Supporting Information

Synthesis of 5,10,15-triazaporphyrins – effect of benzo-annulation on the electronic structures

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i. Experimental

General procedure: Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer. Magnetic circular dichroism (MCD) spectra were recorded on a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet, which produces magnetic fields of up to 1.09 T (1 T = 1 tesla) with both parallel and antiparallel fields. The magnitudes were expressed in terms of molar ellipticity per tesla (\([\theta]_M / \text{deg dm}^3 \text{mol}^{-1} \text{cm}^{-1} \text{T}^{-1}\)). Fluorescence spectra were measured on a Hitachi F-4500 spectrofluorimeter. 1H NMR spectra were recorded on a JEOL ECA-600 spectrometer (operating at 594.17 MHz) and a Bruker AVANCE 400 spectrometer (operating at 400.33 MHz) using a residual solvents as internal references for 1H (\(\delta = 7.26 \text{ ppm for CDCl}_3 \) and 2.09 ppm for toluene-\(d_8\)). High resolution mass spectra were recorded on a Bruker Daltonics Apex-III spectrometer or on an AB SCIEX 4800 Plus MALDI TOF/TOF Analyzer. Preparative separations were performed by alumina gel column chromatography (Wako), preparative thin layer plate (Silica gel 60, F254, Merck), and recycling preparative GPC-HPLC (JAI LC-9201 with preparative JAIGEL-2H, 2.5H, and 3H columns). All reagents and solvents were of commercial reagent grade and were used without further purification except where noted.

Crystallographic data collection and structure refinement: Suitable crystals of 1 and ruthenium complex of 3a were obtained from slow evaporation of dichloromethane in the presence of water and slow diffusion of hexane into a chloroform solution in the presence of a slight amount of pyridine, respectively. Data collection for 1 and ruthenium complex of 3a was carried out at at –173 ºC on a Bruker APEXII CCD diffractometer with MoKα radiation (\(\lambda = 0.71073 \ \text{Å}\)). The structures were solved by direct methods (SHELXS-97\(^1\) or Sir 2004\(^2\)) and refined using a full-matrix least square technique (SHELXL-97\(^3\)). Yadokari-XG\(^3\) software was used as a GUI for SHELXL-97. CCDC-862131 and 864016 contain the supplementary crystallographic data for 1 and ruthenium complex of 3a, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via
There is one residual electron density larger than 1 in the unit cell of 1 probably due to the effect of electron-rich bromine atoms. Because of the presence of \( \text{C}_2 \) symmetry axis, the position of NH-hydrogen atom could not be determined and refined positionally restrained conditions using DFIX command. There are three DFIX restraints in the final refinement.

Some large Q peaks were found due to disorder of solvent molecule(s) in the case of ruthenium complex of 3a, which is (are) mostly chloroform. As we failed to model them properly, the rest molecules were refined without the effect of the solvent molecule(s) by the Platon squeeze technique. Despite using Platon squeeze for smoothing, two residual Q peaks having electron densities greater than 1.0 (1.29) are still observed close to the central ruthenium mainly due to its large electron density. The tert-butyl substituents were also disordered.

**Computational methods:** The Gaussian 09\textsuperscript{4} software package was used to carry out DFT and TDDFT calculations at the B3LYP/6-31G(d) level. Structural optimization was performed on model compounds of 3a, 3b, and 3c in which the peripheral tert-butylphenyl substituents were replaced by hydrogen atoms or phenyl groups for simplicity.

**General synthetic procedures:**

**5-Pentafluorophenyl-1,9-dibromodipyrromethene** 1: To a dry THF solution (30 mL) of 5-pentafluorophenylidipyrromethane (0.50 g, 1.6 mmol) at ~78 °C was added dropwise a THF solution (15 mL) of N-bromosuccinimide (0.63 g, 3.5 mmol). After the consumption of the starting material, 50 mL of aqueous Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} was added to the reaction mixture. The organic phase was extracted with dichloromethane, and the resultant mixture was dried over MgSO\textsubscript{4}. A brown oil was obtained after removing solvent under reduced pressure. The oil was dissolved in THF (30 mL) and DDQ (0.50 g, 2.2 mmol) was added. The mixture was stirred for 10 min at r.t., and then passed through an alumina column. The target compound was purified by silica gel column chromatography, and 1 was obtained as a red powder (0.58 g, 1.2 mmol, 77%). MALDI-TOF-MS (m/z): 468.9 (calcd for C\textsubscript{15}H\textsubscript{6}N\textsubscript{2}F\textsubscript{5}Br\textsubscript{2} = 468.8 [M\textsuperscript{+}+H]); \(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz, 298 K): \( \delta = 6.37 \) ppm (s, 4H; \( \beta \)-pyrrole); UV/vis (CHCl\textsubscript{3}): \( \lambda_{\text{max}} \) [nm] = 456.

