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PAPER

Novel syntheses and properties of *meso*-tetraaryl-octabromo-tetranaphtho-[2,3]porphyrins (Ar_4Br_8TNPs)†

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o-Quinodimethane (*o*-QDM) generated from benzosultine was used to extend the pyrrole system for the preparation of octabromo-tetranaphtho[2,3]porphyrins *via* oxidative aromatization. The properties of these bromoporphyrins were presented and chemical transformation *via* Pd-catalyzed Suzuki reaction was also effectively achieved.

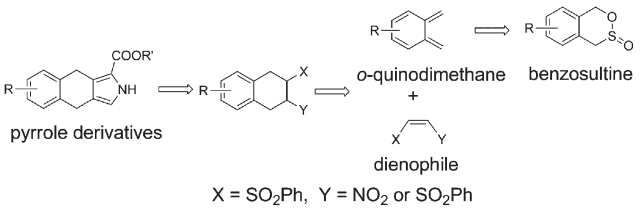
Introduction

π-Extended porphyrins continued to be an active research field due to their strong intermolecular interaction, and the unique optical and electronic properties they possess, which mean they have many potential applications for the preparation of molecular scale electronic and optoelectronic devices,[1] photo-sensitizers for photodynamic therapy,[2] nonlinear optical (NLO) materials,[3] and dye-sensitized solar cells (DSSCs).[4] Among the π-extended porphyrins, the linear fusion of aromatic rings to the porphyrins exhibited significant red-shift and intensification of Q-band.[5] Especially, naphtho[2,3]porphyrins, which began to absorb at the near-infrared region, had been applied in the fields including organic field effect transistors (OFETs), near-infrared electrophosphorescence, the process of blue green up-conversion, and phosphorescent probes for oxygen imaging in biological systems.[6]

However, the naphtho[2,3]porphyrins have only been synthesized and investigated by a few groups because of their synthetic difficulty and low solubility in most solvents. Due to the extreme instabilities of isoindoles and their π-expanded analogues, the conjugation has to be completed after the formation of porphyrin macrocycle. So far, two synthetic strategies have been employed to construct this conjugated architecture: retro-Diels–Alder reaction developed by Ono's group,[7] and oxidative aromatization used by Vinogradov and Cheprakov's groups.[8] Nevertheless, limited by the synthetic accessibility of versatile precursors, known extended porphyrins with extra substituents in the annelated rings are very scarce.[8e] It still remains a challenge to introduce various substituents into the annelated rings, which would tune the properties of the π-extended porphyrins more profoundly.

o-Quinodimethane (*o*-QDM), as a highly reactive diene, had been extensively exploited to extend the aromatic system,[9] which inspired us to extend the conjugated system of porphyrin with a readily accessible diversity of *o*-QDM. Benzosultine could generate *o*-QDM under relatively mild conditions, and then react with an electron-deficient dienophile to afford the synthetic equivalent of nitroalkene, a very useful precursor for the classic Barton–Zard pyrrole synthesis (Scheme 1).

Considering the facile and various transformation of carbon–bromine bond in synthetic chemistry,[10] the β-bromo substituted naphtho[2,3]porphyrins could be quite desirable in the π-extended molecular architectures, since the multiple β substituents may enlarge the conjugated system more efficiently. To the best of our knowledge, β-bromo substituted naphthoporphyrins have never been reported in the literature until now, despite the bromo-substituted porphyrins on *meso*- or β-position have been extensively investigated.[10a,11] Accordingly, exploring a valid synthetic procedure for the introduction of bromine is of great significance. Herein we present a novel route to the synthesis of a series of symmetrical tetraaryl-octabromo-tetranaphtho[2,3]-porphyrins (Ar_4Br_8TNPs). Furthermore, the Pd-catalyzed Suzuki coupling reaction of bromo-substituted naphtho[2,3]porphyrin was also effectively achieved in good yield.



Scheme 1 Synthetic procedure.

