Basic Photophysical Properties of *meso*-Bis(pyren-2-yl)porphyrin: An Isomer of Pyrene-Substituted Porphyrins

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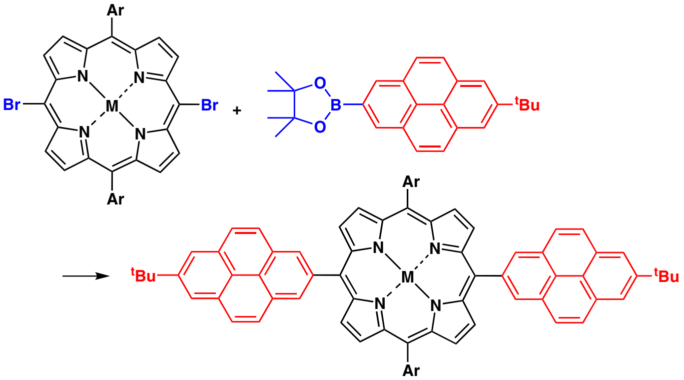

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Abstract The Suzuki–Miyaura coupling reaction of pyren-2-yl boronic acid ester with a *meso*-dibromodiphenylporphyrin derivative was carried out to give another pyrene-substituted porphyrin. The electrophilic substitution reaction occurred selectively on the porphyrin nucleus of this molecule. The introduced pyrenes acted as a light-harvesting antenna.

Key words porphyrin, pyrene, Suzuki–Miyaura coupling, light-harvesting

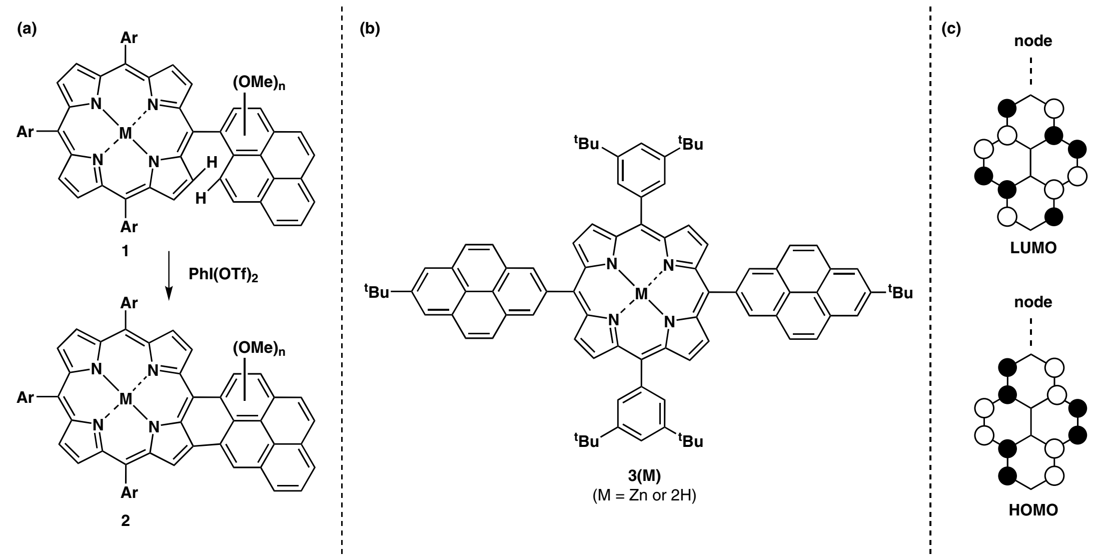
The molecular design and synthesis of porphyrinoid compounds have been attracting much attention[1] and, thanks to advances in analytical instrumentation, the synthetic chemistry of large porphyrin-based advanced materials has become an interdisciplinary science.[2] To enhance the functions of porphyrins, the introduction of a suitable substituent on the *meso*-position is a promising approach because this position has large HOMO and LUMO coefficients. Various functional groups have been introduced, including arenes such as oligo-*p*-phenylenes[3] and polycyclic aromatic hydrocarbons (PAHs), namely anthracene,[4] perylene,[5] coronene,[5] and hexa-*peri*-hexabenzocoronene.[6] We have also contributed to this research field: our pyren-1-yl-substituted porphyrin **1** opened the door to PAH-fused porphyrin chemistry (Scheme1); thus, the oxidation of **1** afforded extremely π-expanded porphyrins **2**.[7] After the publication of our work, many reports of PAH-fused π-expanded porphyrins appeared, which used PAH-substituted porphyrins as precursors.[2] In this study, we designed another pyrene-substituted porphyrin, namely *meso*-bis(pyrene-2-yl)porphyrin derivative **3(M)** (Scheme 1).

