (m, 4H), −2.78 (s, 2H); IR (neat) 1668, 1679 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 ×10^4 cm^{-1} M^{-1}) 420.5 (27.96), 513.5 (3.54), 550.0 (2.07), 589.0 (1.08); FABMS m/z 1040 (M + 2)$^+$. Compound was insufficiently stable to obtain satisfactory analytical results.

***meso*-Tetrakis[3-(2,5-benzoquinonyl)phenyl]porphyrin (26b)** (79% yield): R_f = 0.37 (CH_2Cl_2); ^{1}H NMR δ 8.94 (s, 8H), 8.31 (s, 8H), 7.75 (br s, 8H), 7.00 (s, 4H), 6.69 (d, 4H, J = 9.9 Hz), 6.61 (d, 4H, J = 9.9 Hz), −2.80 (s, 2H); IR (neat) 1664, 1680 cm^{-1}; UV/vis (λ_{max}, nm, CH_2Cl_2 ×10^4 cm^{-1} M^{-1}) 421.5 (27.16), 514.0 (3.46), 550.5 (2.10), 590.0 (1.07); FABMS m/z 1040 (M + 2)$^+$. Compound was insufficiently stable to obtain satisfactory analytical results.

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