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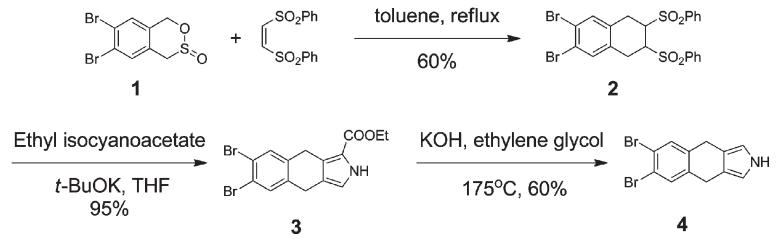
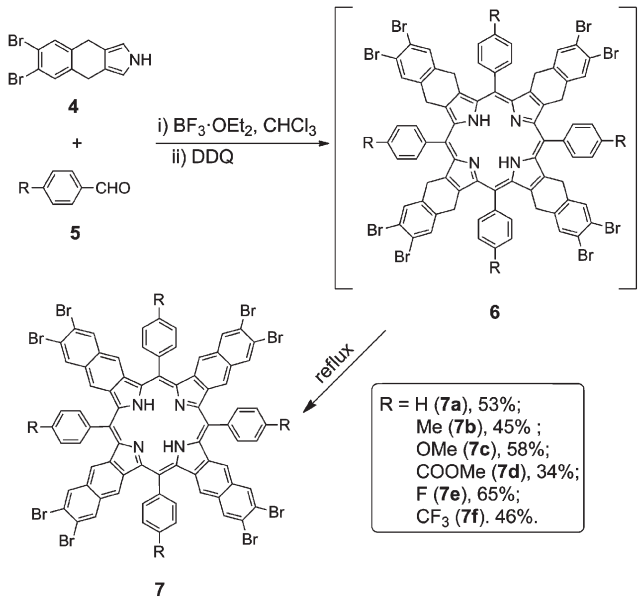
† Electronic supplementary information (ESI) available: Characterization data and spectra. CCDC 823739. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob00041e



Scheme 2 Synthesis of pyrrole **4**.



Scheme 3 Synthesis of naphtho[2,3]porphyrin.

Results and discussion

Syntheses of Ar_4Br_8TNPs

As shown in Scheme 2, dibromo-benzosultine **1** was chosen as a precursor for the generation of *o*-QDM, because it could be conveniently prepared from easily available reagents, and react thermally with dienophile under mild conditions. Thus, bis-sulfone **2** was prepared *via* Diels–Alder cycloaddition of *cis*-1,2-bis-(phenylsulfonyl)ethylene and benzosultine **1** in refluxing toluene. Then, the condensation of bis-sulfone **2** and isocyanoacetate was conducted *via* Barton–Zard reaction by the elimination of phenylsulfone with *t*-BuOK to provide pyrrole ester **3** in excellent yield. Pyrrole **4**, the key precursor for the syntheses of naphthoporphyrins, was obtained by the saponification and decarboxylation of **3** using KOH as a base in ethylene glycol at 175 °C in moderate yield.

With pyrrole **4** in hand, we succeeded in the preparation of *meso*-tetraaryl-tetranaphtho[2,3]porphyrins (Ar_4Br_8TNPs) by the conventional Lindsey condensation.[12] As shown in Scheme 3, pyrrole **4** reacted with benzaldehyde in $CHCl_3$ in the presence of $BF_3{\cdot}OEt_2$, followed by oxidation with 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) at room temperature for additional 3 hours to afford octahydronaphthalene fused porphyrin **6a**. The ^1H NMR showed a single broad peak at 3.70 ppm with sixteen protons assigned to the eight methylene groups connecting the phenyl with porphyrin ring, and a single broad peak at −2.29 ppm with two protons assigned to the NH group, which proved the only formation of the non-extended porphyrin core. After further dehydrogenation by DDQ at elevated temperature to reflux, naphtho[2,3]porphyrin **7a** was obtained in 53% yield. The aromatization was identified by the disappearance of methylene groups at 3.70 ppm and the appearance of a new singlet peak at the aromatic zone corresponding to eight protons on the naphthalene ring in ^1H NMR spectrum. Additionally, it also resulted in downfield shift of protons adjacent to bromine due to the enlargement of π-conjugation. It was noteworthy that a well-resolved ^1H NMR spectrum was obtained by the addition of a trace of trifluoroacetic acid (TFA) and the comparison among them was shown in Fig. 1. MALDI-TOF mass spectra gave the additional evidence for the formation of **6a** and **7a** (ESI†).

