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Efficient Rhodium-Catalyzed Installation of Unsaturated Ester Functions onto Porphyrins: Site-Specific Heck-Type Addition versus Conjugate Addition

Hiromi Baba, Jinping Chen, Hiroshi Shinokubo,* and Atsuhiro Osuka*[a]

Abstract: A facile introduction of α,β- or α,β,γ,δ-unsaturated ester functions onto porphyrins was achieved through rhodium-catalyzed addition of β-borylporphyrins to acrylate or 2,4-pentadienoate esters. The reaction of *meso*-borylporphyrins with acrylates exclusively afforded saturated esters by 1,4-conjugate addition under the same reaction conditions. Thus, the reaction mode (Heck-type versus conjugate addition) is highly dependent on the reaction site (β versus *meso*). This functionalization has a significant impact on the electronic properties of the π system of porphyrins, which induces a substantial redshift and broadening in the absorption spectra by effective conjugation through the β positions. The coplanar structure of the unsaturated ester moieties with respect to the porphyrin core has been unambiguously elucidated by X-ray crystallographic analysis.

Keywords: boron · C–C coupling · Heck reaction · porphyrinoids · rhodium

Introduction

Peripheral functionalization is important for the modification of porphyrins and thus the fine-tuning of their electronic and photophysical properties. Most porphyrin functionalizations rely on classical but still useful electrophilic substitution such as halogenation, formylation, and nitration.[1] As for modern transition metal-catalyzed reactions, palladium-catalyzed cross coupling[2] as well as Sonogashira[3] and Heck reactions[4] are powerful tools for the further derivatization of haloporphyrins.[5] However, rhodium-catalyzed transformations have never been employed in porphyrin synthesis, although they have proven to be highly versatile in organic synthesis.[6] In particular, the chemistry of organoboranes combined with rhodium catalysis has been extensively explored in the search for new types of carbon–carbon bond formation with high levels of asymmetric induction.[7]

For the synthesis of a functionalized porphyrin, protected functional groups are often introduced into the porphyrin precursor, such as dipyrromethanes and aldehydes, before cyclization. However, the protected functional group is sometimes decomposed to some extent under the acidic and oxidative conditions of porphyrin synthesis. We propose the post-modification of relatively simple porphyrins by organometallic and catalytic means.[8] Herein, we report facile and efficient installation of carboxylic ester functions at the *meso* and β positions of porphyrins by the rhodium-catalyzed addition of organoboranes to acrylates as the first application of rhodium catalysis to porphyrin synthesis. In particular, the use of β-boryl porphyrins allows the multiple introduction of α,β- and α,β,γ,δ-unsaturated ester groups, which are effectively conjugated to the porphyrin π system, at the β positions in a sterically unhindered manner.[9]

Selective introduction of ester groups at desired positions in porphyrins is quite important because carboxylic acid groups attached to porphyrins serve as anchoring moieties to ensure efficient absorption on the surface of TiO_2, a process that enhances the efficiency of dye-sensitized solar cells (DSSC).[10,11] Furthermore, carboxylic acid functions act as hydrophilic sites in water-soluble porphyrins, which are useful materials in photodynamic therapy and often exhibit intriguing aggregation properties in water.[12]

[a] H. Baba, Dr. J. Chen, Prof. Dr. H. Shinokubo, Prof. Dr. A. Osuka
Department of Chemistry
Graduate School of Science
Kyoto University
Sakyo-ku, Kyoto 606-8502 (Japan)
Fax: (+81) 75-753-3970
E-mail: hshino@kuchem.kyoto-u.ac.jp
osuka@kuchem.kyoto-u.ac.jp

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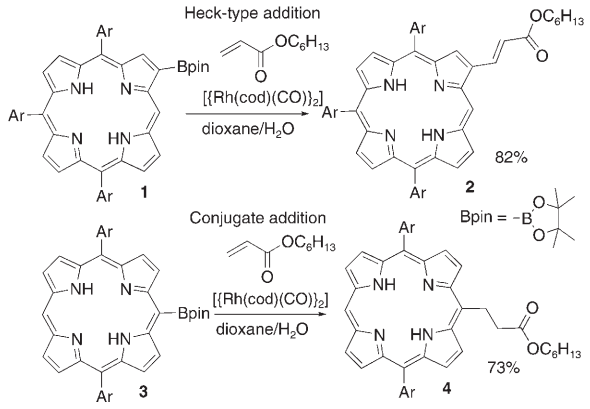
Results and Discussion

Site-specific Rh-catalyzed addition of β- and *meso*-boryl porphyrins: β-Boryl porphyrins were prepared by means of direct, regioselective iridium-catalyzed β-borylation of porphyrins.[8a,c] *meso*-Boryl porphyrins were synthesized according to Therien's protocol.[13] β-Boryl porphyrin **1** was heated at 100 °C for 15 h in aqueous 1,4-dioxane with hexyl acrylate (10 equiv) in the presence of 10 mol % of [{Rh(cod)(OH)}$_2$] (cod = 1,5-cyclooctatriene). After chromatographic separation, unsaturated ester **2** was obtained in 82 % yield along with a small amount of saturated product (< 3 %), which clearly indicated that predominant addition–elimination, namely Heck-type addition, had proceeded (Scheme 1).[14]