The greatest motivation for this study was the comparison with the chemistry of the pyren-1-yl porphyrins **1** because the HOMO and LUMO coefficients of the 1- and 2-positions of pyrene are markedly different; that is, the 1-position has large coefficients whereas the 2-position is the node (Scheme 1, c).[7] Here we report the synthesis of **3(M)** and describe its electrophilic reactivity and basic properties.

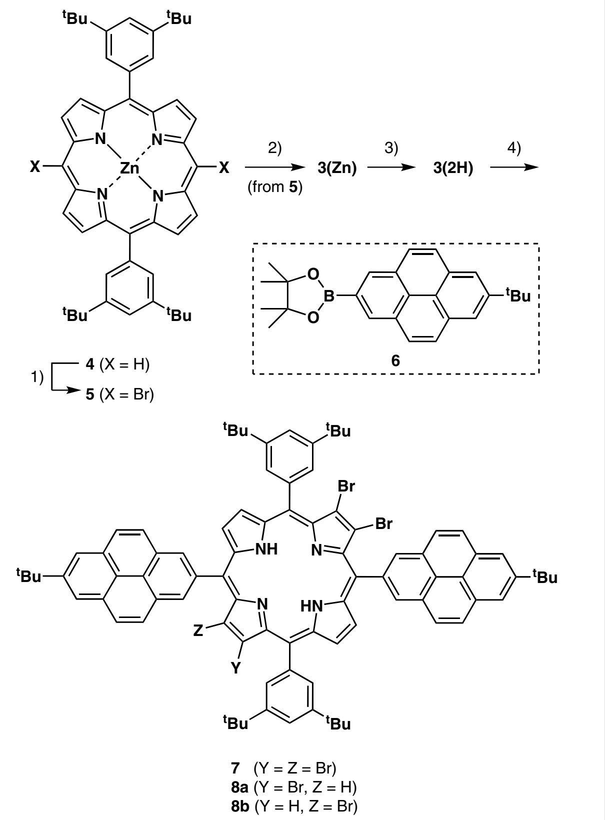
The reactions are summarized in Scheme 2. The key reaction is the Suzuki–Miyaura reaction. In contrast to the synthesis of pyren-1-yl porphyrins **1**,[7] which involved the coupling of a porphyrin having a boronic acid ester with bromopyrenes, the reaction of boronic acid of pyrene **6**[8] with *meso*-dibromoporphyrin **5**[9] was designed. The reaction proceeded smoothly (50% yield) and gave a similar yield to that of **1** (ca. 70%).[7] The six *tert*-butyl groups on pyrenes and phenyls led to a reasonable solubility of **3** in common organic solvents. The corresponding free base **3(2H)** was obtained by treatment of **3(Zn)** with mineral acid.[10]

The functionalization of **3(2H)** was examined with an eye to the future application of **3**. Given that the 1-, 3-, 6-, and 8-positions of pyrene have high reactivities in the electrophilic aromatic substitution reaction, a concerted reaction between pyrene and/or porphyrin functionalizations was examined. We then carried out the bromination of **3(2H)**. To our surprise, the substitution occurred selectively on the β-position of the porphyrin. Treatment with NBS (6 equiv) afforded tetrabromo derivative **7** as the main product in an acceptable yield (63%) along with byproducts **8a** and **8b** (20% yield).[11,12]

The absorption spectra of **3(Zn)** and reference compound **4** are shown in Figure 1 (a). A sharp and intense absorption band was observed at 429 nm (23,300 cm^{-1}) for **3(Zn)**.