With the same procedure, five different naphthoporphyrins **7b–f** were successfully synthesized as illustrated in Scheme 3. Both aldehydes containing electron-donating and electron-withdrawing substituent could afford the desired naphtho[2,3]-porphyrins in acceptable yields. For the sake of convenience, all these naphthoporphyrins were prepared in one step without isolation of the intermediate porphyrins corresponding to **6**.

The π-extended molecular skeleton was also unambiguously identified by the X-ray crystallographic structure of **7e**‡ and the saddle type distortion conformation has formed as shown in Fig. 2. The dihedral angle between the two opposite pyrroles fused with naphthalene was about 136°, which was similar to the reported Pd-complex of naphtho[2,3]porphyrin derivatives.[8a]

UV-vis absorption and thermal behaviors

In spite of the lower solubility of naphtho[2,3]porphyrins **7a–f** due to the molecular aggregation, their electronic absorption spectra could still be obtained as free-base at the concentration of 10^{-5} M in CH_2Cl_2 as orange-yellow solution. As shown in Fig. 3, all naphthoporphyrins **7a–f** showed three split Soret bands, which were presumably caused by the lower symmetry of molecules. Due to the extension of π-system and conformation distortion of the macrocycles, **7a–f** exhibited largely red-shifted and intensified Q-band absorption and the maximum absorption was at 740 nm for **7d**. The maximum molar absorption coefficients of both Soret and Q band could reach 10^5 scale and the spectral data were summarized in Table S1 (ESI†). In order to identify the electronic effect of bromine on the naphthoporphyrin, a direct comparison of electronic absorption was made between **7c** and *meso*-tetrakis(4-methoxyphenyl)tetranaphtho-

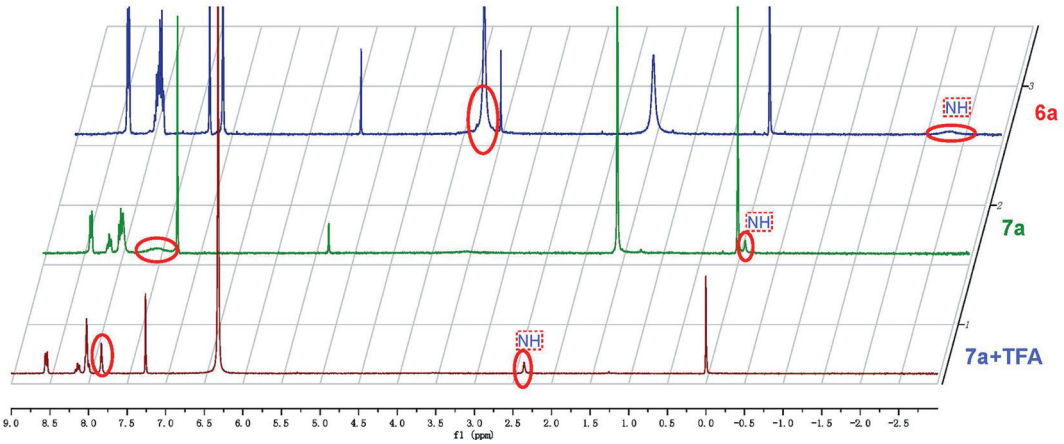


Fig. 1 ^{1}H NMR spectra comparison of porphyrin **6a**, **7a**, and **7a** + TFA.

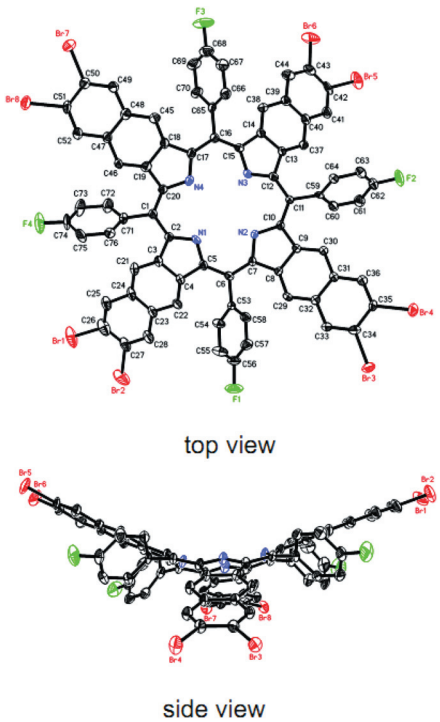


Fig. 2 X-ray crystal structure of **7e**.