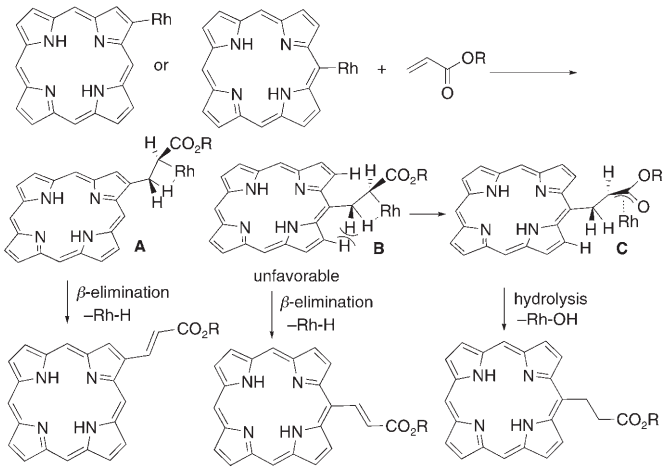


Scheme 1. Site-specific Rh-catalyzed addition of β- and *meso*-boryl porphyrins to acrylate. Ar = 3,5-di-*tert*-butylphenyl.

In contrast, the reaction of *meso*-boryl porphyrin **3** under exactly the same conditions exclusively provided saturated product **4** in 73 % yield by 1,4-conjugate addition).[15] Notably, the reaction mode (Heck-type addition versus conjugate addition) was highly dependent on the reaction site (β versus *meso*).

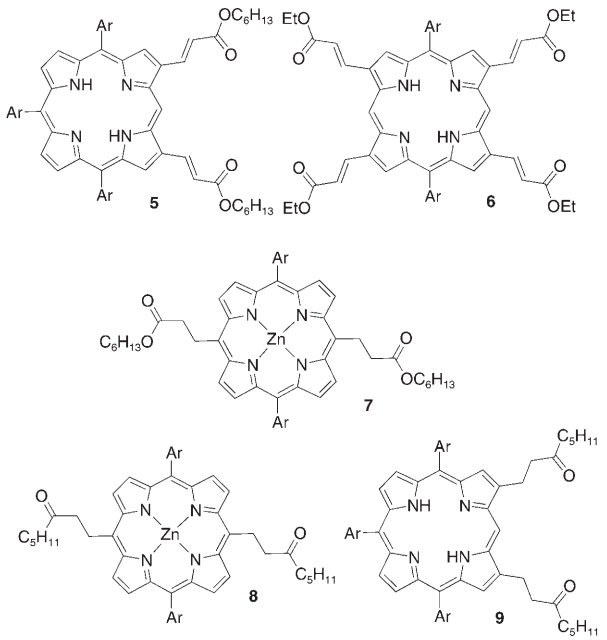
In view of the reaction mechanism, it is worth noting that the reaction mode of these rhodium-catalyzed addition reactions is highly dependent on the reaction site in the porphyrins. The transition states for the β-elimination steps were calculated by DFT at the B3LYP/LANL2DZ level (see the Supporting Information). Calculations were carried out by using the Gaussian 03 program.[16] Whereas β elimination occurs smoothly in transition-state **A** from β-boryl porphyrin, β elimination is not favorable from the *meso*-boryl porphyrin due to steric repulsion between the adjacent β proton in transition-state **B** (Scheme 2). The intermediate is then hydrolyzed to provide the conjugate addition product via oxa-π-allylrhodium species **C**.

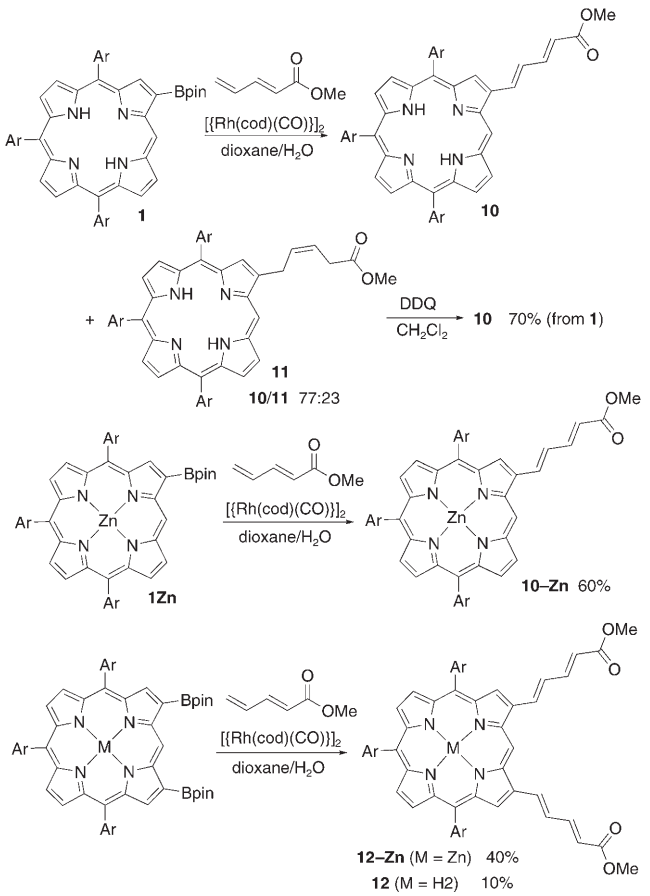
The use of β,β′-diboryl- and β,β′β″,β‴-tetraborylporphyrin provided diester **5** and tetraester **6** in 72 and 68 % yield, respectively, by Heck-type addition. *meso*,*meso*′-Diboryl porphyrin underwent exclusive 1,4-conjugate addition to furnish the corresponding saturated ester **7** in 61 % yield. Interestingly, the reaction with the α,β-unsaturated ketone, oct-1-



Scheme 2. Reaction mechanism.