Scheme 1 (a) Molecular structure of **1** and its oxidative intramolecular ring-closure reaction. (b) Molecular structure of **3(M)**. (c) Frontier orbitals (HOMO and LUMO) of pyrene.



Scheme 2 Synthesis of pyren-2-yl-substituted porphyrins. *Reagents and conditions*: (1) NBS, pyridine, $CHCl_3$; (2) **6**, $Pd(PPh_3)_4$, K_2CO_3, DMF; (3) HCl, toluene/THF; (4) NBS, $CHCl_3$.

This Soret band was shifted 1100 cm^{-1} to the lower energy region compared with that of **4** (409 nm, 24,400 cm^{-1}). Although the substitution position of pyrene is the node of this molecule and the pyrene molecules are connected nearly perpendicularly to porphyrin, a small but significant conjugation occurred between the porphyrin. The Q-band also showed bathochromic shifts (see the Supporting Information, SI1). Along with the absorptions characteristic of zinc porphyrins, three new bands were observed in the UV region, which were attributable to the excitations of pyrene; namely, Band-I, with structures around 339 nm (29,500 cm^{-1}), Band-II, with structures around 278 nm (35,000 cm^{-1}), and broadened Band-III around 249 nm (39,000 cm^{-1}). Compared with the known photophysical properties of pyrene,[13,14] those bands were assigned to the transitions of ^1L_a (transition from the pyrene HOMO to the pyrene LUMO; i.e., LUMO ← HOMO), ^1B_b (LUMO ← HOMO-1), and ^1B_a (LUMO+1 ← HOMO-1), respectively.

One of the important functions of PAH-substituted porphyrin is light harvesting; that is, the photoexcited energies of PAH moieties are transferred to porphyrin and the formed excited state of porphyrin emits light. Steady-state qualitative experiments of **3(Zn)** were carried out (Figure 1, b). Irradiation of the Q-band of **3(Zn)** at 551 nm afforded emissions at 601 and 649 nm, which are characteristic of zinc porphyrins. Irradiation of the ^1B_b band of the pyrenes at 277 nm also afforded a similar emission with 48% intensity. The irradiation at 277 nm of **4**, the reference compound having no pyrene, gave a very weak emission. This suggests that the two pyrenes acted as antenna chromophores in **3(Zn)**.[15]

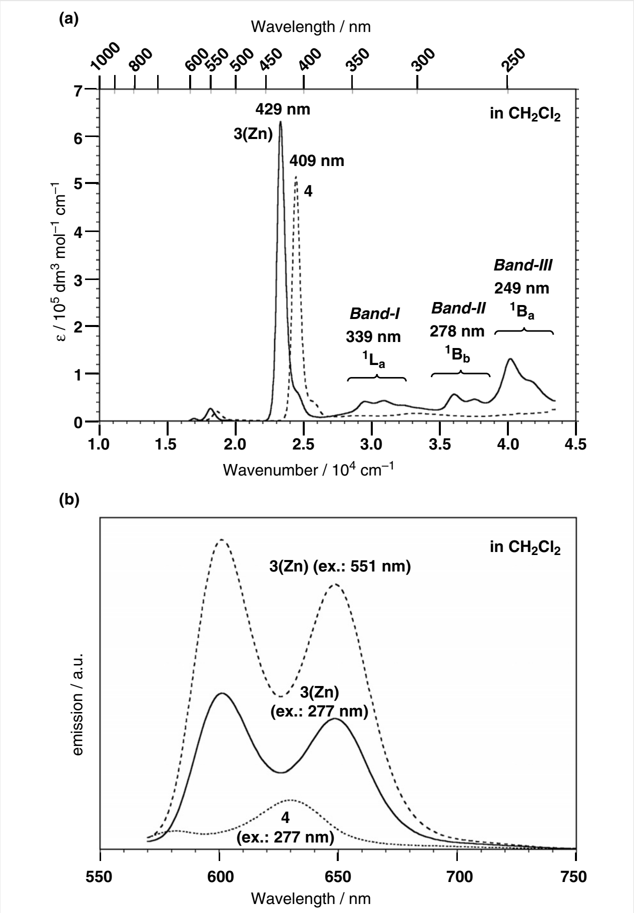


Figure 1 (a) Absorption spectra of **3(Zn)** and **4** (in CH_2Cl_2). (b) Steady-state emission spectra of **3(Zn)** excited at 551 and 277 nm and **4** excited at 277 nm (in CH_2Cl_2).