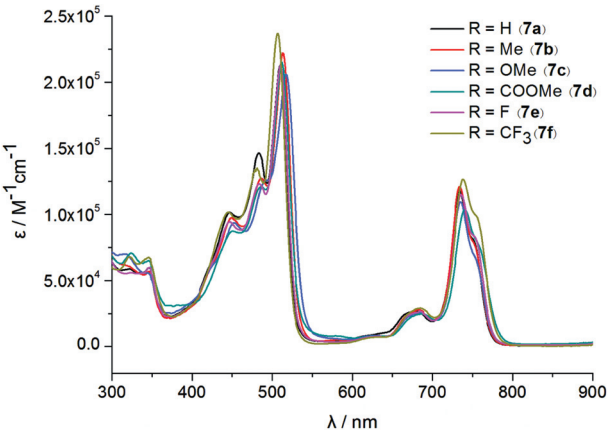


Fig. 3 UV-vis absorption spectra of **7a–f** as free-base.

[2,3]porphyrin (TMPTNP) in CH_2Cl_2 (see Fig. S2 in ESI†). The introduction of bromine atoms induced a red-shift of the Soret band by 14 nm and the Q-band by 7 nm, which might be caused by the lower of LUMO energy level due to the presence of an electron-withdrawing group. Additionally, it is worth noting that the maximum absorption coefficient ratio of Q-band to Soret-band was also enhanced from 0.48 to 0.54. The UV-vis absorption spectra of the corresponding dications of **7a–f** in CH_2Cl_2 as a purple solution showed further red-shift of both Soret and Q-band absorption (see Table S2 and Fig. S1 in ESI†), which suggested the formation of a more distorted and "frozen" saddle-shaped conformation.

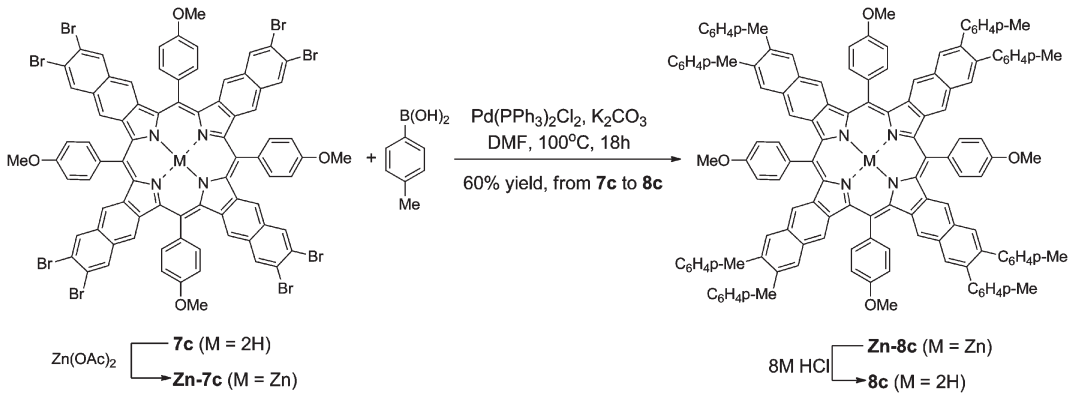
The thermal behaviors of naphtho[2,3]porphyrins **7a–f** were investigated by thermogravimetric analysis. All these naphthoporphyrins, especially fluorine-containing naphthoporphyrins **7e** and **7f** with fast decomposition temperature at 560 °C and beyond 600 °C, respectively, exhibited excellent thermal stability (see Fig. S3 and Table S3 in ESI†).