en-3-one, afforded only saturated products **8** and **9** in 89 and 77 % yields, respectively. This indicates that only conjugate addition occurs in the reaction with the α,β-enone regardless of the position of the boryl group. The reaction with methyl 2,4-pentadienoate allowed further elongation of conjugation through selective 1,6-addition (Scheme 3).[17] Conjugate addition competed with Heck-type addition to provide a mixture of products **10** and **11**, but the crude mixture was selectively transformed into fully conjugated product **10** in 70 % overall yield upon treatment with DDQ. Interestingly, the use of Zn^{II}–porphyrin **1–Zn** resulted in exclusive formation of conjugated product **10–Zn**.[18] Clearly, the central metal has a significant effect on the selectivity of the reaction course, probably by changing the electron density of the porphyrin core. This is also the case for diborylporphyrins: Zn^{II}–porphyrin furnished the desired conjugated porphyrin in 40 % yield in a single step, whereas the product was ob-





Scheme 3. Rh-catalyzed addition of β-boryl porphyrins to methyl pentadienoate. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; Ar = 3,5-di-*tert*-butylphenyl.

tained in only 10% yield even after the use of DDQ in the reaction with the corresponding free base porphyrin.

X-ray crystallographic analysis and electronic absorption properties: The structures of β,β′- and *meso*,*meso*′-diester porphyrins were unambiguously elucidated by X-ray crystallographic analysis (Figure 1). In the case of **5**, the β-unsaturated ester moieties adopt a rather coplanar conformation and the dihedral angles of C3-C2-C63-C64 and C17-C18-C72-C73 are 2.5 and 22.2°, respectively, because of the lack of steric bulkiness at the *meso* position. This orientation allows effective electronic conjugation in the porphyrin π system, which is confirmed by the shortened $C_{pyrrole}$–C_{vinyl} single bond lengths (1.447(7) and 1.448(7) Å) relative to the $C_{pyrrole}$–C_{sp3} single bond lengths (1.508(3) Å) in diketo porphyrin **9**. In contrast, the *meso*-ester substituents in **7** are perpendicular to the porphyrin plane to minimize the steric repulsion between the proximal β-hydrogen atoms.

As is evident from the X-ray structure, the lack of bulky *meso*-substituents secures the extension of conjugation at the β positions. In fact, β-enoate porphyrins **2**, **5**, and **6** exhibit substantial redshifts and broadening of the Soret and Q bands in the absorption spectra (Figure 2a,b). Furthermore, the electronic effects of dienoate moieties at the β positions in porphyrins are quite significant and the shapes of the absorption bands of **10** and **12** are much broader and are redshifted, which implies their prospective use as light-harvesting dyes. In comparison with the parent triarylporphyrin, the redshift reaches 44 nm (Soret band) in the case of **12** by the introduction of two conjugated dienoate moieties. The full widths at half maxima (fwhm) of the Soret bands of **10** and **12** are 2350 and 2180 cm^{-1}, respectively. The shape of the absorption spectrum of **10** in dichloromethane does not

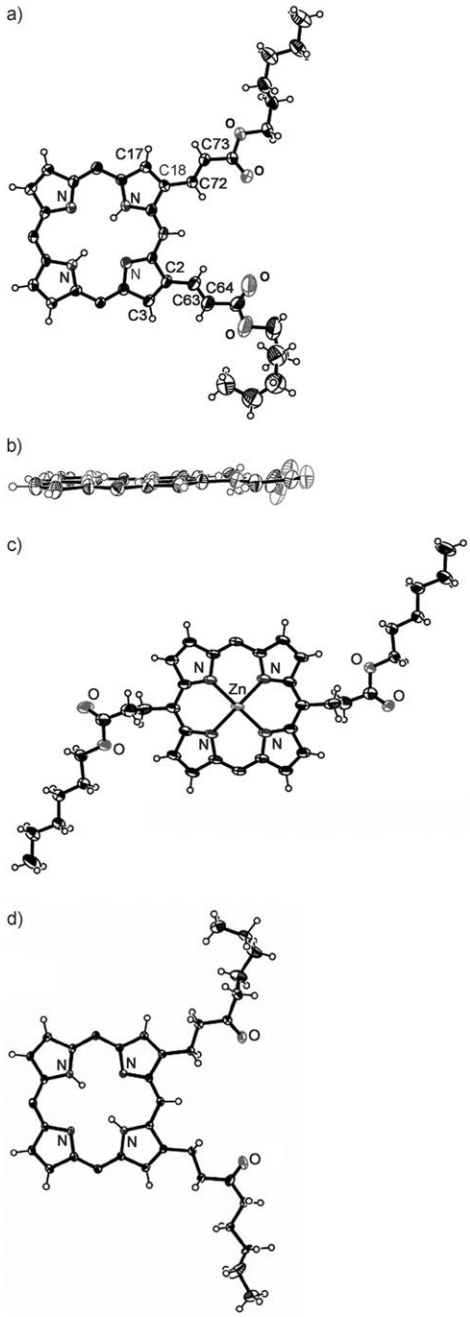


Figure 1. X-ray structures of **5**, **7**, and **9**. a) Top view and b) side view of **5**, c) top view of **7**, and d) top view of **9**. The thermal ellipsoids are at the 50% probability level. The *meso*-aryl and alkyl groups in b) are omitted for clarity.