In conclusion, pyren-2-yl-substituted porphyrin **3(M)** was designed and prepared. Similar to our other pyren-2-yl-substituted arenes,[14] the corresponding boronic acid ester of pyrene **6** acted as a good synthon of pyrene and conveniently afforded **3(2H)**. PAH-substituted porphyrins **3(M)** show much potential in advanced materials chemistry because they can be used as light-harvesting materials, PAH-fused porphyrins,[7,16] sponge molecules incorporating solvents,[10] and so on. We are investigating these topics further with emphasis on the comparison of pyren-1-yl porphyrins.

The syntheses of dibromoporphyrin **4** and **5**[9] and boronic acid ester **6**[8] were carried out according to the reported method. The following reagents were used as received: K_2CO_3 (Nacalai Tesque, Inc.), $Pd(PPh_3)_4$ (Tokyo Chemical Industry Co., Ltd.), conc. HCl (Kanto Chemical Co., Inc.), THF (Kanto Chemical Co., Inc.), $NaHCO_3$ (Kanto Chemical Co., Inc.), and NBS (Wako Pure Chemical Industries, Ltd.). DMF (Wako Pure Chemical Industries, Ltd.) was distilled over KOH under N_2. The ^1H NMR spectra were recorded with a Bruker Avance III 500 (500 MHz for ^1H) spectrometer in $CDCl_3$ (Acros Organics Co., Inc.) with TMS as the internal standard. Infrared spectra were recorded with a Shimadzu FTIR-8400 instrument using KBr pellet techniques in the range of 500 to 4000 cm^{-1}. The absorption spectra were recorded with a Shimadzu UV-3600 using spectrophotometric grade CH_2Cl_2. The fluorescence spectra were recorded with a JASCO FP-6500. Mass spectra were recorded with a Bruker micrOTOF II SDT1. Melting points were measured with a YANAKO MP-S3 apparatus. The observed melting points are uncorrected. Silica gel thin-layer chromatography (Merck & Co., Inc.) was performed using Silica Gel 60 F_{254} aluminum sheets from Merck Co. Ltd. Column chromatography was performed using Neutral Silica Gel 60N from Kanto Chemical Co., Inc. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Other experimental details were reported previously.[17]

Compound 3(Zn)

A mixture of dibromoporphyrin **5** (90.8 mg, 100 μmol),[9] boronic acid of pyrene **6** (96.1 mg, 250 μmol, 2.5 equiv),[8,18] K_2CO_3 (55.4 mg, 400 μmol, 4 equiv), and freshly distilled DMF (20 mL) was introduced into a Schlenk flask and purged with N_2. Against the stream of N_2, $Pd(PPh_3)_4$ (11.6 mg, 10 μmol, 0.1 equiv) was added. The reaction mixture was stirred and heated at 70 °C under N_2 for 17 h. TLC analysis showed the disappearance of **5** and the formation of a new product ($R_f = 0.21$; *n*-hexane/$CHCl_3$/pyridine, 2:1:0.02). The reaction mixture was diluted with toluene and then washed with water three times and brine once. The organic layer was dried and the solvent was removed under reduced pressure. The crude product was purified by chromatography on SiO_2 (*n*-hexane/$CHCl_3$/pyridine, 2:1:0.02) to give the desired product. An analytical sample was obtained by recrystallization from $CHCl_3$.

Yield: 63.0 mg (50%); purple solid; mp >300 °C.

^1H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 9.06$ (s, 4 H), 9.90 (d, $J = 4.7$ Hz, 4 H), 8.00 (d, $J = 4.7$ Hz, 4 H), 8.39 (s, 4 H), 8.29 (d, $J = 8.8$ Hz, 4 H), 8.25 (d, $J = 8.8$ Hz, 4 H), 8.11 (d, $J = 1.9$ Hz, 4 H), 7.77 (t, $J = 1.9$ Hz, 2 H), 1.68 (s, 18 H), 1.50 (s, 36 H).