Chemical transformation *via* Suzuki coupling reaction

To illustrate the synthetic potential of these bromo-containing porphyrins, the zinc complex of **7c** was prepared and its Pd-catalyzed coupling reaction with phenylboronic acid was performed (Scheme 4). Under the usual Suzuki reaction conditions, the reaction took place readily and the corresponding octa-phenylated product **8c** was obtained in 60% yield. As expected, product **8c** did possess much better solubility in common organic solvents such as CH_2Cl_2, toluene, and THF, which made it convenient to explore the multiple properties of these analogues in solutions.

Conclusions

In summary, we have developed a reliable and effective method for the linear extension of porphyrin and successful introduction of bromine on the naphthoporphyrin periphery using a highly



Scheme 4 Chemical transformation of **7c** *via* Suzuki coupling reaction.

reactive *o*-QDM intermediate generated from benzosultine. A series of novel bromo-substituted naphtho[2,3]porphyrins (Ar_4Br_8TNPs) were synthesized, and their structures were identified by single crystal X-ray diffraction, as well as significantly red-shifted and intensified Q-band absorption. Further transformation of the carbon–bromine bond *via* Suzuki coupling reaction has also been successfully demonstrated. The potential applications of these large conjugated molecules in biological and materials fields are under investigation in our laboratory.

Experimental section

General procedures

Melting points were measured on a Melt-Temp apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 (300 MHz) spectrometer with TMS as the internal standard. ^{19}F NMR spectra were recorded on a Bruker AM-300 (282 MHz) spectrometer with $CFCl_3$ as external standard (negative for upfield). ^{13}C NMR spectra were recorded on a Bruker AM-400 (100 MHz) spectrometer. Mass spectra were taken on a HP5989A spectrometer. High-resolution mass data were obtained on a high-resolution mass spectrometer in the EI or MALDI-TOF mode. UV-vis spectra were measured with a Varian Cary 100 spectrophotometer. Elementary analyses were obtained on Perkin Elmer 2400 Series II Elemental Analyzer. Thermogravimetric analysis was conducted on TA instruments TGA 500 under N_2 atmosphere (heating rate of 20 °C min^{-1}).

THF was freshly distilled over Na–benzophenone. DMF was distilled over CaH_2 under reduced pressure. Unless otherwise stated, all commercial reagents were used as received without further purification.

1,2-Bis(bromomethyl)-4,5-dibromobenzene,[13] 1,2-bis(phenylsulfonyl)ethene[14] and 6,7-dibromo-1,4-dihydro-2,3-benzoxathiin-3-oxide (**1**)[15] were synthesized according to the literature procedures.

6,7-Dibromo-2,3-bis(phenylsulfonyl)-1,2,3,4-tetrahydronaphthalene (2). 1,2-Bis(phenylsulfonyl)ethene (1.445 g, 4.5 mmol) in toluene (40 mL) was slowly added over one hour to a solution of **1** (1.367 g, 4.5 mmol) in toluene (10 mL) under reflux. The mixture was refluxed for an additional 3 hours and cooled to room temperature. The precipitate was collected by suction filtration to give 1.515 g of the desired product **2** (yield 60%). White solid; mp 277–279 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99–7.96 (m, 4H), 7.71–7.56 (m, 6H), 7.33 (s, 2H), 4.06–4.02 (m, 2H), 3.60 (dd, J = 7.5 Hz, 17.7 Hz, 2H), 2.99 (dd, J = 7.5 Hz, 17.7 Hz, 2H); ESI MS (m/z): 592.8 (M + Na$^+$); HRMS (ESI): calcd for $C_{22}H_{18}Br_2O_4S_2Na^{+1}$ [M + Na$^+$]: 590.8911; Found: 590.8924; Anal. Calcd for $C_{22}H_{18}Br_2O_4S_2$: C, 46.33; H, 3.18. Found: C, 46.21; H, 3.27.