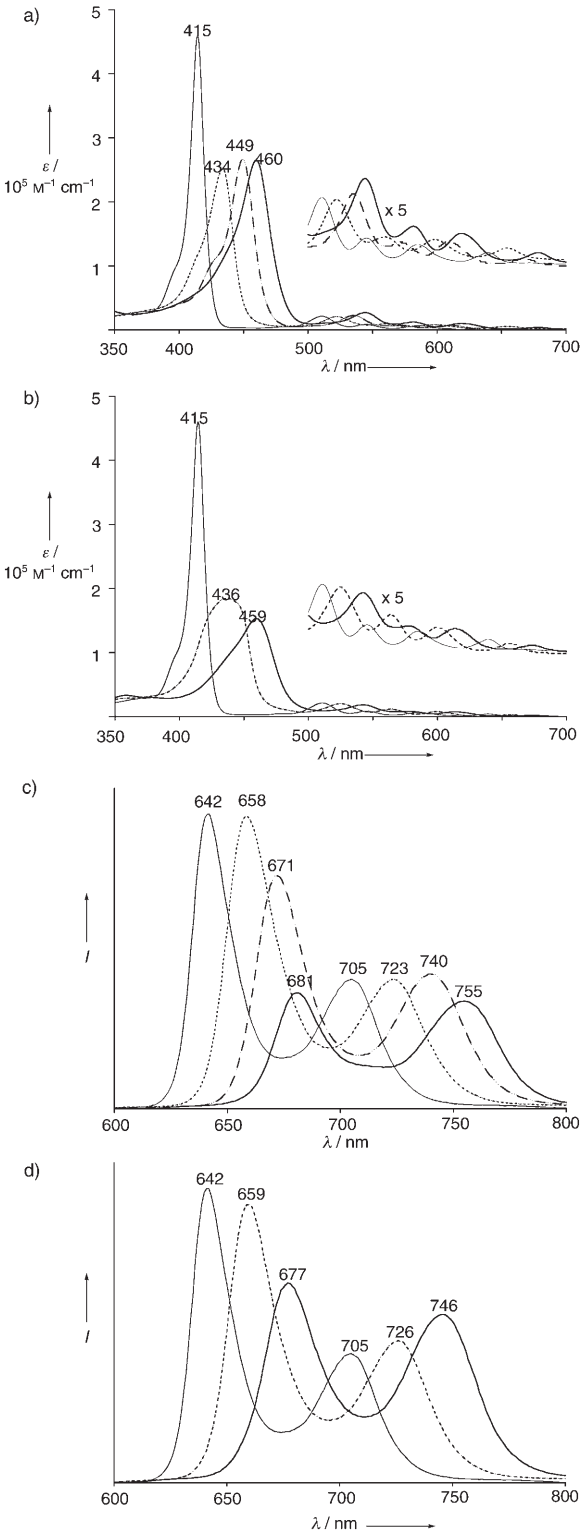


Figure 2. UV/Vis absorption spectra (CH_2Cl_2) of a) **2** (-----), **5** (– – –), and **6** (——) and b) **10** (-----; M = H2) and **12** (——; M = H2) and fluorescence spectra (CH_2Cl_2) of c) **2** (-----), **5** (– – –), and **6** (——) and d) **10** (-----; M = H2) and **12** (——; M = H2). The corresponding spectra of 5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrin (——) are shown in all cases.

show any notable change in the range from 4.0×10^{-7} to 8.0×10^{-6} mol L^{-1}. The considerable broadening in the spectrum is probably explained by its lower symmetry and the electronic effect of the enoate moiety rather than by the formation of aggregates of **10**. Fluorescence spectra of these porphyrins are also redshifted by the introduction of the unsaturated substituents (Figure 2c,d). In contrast, no significant affects on the absorption properties by *meso*-substitution were observed in **7** and **8** (see the Supporting Information).

Synthesis of water-soluble porphyrin 13: Saponification of tetraester porphyrin **6** under standard conditions provided tetraacid **13** in quantitative yield. Absorption spectra of tetraacid **13** in THF and basic water are shown in Figure 3. The blueshift of the Soret band in basic water can be accounted for by formation of H-aggregates due to the hydrophobic effect and π–π stacking interactions.

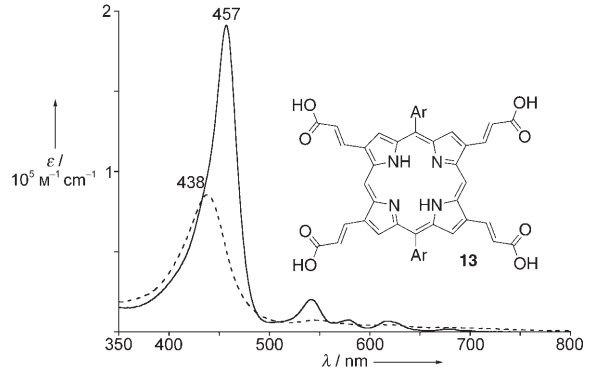


Figure 3. UV/Vis absorption spectra of **13** in THF (——) and basic water (-----).

Conclusion

We have demonstrated an efficient introduction of ester functions onto porphyrins by the addition of borylporphyrins to acrylates. This is the first application of rhodium-catalyzed transformations of organoboranes in porphyrin synthesis. Interestingly, the reaction mode (Heck-type versus conjugate addition) depends heavily on the reaction site (β versus *meso*) in the porphyrins. The unsaturated ester moiety has a significant impact on the electronic system of the porphyrin by effective conjugation at the β positions. This reaction will be useful for the introduction of long alkyl chains to enhance solubility and control aggregation properties in the condensed phase by the use of properly designed acrylate esters. Moreover, the unsaturated ester moieties introduced in this way would be a nice foothold for further functionalization. Application of the materials obtained here in dye-sensitized solar cells is currently underway.