IR (KBr): 3040 (m), 2963 (s), 2904 (m), 2868 (m), 1592 (m), 1363 (m), 1226 (m), 1004 (m), 941 (m), 801 (m), and 715 (s) cm^{-1}.

UV/Vis (CH_2Cl_2): λ_{max} (ε, $dm^3mol^{-1}cm^{-1}$) = 551 (26,600), 537 (98,800), 429 (631,800), 408 (shoulder, 62,200), 339 (41,400), 323 (42,300), 278 (56,800), 267 (46,100), 249 (131,400), 238 (78,500) nm.

HRMS (ESI): *m*/*z* $[M + 1]^+$ calcd for $C_{88}H_{84}N_4Zn + H$: 1261.6060; found: 1261.5991 (100%).

Anal. Calcd for $C_{88}H_{84}N_4Zn$: C, 83.68; H, 6.70; N, 4.44. Found: C, 82.97; H, 6.72; N, 4.41.

Compound 3(2H)

A mixture of **3(Zn)** (45.0 mg, 0.035 mmol), toluene (80 mL), and THF (10 mL) was stirred at r.t. Five drops of concd HCl were added and the reaction mixture was stirred at r.t. The color of the reaction mixture changed from red-purple to dark-purple and finally green. After 15 min, the reaction mixture was washed with water, aq. $NaHCO_3$, and brine. This solution was passed through a short SiO_2 column to afford **3(2H)** (170.6 mg, 95%). An analytical sample was obtained by recrystallization from $CHCl_3$.

Purple solid; mp >300 °C.

^1H NMR (500 MHz, $CDCl_3$, TMS): $\delta = 9.05$ (s, 4 H), 9.89 (d, $J = 4.7$ Hz, 4 H), 8.77 (d, $J = 4.7$ Hz, 4 H), 8.39 (s, 4 H), 8.29 (d, $J = 8.8$ Hz, 4 H), 8.26 (d, $J = 8.8$ Hz, 4 H), 8.11 (d, $J = 1.9$ Hz, 4 H), 7.77 (t, $J = 1.9$ Hz, 2 H), 1.68 (s, 18 H), 1.50 (s, 36 H), –2.40 (s, 2 H).

IR (ATR): 3312 (m), 3042 (m), 2961 (s), 2925 (m), 2854 (m), 1597 (m), 1477 (m), 1362 (m), 1240 (m), 916 (m), 885 (m), 803 (s), and 713 (s) cm^{-1}.

UV/Vis (CH_2Cl_2): λ_{max} (ε, $dm^3mol^{-1}cm^{-1}$): 649 (6,100), 592 (7,400), 555 (12,800), 519 (23,300), 428 (469,500), 408 (shoulder, 104,800), 369 (30,300), 339 (53,200), 324 (49,000), 300 (33,000), 278 (65,600), 267 (56,800), 249 (124,600), 241 (90,400) nm.

HRMS (ESI): *m*/*z* $[M + 1]^+$ calcd for $C_{88}H_{86}N_4$ + H: 1199.6925; found: 1199.6847 (100%).

Anal. Calcd (%) for $C_{88}H_{86}N_4$: C, 88.10; H, 7.23; N, 4.67. Found: C, 87.02; H, 7.33; N, 4.58.

Compound 7

A solution of purified NBS (85.7 mg of NBS dissolved in 6 mL of distilled $CHCl_3$, 481.5 mol, 6 equiv) was added to a solution of **3(2H)** (96.1 mg, 80.1 μmol, dissolved in 50 mL of distilled $CHCl_3$) at r.t. over 10 min. After the addition of the NBS solution, the reaction mixture was heated to reflux for 8 h. TLC analysis indicated the disappearance of **3(2H)** (R_f = 0.17; *n*-hexane/toluene, 2:1) and the formation of desired product **7** (R_f = 0.14) and tribromo compound (see below). The mixture was cooled to r.t. and the reaction was terminated by adding acetone (15 mL). The solvent was removed under reduced pressure and imide was removed by short SiO_2 column chromatography using $CHCl_3$ as eluent. Further purification was carried out by SiO_2 column chromatography (*n*-hexane/$CHCl_3$, 1:2) to give **7** (75.7 mg, 63%) and trisubstituted derivative (22.7 mg, 20%). An analytical sample of **7** was obtained by recrystallization from hot toluene.