Ethyl 6,7-dibromo-4,9-dihydro-2*H*-benzo[*f*]isoindole-1-carboxylate (3). 0.5M *t*-BuOK solution in THF (25 mL, 12.5 mmol) was added over 2 hours to a stirred mixture of **2** (3.0 g, 5.3 mmol) and ethyl isocyanoacetate (0.85 mL, 7.7 mmol) in dry THF (30 mL) at room temperature under N_2 atmosphere. After the addition was completed, the mixture was stirred for additional 3 hours and aq. HCl solution (30 mL, 5%) was dropped slowly into the reaction system. The precipitate was collected by suction filtration and dried to afford 2.020 g of the desired product **3** (yield 95%). Pale yellow solid; mp 209–211 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.97 (br, 1H), 7.57 (s, 1H), 7.50 (s, 1H), 6.81 (d, J = 2.1 Hz, 1H), 4.35 (q, J = 7.5 Hz, 2H), 4.09 (s, 2H), 3.82 (s, 2H), 1.40 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.82, 136.52, 136.23, 134.05, 133.73, 128.26, 124.86, 121.70, 121.55, 119.28, 118.02, 60.30, 27.60, 26.38, 14.65; EIMS (m/z, %): 400 (M$^+$ + H, 8.90), 399 (M$^+$, 39.32), 370 (M$^+$ − Et, 100.00); HRMS (EI): calcd for $C_{15}H_{13}Br_2NO_2$ [M$^+$]: 396.9313; Found: 396.9308. Anal. Calcd for $C_{15}H_{13}Br_2NO_2$: C, 45.14; H, 3.28; Br, 40.04; N, 3.51. Found: C, 45.39; H, 3.64; Br, 39.96; N, 3.51.

6,7-Dibromo-4,9-dihydro-2*H*-benzo[*f*]isoindole (4). A suspension of **3** (1.475 g, 3.7 mmol) and KOH (1.1 g, 19.6 mmol) in ethylene glycol (30 mL) was heated at 175 °C for 40 minutes under N_2 atmosphere. After cooling to room temperature, the dark solution was poured into ice water (30 mL) and extracted with CH_2Cl_2 (100 mL). The organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (eluting with 1 : 5 EtOAc–petroleum) to give 0.720 g of **4** as a pale white solid (yield 60%). mp 175–177 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (br, 1H), 7.50 (s, 2H), 6.65 (s, 2H), 3.82 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.80, 133.62, 121.13, 117.29, 112.88, 26.96; EIMS

(*m*/*z*, %): 327 (M^+, 97.01), 326 (M^+ − H, 100.00), 247 (M^+ − Br–H, 34.22), 167 (M^+ − 2Br–H, 50.48); HRMS (EI): calcd for $C_{12}H_9Br_2N$: 324.9102; Found: 324.9107.

Procedure for the synthesis of naphthoporphyrin precursor *via* modified Lindsey method[8a,12]

Synthesis of porphyrin 6a. A round bottom flask shaded from light was charged with $CHCl_3$ (80 mL) followed by the addition of benzaldehyde (0.084 mL, 0.8 mmol) and pyrrole **4** (0.267 g, 0.8 mmol) under N_2 atmosphere. The mixture was stirred for ten minutes, and $BF_3{\cdot}OEt_2$ (0.08 mmol) was added with a micro-scale syringe. Three hours later, triethylamine (TEA) (one drop) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (0.150 g, 0.6 mmol) were added. After stirring for an additional two hours at room temperature, the solvent was evaporated *in vacuo* and the residue was purified by silica gel chromatography (eluting with CH_2Cl_2). The green band was collected and recrystallized from CH_2Cl_2–CH_3OH to give **6a** as a blue solid. yield 38%; mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, J = 6.0 Hz, 8H), 7.97–7.85 (m, 12H), 7.08 (s, 8H), 3.70 (br, 16H), −2.29 (br, 2H, NH); UV-vis: CH_2Cl_2, λ nm (relative intensity): 465 (31), 550 (1), 621 (1), 673 (2); MS (MALDI) *m*/*z*: 1654.7 (M^+); HRMS (MALDI): Found: 1646.7262. Calcd for $C_{76}H_{47}Br_8N_4$: 1646.7268; Anal. Calcd for $C_{76}H_{46}Br_8N_4{\cdot}CH_2Cl_2$: C, 53.17; H, 2.78; N, 3.22. Found: C, 52.88; H, 2.85; N, 3.20.