Experimental Section

Instrumentation and materials: ^{1}H NMR (600 MHz) spectra were measured on a JEOL ECA-600 spectrometer, and chemical shifts were reported on the δ scale in ppm relative to $CHCl_3$ ($\delta = 7.260$ ppm). UV/Vis absorption spectra were recorded on a Shimadzu UV-3150 spectrometer. Mass spectra were recorded on a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer by using the positive-MALDI ionization method. High resolution ESI-TOF mass spectra were measured on a Bruker microTOF instrument. Recycling preparative GPC-HPLC was carried out on a JAI LC-908 instrument with preparative JAIGEL-2H and 2.5H columns. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Crystallographic data collection and structure refinement: Data collection was carried out at low temperature (−153 °C) on a Rigaku RAXIS-RAPID instrument with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Details of the crystallographic data are listed in Table 1. The structures were solved by direct methods (SHELXS-97[19]) by using the full-matrix least square technique (SHELXL-97).[19] CCDC 646245 (**5**), 646246 (**7**), and 646247 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General procedure: Borylated porphyrin (**1**, 40.9 mg, 41 μmol) and [{Rh(cod)(OH)}$_2$] (1.8 mg, 4 μmol) were placed in a Schlenk flask, which was evacuated and then purged with argon five times. Hexyl acrylate (70 μL, 0.4 mmol) followed by 1,4-dioxane/water (1.5/0.15 mL) were introduced by using a syringe. The mixture was then stirred at 100 °C for 16 h. The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2, and filtered through a small plug of silica gel with copious washings (CH_2Cl_2). After removal of the solvent in vacuo, the residue was purified by silica-gel, column chromatography (hexane/CH_2Cl_2) and careful recrystallization (methanol/dichloromethane) to afford the Heck product **2** (34.7 mg, 34 μmol; 82 %).

***n*-Hexyl (*E*)-3-[5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrin-2-yl]prop-2-enoate (2)**: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = -2.72$ (s, 2H; NH), 0.97 (t, $J = 7.1$ Hz, 3H; Hex), 1.40–1.43 (m, 4H; Hex), 1.50–1.52 (m, 2H; Hex), 1.54 (s, 36H; *t*Bu), 1.56 (s, 18H; *t*Bu), 1.84–1.89 (m, 2H; Hex), 4.41 (t, $J = 6.9$ Hz, 2H; Hex), 7.14 (d, $J = 15.6$ Hz, 1H), 7.79 (t, $J = 1.4$ Hz, 1H; Ar-*para*-H), 7.81 (t, $J = 1.4$ Hz, 1H; Ar-*para*-H), 7.84 (t, $J = 1.8$ Hz, 1H; Ar-*para*-H), 8.04 (d, $J = 1.4$ Hz, 2H; Ar-*ortho*-H), 8.09 (t, $J = 1.9$ Hz, 4H; Ar-*ortho*-H), 8.86 (d, $J = 4.6$ Hz, 1H; β-H), 8.89 (d, $J = 4.6$ Hz, 1H; β-H), 8.91 (d, $J = 5.0$ Hz, 1H; β-H), 8.93 (d, $J = 4.6$ Hz, 1H; β-H), 9.07 (d, $J = 4.1$ Hz, 1H; β-H), 9.23 (s, 1H; β-H), 9.38 (d, $J = 15.1$ Hz, 1H), 9.40 (d, $J = 6.0$ Hz, 1H; β-H), 10.37 ppm (s, 1H; *meso*); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 434 (2.52×10^5), 522 (2.08×10^4), 559.5 (9.11×10^3), 598 (8.22×10^3), 654.5 nm (5.59×10^3 M^{-1} cm^{-1}); fluorescence (CH_2Cl_2), $\lambda_{ex} = 434$; $\lambda_{em} = 658$, 723 nm; HRMS (ESI): *m*/*z*: calcd for $C_{71}H_{88}N_4O_2Na$: 1051.6799 $[M+Na]^+$; found: 1051.6799.

***n*-Hexyl 3-[10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin-5-yl]propanoate (4)**: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = -2.97$ (s, 2H; NH), 0.81 (t, $J = 6.8$ Hz, 3H; Hex), 1.19–1.23 (m, 4H; Hex), 1.27–1.30 (m, 2H; Hex), 1.56 (s, 36H; *t*Bu), 1.58–1.63 (m, 2H; Hex), 3.58 (t, $J = 8.3$ Hz, 2H), 4.20 (t, $J = 6.9$ Hz, 2H), 5.47 (t, $J = 8.3$ Hz, 2H), 7.83 (t, $J = 1.8$ Hz, 2H; Ar-*para*-H), 8.10 (d, $J = 1.86$, 4H; Ar-*ortho*-H), 9.01 (d, $J = 4.6$ Hz, 2H; β-H), 9.04 (d, $J = 4.6$ Hz, 2H; β-H), 9.28 (d, $J = 4.1$ Hz, 2H; β-H), 9.58 (d, $J = 4.6$ Hz, 2H; β-H), 10.12 ppm (s, 1H; *meso*); HRMS (ESI): *m*/*z*: calcd for $C_{57}H_{71}N_4O_2$: 843.5572 $[M+H]^+$; found: 843.5551.