Purple solid; mp > 300.0 °C.

^1H NMR (500 MHz, $CDCl_3$, TMS): δ = 8.99 (s, 4 H), 8.78 (d, *J* = 4.7 Hz, 2 H), 8.62 (d, *J* = 4.7 Hz, 2 H), 8.39 (s, 4 H), 8.31 (d, *J* = 8.8 Hz, 4 H), 8.29 (d, *J* = 8.8 Hz, 4 H), 8.01 (d, *J* = 1.9 Hz, 4 H), 7.80 (t, *J* = 1.9 Hz, 2 H), 1.68 (s, 18 H), 1.52 (s, 36 H), –2.74 (s, 2 H).

IR (KBr): 3373 (m), 3042 (m), 2960 (s), 1594 (m), 1475 (m), 1362 (m), 1226 (m), 1002 (s), 953 (m), 929 (m), 713 (m) cm^{-1}.

UV/Vis (CH_2Cl_2): λ_{max} (ε, $dm^3mol^{-1}cm^{-1}$) = 679 (10,900), 536 (20,400), 440 (289,000), 340 (63,500), 325 (49,000), 279 (66,400), 267 (65,800), 248 (105,200) nm.

HRMS (ESI): *m*/*z* $[M + 1]^+$ calcd for $C_{88}H_{82}Br_4N_4$ + H: 1515.3327; found: 1515.3303 (100%).

Anal. Calcd for $C_{88}H_{82}Br_4N_4$: C, 69.75; H, 5.45; N, 3.70. Found: C, 70.06; H, 5.75; N, 3.55.

The fraction eluting first having R_f = 0.22 was characterized as a mixture of the isomers of tribiromo derivatives on the basis of mass spectra and complicated ^1H NMR signals; MS (ESI): *m*/*z* (%) = 1436.4 (100) $[M + 1]^+$.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588715.

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However, the marked disorder of solvent molecules prevented the complete analysis. Provisional results are shown in the Supporting Information SI2. CCDC 1520375 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

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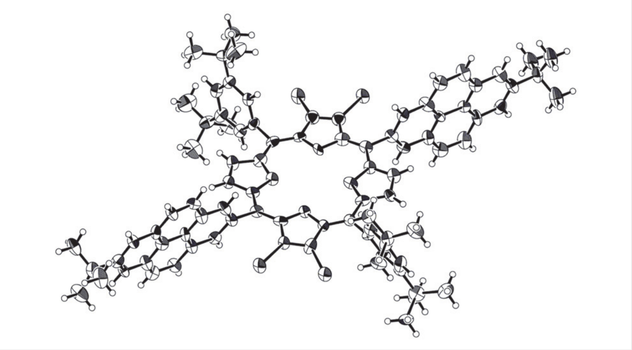

Figure 2

(15) Similar experiments were carried out in polar solvent DMF and similar results were obtained; that is, energy transfer occurred from pyrenes to porphyrin.

(16) One of the objectives of this study was to synthesize pyrene-fused porphyrins. Attempts to obtain such porphyrins under oxidative conditions, such as $FeCl_3$ in $MeNO_2$, DDQ/$Sc(OTf)_3$, etc., were unsuccessful. Furthermore, Pd-catalyzed intramolecular C–C bond formation reactions on tetrabromide **7** also failed, see: Saegusa, Y.; Ishizuka, T.; Komamura, K.; Shimizu, S.; Kotani, H.; Kobayashi, N.; Kojima, T. *Phys. Chem. Chem. Phys.* **2015**, *17*, 15001; details of the oxidation reactions of **3(M)** will be reported elsewhere.

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