Typical procedure for the synthesis of naphthoporphyrins 7a–f without isolation of the intermediate porphyrins

A round bottom flask shaded from light was charged with $CHCl_3$ (50 mL) followed by the addition of aromatic aldehyde (0.5 mmol) and precursor pyrrole **4** (0.5 mmol) under N_2 atmosphere. The mixture was stirred for ten minutes, and $BF_3{\cdot}OEt_2$ (0.05 mmol) was added with a micro-scale syringe. Three hours later, TEA (one drop) and DDQ (0.2 g, 0.88 mmol) were added. The mixture was stirred under reflux for an additional three hours. When cooled to room temperature, the crude dark purple mixture was charged into the top of a long silica gel column and eluted with CH_2Cl_2. The first dark band was collected and precipitated by adding methanol. After filtration and drying, the solid was pure enough for element analysis.

7a Green solid; yield 53%; mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + TFA): δ 8.56–8.54 (m, 8H), 8.16–7.99 (m, 20H), 7.83 (s, 8H), 2.38 (br, 4H); UV-vis: CH_2Cl_2, λ nm (lg ε): 447 (5.01), 483 (5.16), 510 (5.33), 684 (4.43), 734 (5.07); MS (MALDI) *m*/*z*: 1647.5 (M^+ + 1); HRMS (MALDI): calcd for $C_{76}H_{38}Br_8N_4$: 1637.6563; Found: 1637.6558. Anal. Calcd for $C_{76}H_{38}Br_8N_4{\cdot}0.4CH_2Cl_2$: C, 54.61; H, 2.33; N, 3.33. Found: C, 54.64; H, 2.39; N, 3.44.

7b Green solid; yield 45%; mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + TFA): δ 8.42 (d, J = 7.2 Hz, 8H), 8.03 (s, 8H), 7.86 (s, 8H), 7.79 (d, J = 7.2 Hz, 8H), 2.89 (s, 12H), 2.60 (br, 4H); UV-vis: CH_2Cl_2, λ nm (lg ε): 449 (4.98), 486 (5.10), 513 (5.35), 682 (4.44), 734 (5.08); MS (MALDI) *m*/*z*: 1701.7 (M^+ − 1); Anal. Calcd for $C_{80}H_{46}Br_8N_4$: C, 56.44; H, 2.72; N, 3.29. Found: C, 56.64; H, 2.58; N, 3.13.

7c Green solid; yield 58%; mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + TFA): δ 8.44 (d, J = 8.4 Hz, 8H), 8.07 (s, 8H), 7.92 (s, 8H), 7.49 (d, J = 8.4 Hz, 8H), 4.24 (s, 12H), 2.65 (br, 4H); UV-vis: CH_2Cl_2, λ nm (lg ε): 453 (4.97), 486 (5.08), 517 (5.31), 686 (4.42), 735 (5.04); MS (MALDI) *m*/*z*: 1765.1 (M^+ − 1); HRMS (MALDI): calcd for $C_{80}H_{46}Br_8N_4O_4$: 1757.6986; Found: 1757.6980; Anal. Calcd for $C_{80}H_{46}Br_8N_4O_4$: C, 54.39; H, 2.62; N, 3.17; Found: C, 54.50; H, 2.90; N, 3.07.

7d Green solid; yield 34%; mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + TFA): δ 8.68 (s, 16H), 8.02 (s, 8H), 7.79 (s, 8H), 4.24 (s, 12H), 2.95 (br, 4H); UV-vis: CH_2Cl_2, λ nm (lg ε): 451 (4.94), 486 (5.08), 512 (5.33), 686 (4.39), 740 (5.02); MS (MALDI) *m*/*z*: 1877.7 (M^+ − 1); Anal. Calcd for $C_{84}H_{46}Br_8N_4O_8$: C, 53.71; H, 2.47; N, 2.98. Found: C, 53.66; H, 2.42; N, 2.76.