Di-*n*-hexyl (*E*,*E*)-3,3′-[5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrin-2,18-diyl]diprop-2-enoate (5): ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = -2.53$ (s, 2H; NH), 0.94 (t, $J = 6.9$ Hz, 6H; Hex), 1.38–1.42 (m, 8H; Hex), 1.49–1.53 (m, 4H; Hex), 1.53 (s, 18H; *t*Bu), 1.54 (s, 36H; *t*Bu), 1.84–1.89 (m, 4H; Hex), 4.41 (t, $J = 6.9$ Hz, 4H; OCH_2), 7.15 (d, $J = 15.6$ Hz, 2H), 7.77 (t, $J = 1.9$ Hz, 1H; Ar-*para*-H), 7.84 (t, $J = 1.9$ Hz, 2H; Ar-*para*-H), 8.01 (d, $J = 1.9$ Hz, 2H; Ar-*ortho*-H), 8.06 (d, $J = 1.9$ Hz, 4H; Ar-*ortho*-H), 8.84 (d, $J = 4.6$ Hz, 2H; β-H), 8.85 (d, $J = 4.6$ Hz, 2H; β-H), 9.22 (s, 2H; β-H), 9.37 (d, $J = 15.6$ Hz; 2H), 10.43 ppm (s, 1H; *meso*); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 449 (2.67×10^5), 535 (2.25×10^4), 571 (7.48×10^3), 609.5 (7.48×10^3), 668 nm (2.08×10^3 M^{-1} cm^{-1}); fluorescence (CH_2Cl_2): $\lambda_{ex} = 449$; $\lambda_{em} = 671$, 740 nm; HRMS (ESI): *m*/*z*: calcd for $C_{80}H_{102}N_4O_4Na$: 1205.7793 $[M+Na]^+$; found: 1205.7791.

Tetraethyl (*E*,*E*,*E*,*E*)-3,3′,3″,3‴-[5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin-2,8,12,18-tetrayl]tetraprop-2-enoate (6): ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = -2.39$ (s, 2H; NH), 1.52 (t, $J = 6.9$ Hz, 12H; CH_3), 1.59 (s, 36H; *t*Bu), 4.49 (q, $J = 6.8$ Hz, 8H; OCH_2), 7.15 (d, $J = 15.6$ Hz, 4H), 7.91 (t, $J = 1.8$ Hz, 2H; Ar-*para*-H), 8.06 (d, $J = 1.9$ Hz, 4H; Ar-*ortho*-H), 9.20 (s, 4H; β-H), 9.33 (d, $J = 15.6$ Hz, 4H), 10.43 ppm (s, 2H; *meso*); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 460 (2.65×10^5), 544 (2.73×10^4), 581.5 (1.24×10^4), 619 (1.01×10^4), 678.5 nm (4.17×10^3 M^{-1} cm^{-1}); fluorescence (CH_2Cl_2): $\lambda_{ex} = 460.5$; $\lambda_{em} = 681$, 755 nm; HRMS (ESI): *m*/*z*: calcd for $C_{68}H_{78}N_4O_8Na$: 1101.5712 $[M+Na]^+$; found: 1101.5728.

Di-*n*-hexyl 3,3′-[10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinate(zinc)-5,15-diyl]dipropanoate (7): $\delta = {}^1$H NMR (600 MHz, $CDCl_3$): $\delta = 0.80$ (t, $J = 7.1$ Hz, 6H; Hex), 1.19–1.23 (m, 8H; Hex), 1.26–1.30 (m, 4H; Hex), 1.56 (s, 36H; *t*Bu), 1.59–1.63 (m, 4H; Hex), 3.58 (t, $J = 8.3$ Hz, 4H), 4.19 (t, $J = 6.6$ Hz, 4H; Hex), 5.41 (t, $J = 8.3$ Hz, 4H), 7.82 (t, $J = 1.9$ Hz, 2H; Ar-*para*-H), 8.07 (d, $J = 1.4$ Hz, 4H; Ar-*ortho*-H), 9.05 (d, $J = 4.6$ Hz, 4H; β-H), 9.59 ppm (d, $J = 4.6$ Hz, 4H; β-H); HRMS (ESI): *m*/*z*: calcd for $C_{66}H_{85}N_4O_4Zn$: 1061.5857 $[M+H]^+$; found: 1061.5854.

Table 1. Crystallographic data for **5**, **7**, and **9**.

	5	**7**	**9**
empirical formula	$C_{80.98}H_{103.96}Cl_{0.98}N_4O_4$	$C_{66}H_{83.80}N_4O_4Zn$	$C_{80}H_{106}Cl_2N_4O_2$
M	1232.24	1062.54	1226.59
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a [Å]	11.955(3)	5.774(3)	12.937(5)
b [Å]	17.381(5)	14.425(7)	17.159(7)
c [Å]	18.601(6)	17.283(9)	17.616(9)
α [°]	84.117(10)	94.571(18)	82.555(17)
β [°]	80.176(9)	90.653(17)	68.410(14)
γ [°]	71.333(9)	90.721(16)	74.705(12)
V [Å^3]	3603.1(18)	1434.6(11)	3505(3)
Z	2	1	2
ρ_{calcd} [g cm^{-3}]	1.136	1.230	1.142
μ [mm^{-1}]	0.104 ($Mo_{K\alpha}$)	0.480 ($Mo_{K\alpha}$)	0.142 ($Mo_{K\alpha}$)
F(000)	1333	570	1328
crystal size [mm^3]	0.10 × 0.10 × 0.10	0.45 × 0.10 × 0.10	040 × 0.40 × 0.20
$2\theta_{max}$ [°]	55.0	55.0	55.0
T [K]	123(2)	123(2)	123(2)
total reflections	12504	14121	31920
unique reflections	5405	6463	15340
reflection used	5405	6463	15340
parameters	918	375	903
absorption correction	none	none	none
R_1	0.0959	0.0836	0.0605
wR_2	0.2893	0.2426	0.2189
GOF	1.011	1.065	0.985

5,15-Bis(3,5-di-*tert*-butylphenyl)-10,20-bis(3-oxooctyl)porphyrinate zinc(II) (8): ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.85$ (t, $J = 6.9$ Hz, 6H; Pen), 1.25–1.28 (m, 8H; Pen), 1.55 (s, 36H; *t*Bu), 1.64–1.69 (m, 4H; Pen), 2.48 (t, $J = 7.3$ Hz, 4H), 3.69 (t, $J = 8.2$ Hz, 4H), 5.34 (t, $J = 7.8$ Hz, 4H), 7.82 (d, $J = 1.8$ Hz, 2H; Ar-*para*-H), 8.06 (d, $J = 1.9$ Hz, 4H; Ar-*ortho*-H), 9.03 (d, $J = 4.6$ Hz, 4H; β-H), 9.53 ppm (d, $J = 4.6$ Hz, 4H; β-H); HRMS (ESI): *m*/*z*: calcd for $C_{64}H_{80}N_4O_2ZnNa$: 1023.5465 $[M+Na]^+$; found: 1023.5462.

5,10,15-Tris(3,5-di-*tert*-butylphenyl)-2,18-bis(3-oxooctyl)porphyrin (9): ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = -2.85$ (s, 2H; NH), 0.86 (t, $J = 6.4$ Hz, 6H; Pen), 1.25–1.33 (m, 8H; Pen), 1.52 (s, 18H; *t*Bu), 1.57 (s, 36H; *t*Bu), 1.65–1.69 (m, 4H; Pen), 2.57 (t, $J = 7.3$ Hz, 4H), 3.48 (t, $J = 7.8$ Hz, 4H), 4.44 (t, $J = 7.8$ Hz, 4H), 7.79 (s, 1H; ArH), 7.82 (s, 2H; ArH), 8.07 (s, 2H; ArH), 8.09 (s, 4H; ArH), 8.71 (s, 2H; β-H), 8.89 (s, 4H; β-H), 10.18 ppm (s, 1H; *meso*); HRMS (ESI): *m*/*z*: calcd for $C_{78}H_{102}N_4O_2$: 1149.7895 $[M+Na]^+$; found: 1149.7840.

Methyl (2*E*,4*E*)-5-[5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrin-2-yl]penta-2,4-dienoate (10): ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = -2.70$ (s, 2H; NH), 1.50 (s, 18H; *t*Bu), 1.54 (s, 18H; *t*Bu), 1.56 (s, 18H; *t*Bu), 3.88 (s, 3H; OCH_3), 6.25 (d, $J = 15.1$ Hz, 1H), 7.60 (dd, $J = 15.6$, 11.5 Hz, 1H), 7.78 (t, $J = 1.9$ Hz, 1H; Ar-*para*-H), 7.81 (t, $J = 1.8$ Hz, 1H; Ar-*para*-H), 7.84 (t, $J = 1.8$ Hz, 1H; Ar-*para*-H), 7.97 (dd, $J = 15.1$, 11.9 Hz, 1H), 8.04 (d, $J = 1.9$ Hz, 2H; Ar-*ortho*-H), 8.09 (d, $J = 1.8$ Hz, 2H; Ar-*ortho*-H), 8.11 (d, $J = 1.9$ Hz, 2H; Ar-*ortho*-H), 8.64 (d, $J = 14.6$ Hz, 1H), 8.86 (d, $J = 4.6$ Hz, 1H; β-H), 8.90 (d, $J = 4.6$ Hz, 2H; β-H), 8.92 (d, $J = 4.6$ Hz, 1H; β-H), 9.06 (d, $J = 4.6$ Hz, 1H; β-H), 9.18 (s, 1H; β-H), 9.37 (d, $J = 4.1$ Hz, 1H; β-H), 10.28 ppm (s, 1H; *meso*); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 304.0 (2.67×10^4), 436.0 (1.85×10^5), 524.5 (2.08×10^4), 563.5 (1.21×10^4), 599.5 (7.99×10^3), 655.5 nm (3.00×10^3 м$^{-1}$ cm^{-1}); fluorescence (CH_2Cl_2): λ_{ex} = 435.5 nm; λ_{em} = 659, 726 nm; HRMS (ESI): *m*/*z*: calcd for $C_{68}H_{81}N_4O_2$: 985.6354 $[M+H]^+$; found: 985.6382.

Methyl (3*Z*)-5-[5,10,15-Tris(3,5-di-*tert*-butylphenyl)porphyrin-2-yl]pent-3-enoate (11): ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = -2.87$ (s, 2H; NH), 1.50 (s, 18H; *t*Bu), 1.55 (s, 36H; *t*Bu), 3.60 (d, $J = 7.3$ Hz, 2H), 3.75 (s, 3H; OCH_3), 4.93 (d, $J = 6.9$ Hz, 2H), 6.02 (dtt, $J = 10.6$, 7.3, 1.8 Hz, 1H), 6.52 (dtt, $J = 10.6$, 7.3, 1.9 Hz, 1H), 7.78 (t, $J = 1.8$ Hz, 1H; Ar-*para*-H), 7.79–7.81 (m, 2H; Ar-*para*-H), 8.06 (d, $J = 1.8$ Hz, 2H; Ar-*ortho*-H), 8.09 (d, $J = 1.8$ Hz, 2H; Ar-*ortho*-H), 8.10 (d, $J = 1.9$ Hz, 2H; Ar-*ortho*-H), 8.75 (s, 1H; β-H), 8.90 (m, 3H; β-H), 8.94 (d, $J = 4.6$ Hz, 1H; β-H), 9.04 (d, $J = 4.6$ Hz, 1H; β-H), 9.32 (d, $J = 4.6$ Hz; β-H), 10.15 ppm (s, 1H; *meso*); HRMS (ESI): *m*/*z*: calcd for $C_{68}H_{83}N_4O_2$: 987.6511 $[M+H]^+$; found: 987.6501.