7e Reddish brown solid; yield 65%; mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + TFA): δ 8.57–8.52 (m, 8H), 8.09 (s, 8H), 7.86 (s, 8H), 7.75–7.69 (m, 8H), 2.62 (br, 4H); ^{19}F NMR (282 MHz, $CDCl_3$ + TFA): δ −107.41 (s); UV-vis: CH_2Cl_2, λ nm (lg ε): 447 (4.97), 483 (5.09), 510 (5.33), 684 (4.43), 736 (5.06); MS (MALDI) *m*/*z*: 1717.0 (M^+); HRMS (MALDI): calcd for $C_{76}H_{34}Br_8F_4N_4$: 1709.6187; Found: 1709.6181; Anal. Calcd for $C_{76}H_{34}Br_8F_4N_4$: C, 53.12; H, 1.99; N, 3.26. Found: C, 53.35; H, 2.32; N, 3.30.

7f Green solid; yield 46%; mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + TFA): δ 8.74 (d, J = 7.8 Hz, 8H), 8.30 (d, J = 7.8 Hz, 8H), 8.01 (s, 8H), 7.74 (s, 8H), 2.87 (br, 4H); ^{19}F NMR (282 MHz, $CDCl_3$ + TFA): δ –62.47 (s); UV-vis: CH_2Cl_2, λ nm (lg ε): 445 (5.01), 481 (5.13), 507 (5.37), 684 (4.46), 738 (5.10); MS (MALDI) *m*/*z*: 1919.5 (M + H^+); Anal. Calcd for $C_{80}H_{34}Br_8F_{12}N_4$: C, 50.09; H, 1.79; N, 2.92. Found: C, 50.15; H, 1.54; N, 2.71.

The chemical transformation of porphyrin 7c to 8c *via* Suzuki coupling reaction

Porphyrin **7c** (50 mg, 0.028 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (58 mg, 0.1 mmol) were dissolved in $CHCl_3$ (20 mL) and CH_3OH (2 mL), and the mixture was refluxed for 2 hours. The resulting solution was washed with water and brine. The product **Zn-7c** was obtained as a green solid after purifying on a silica gel column (eluting with 50 : 1 CH_2Cl_2–CH_3OH) and precipitated with CH_3OH. Anhydrous DMF was added to the mixture of **Zn-7c** (44 mg, 0.024 mmol), 4-methylphenylboric acid (100 mg, 0.735 mmol), $Pd(PPh_3)_2Cl_2$ (6 mg, 0.008 mmol) and K_2CO_3 (100 mg, 0.724 mmol) in a Schlenk tube under Ar, and the system was stirred at 100 °C for 18 hours. After extracting with CH_2Cl_2 (20 mL) and acidifying with 6 M HCl (10 mL), the organic phase was washed with brine and purified on a silica gel column (eluting with CH_2Cl_2). The first fraction was collected and precipitated with CH_3OH. The precipitate was filtered and dried to give porphyrin **8c** as a green solid. Yield: 60% (32 mg) for three steps. mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + TFA): δ 8.52 (d, J = 8.4 Hz, 8H), 8.07 (s, 8H), 7.76 (s, 8H), 7.44 (d, J = 8.4 Hz, 8H), 7.07 (s, 32H), 4.15 (s, 12H), 2.77 (br, 4H), 2.33 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.72, 139.19, 138.77, 136.20, 135.69, 134.88, 130.63, 130.48, 129.91, 128.67, 115.01, 113.87, 55.93, 21.20; UV-vis: CH_2Cl_2, λ nm (relative

intensity): 450 (3.665), 518 (7.915), 689 (1.000), 748 (4.192); MS (MALDI) *m/z*: 1855.8 (M^+); Anal. Calcd for $C_{136}H_{102}N_4O_4$: C, 88.00; H, 5.54; N, 3.02; Found: C, 87.85; H, 5.44; N, 3.08.

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Notes and references

‡Crystal data for **7e**: $C_{76}H_{34}Br_8F_4N_4$, M = 1718.35, monoclinic, a = 10.0612(10) Å, b = 18.1279(19) Å, c = 17.8048(18) Å, α = 90.00°, β = 98.285(3)°, γ = 90.00°, V = 3213.5(6) Å^3, T = 296(2) K, space group *Pc*, Z = 2, 31 992 reflections measured, 9390 independent reflections (R_{int} = 0.0418). The final R_1 values were 0.0474 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.1225 ($I > 2\sigma(I)$). The final R_1 values were 0.0593 (all data). The final w$R(F^2)$ values were 0.1317 (all data).

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