Dimethyl (2*E*,2′*E*,4*E*,4′*E*)-5,5′-[5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrin-2,18-yl]dipenta-2,4-dienoate (12): ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = -2.49$ (s, 2H; NH), 1.50 (s, 18H; *t*Bu), 1.56 (s, 36H; *t*Bu), 3.90 (s, 6H; OCH_3), 6.27 (d, $J = 15.1$ Hz, 2H), 7.61 (dd, $J = 15.1$, 11.0 Hz, 2H), 7.78 (dd, $J = 1.9$, 1.8 Hz, 1H; Ar-*para*-H), 7.85 (dd, $J = 1.8$, 1.4 Hz, 2H; Ar-*para*-H), 8.02 (d, $J = 1.4$ Hz, 2H; Ar-*ortho*-H), 8.03 (dd, $J = 15.1$, 11.5 Hz, 2H), 8.09 (d, $J = 1.9$ Hz, 4H; Ar-*ortho*-H), 8.68 (d, $J = 15.6$ Hz, 2H), 8.84 (d, $J = 4.6$ Hz, 2H; β-H), 8.86 (d, $J = 4.6$ Hz, 2H; β-H)), 9.18 (s, 2H; β-H), 10.31 ppm (s, 1H; *meso*); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 302.5 (3.34×10^4), 459.5 (1.53×10^5), 542.5 (1.88×10^4), 576.5 (8.17×10^3), 613.5 (7.34×10^3), 674.0 nm (2.08×10^3 м$^{-1}$ cm^{-1}); fluorescence (CH_2Cl_2): λ_{ex} = 459; λ_{em} = 677, 746 nm; HRMS (ESI): *m*/*z*: calcd for $C_{74}H_{87}N_4O_4$: 1095.6722 $[M+H]^+$; found: 1095.6749.

Dimethyl (2*E*,2′*E*,4*E*,4′*E*)-5,5′-[5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrinato(zinc)-2,18-yl]dipenta-2,4-dienoate (12–Zn): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.51–1.57 (m, 54H; CH_3 in *t*Bu), 3.89 (s, 6H; OCH_3), 6.24–6.27 (d, $J = 15.1$ Hz, 2H; double bond), 7.58–7.61 (dd, $J = 15.1$ Hz, 2H; double bond), 7.78 (s, 1H; Ar-*para*-H), 7.85 (s, 2H; Ar-*para*-H), 8.01–8.04 (dd, $J = 15.1$ Hz, 2H; double bond), 8.03 (s, 2H; Ar-*ortho*-H), 8.09 (s, 4H; Ar-*ortho*-H), 8.70–8.73 (d, J = 15.1 Hz, 2H; double bond), 8.95–8.96 (m, 4H; β-H), 9.27 (s, 2H; porphyrin β-H), 10.38 ppm (s, 1H; porphyrin *meso*-H); MS (MALDI-TOF) *m*/*z*: calcd for $C_{74}H_{84}N_4O_4Zn$: 1156.58 $[M]^+$; found: 1151.

DDQ oxidation of 10 and 11: The mixture of compound **10** and **11** was dissolved in dichloromethane and DDQ was added. The mixture was stirred at room temperature for 1 h. The crude product was purified by short silica gel column chromatography and recrystallization (CH_2Cl_2/MeOH) to provide compound **10**.

(*E*,*E*,*E*,*E*)-3,3′,3″,3‴-[5,15-Bis(3,5-di-*tert*-butylphenyl)porphyrin-2,8,12,18-tetrayl]tetraprop-2-enecarboxylic acid (13): Porphyrin tetraethyl ester **6** (10.8 mg, 0.01 mmol) was dissolved in THF (1 mL). Then, ethanol (1 mL) and aqueous NaOH (0.5 mL, 2 м, 100 equiv) were added. The solution was stirred under a N_2 atmosphere at 70 °C (oil bath) for 20 h. The solvent was removed in vacuo, and the residue was dissolved in water (50 mL). The aqueous solution was extracted with CH_2Cl_2 (×2) to get rid of the unreacted ester. The tetraacid was precipitated by the slow addition of aqueous 1 м HCl to the aqueous solution. The precipitate was filtered and washed thoroughly with water and CH_2Cl_2 to give product **13** (98%) as a dark-brown powder. ^{1}H NMR (600 MHz, [D_5]pyridine): $\delta = -1.95$ (s, 2H; NH), 1.63 (s, 36H; *t*Bu), 7.71–7.74 (d, 4H, $J = 15.9$ Hz; double bond), 8.15 (s, 2H; ArH), 8.51 (s, 4H; ArH), 9.76 (s, 4H; β-H), 9.94–9.97 (d, 4H, $J = 15.5$ Hz; double bond), 11.16 ppm (s, 2H; *meso*-H); MALDI-TOF-MS: *m*/*z*: calcd for $C_{60}H_{62}N_4O_8$ 966.46 $[M]^+$; found: 963; UV/Vis (THF): λ_{max} (ε) = 457 (1.7×10^5), 541 (1.8×10^4), 579 (7.8×10^3), 619 (6.8×10^3), 676 nm (tail, 2.3×10^3 м$^{-1}$ cm^{-1}).

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