**meso-Pentafluorophenyl-substituted dibenzo-5,10,15-triazaporphin** 3a: A mixture of 1 (0.12 g, 0.26 mmol) and 5,6-di-\textit{p}-tert-butylphenyl-1,3-diiminoisoindoline 2a (0.22 g, 0.54 mmol) in p-xylene (1.0 mL) was stirred at r.t. for a few seconds. After addition of dimethylaminomethanol (DMAE, 1.0 mL), the mixture was heated at 145 °C for 1 hour. The reaction mixture was purified by silica gel column chromatography using CH\textsubscript{2}Cl\textsubscript{2}/hexane (1:2 (v/v)), and the final purification was carried out by silica gel thin layer chromatography to provide 3a as a blue powder (42 mg, 15%). HR-ESI-FT-ICR-MS (m/z): 1108.5052 (calcd for C\textsubscript{71}H\textsubscript{63}N\textsubscript{7}F\textsubscript{5} = 1108.5060 [M\textsuperscript{+}+H]); \(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz, 298 K): \( \delta = 9.14 \) ppm (s, 4H; \( \alpha \)-benzo), 8.98 (s, 2H; \( \alpha \)-benzo), 8.45 (d, \( J = 4.30 \) Hz, 2H; \( \beta \)-pyrrole), 8.22 (d, \( J = 4.00 \) Hz, 2H; \( \beta \)-pyrrole).
**meso-Pentafluorophenyl-substituted dinaphtho-5,10,15-triazaporphyrin 3b:** 3b was synthesized from a reaction of 1 (0.15 g, 0.32 mmol) and 6,7-di-p-tert-butylphenyl-1,3-diiminobenz[f]isoindole 2b (0.30 g, 0.65 mmol) in p-xylene (1.0 mL) and DMAE (1.0 mL) and similarly purified as in the case of 3a. 3b was then obtained as a green powder in 1.6% yield (6.0 mg). HR-ESI-FT-ICR-MS (m/z): 1208.5374 (calcd for C$_{79}$H$_{67}$N$_7$F$_5$ = 1208.5373 [M++H]); 1H NMR (toluene-d$_8$, 600 MHz, 298 K): δ = 9.19 (s, 2H; naphtho), 9.15 (s, 2H; naphtho), 8.28 (d, $J$ = 4.20 Hz, 2H; β-pyrrole), 8.22 (s, 2H; naphtho), 8.21 (s, 2H; naphtho), 7.80 (d, $J$ = 3.60 Hz, 2H; β-pyrrole), 7.50 (d, $J$ = 8.40 Hz, 4H; phenyl), 7.45 (d, $J$ = 7.80 Hz, 4H; phenyl), 7.33 (d, $J$ = 8.40 Hz, 4H; phenyl), 7.30 (d, $J$ = 7.80 Hz, 4H; phenyl), 1.31 (s, 18H; t-butyl), 1.29 ppm (s, 18H; t-butyl); UV/vis (CHCl$_3$): $\lambda_{\text{max}}$ [nm] (ε) = 376 (81200), 595 (61600), 633 (76400).

**meso-Pentafluorophenyl-substituted 5,10,15-triazaporphyrin 3c:** 3c was synthesized from a reaction of 1 (1.7 g, 3.6 mmol) and 3,4-di-p-tert-butylphenyl-2,5-pyrrolenediimine 3c (2.5 g, 6.9 mmol) in p-xylene (6.0 mL) and DMAE (6.0 mL) and similarly purified as in the case of 3a. 3c was then obtained as a purple powder in 0.11% yield (4.0 mg). HR-ESI-FT-ICR-MS (m/z): 1008.4745 (calcd for C$_{63}$H$_{59}$N$_7$F$_5$ = 1008.4747 [M++H]); 1H NMR (CDCl$_3$, 600 MHz, 298 K): δ = 9.16 (d, $J$ = 4.80 Hz, 2H; β-pyrrole), 8.74 (d, $J$ = 4.80 Hz, 2H; β-pyrrole), 8.33 (d, $J$ = 7.80 Hz, 4H; phenyl), 8.28 (d, $J$ = 8.40 Hz, 2H; phenyl), 7.72 (d, $J$ = 6.60 Hz, 4H; phenyl), 7.61 (d, $J$ = 8.40 Hz, 4H; phenyl), 1.53 (s, 18H; t-butyl), 1.52 (s, 18H; t-butyl), –1.29 ppm (s, 2H; inner-NH); UV/vis (CHCl$_3$): $\lambda_{\text{max}}$ [nm] (ε) = 367 (62700), 564 (29300), 637 (43700).

**Ruthenium complex of 3a:** By following the literature procedure, 5 3a was reacted with triruthenium dodecacarbonyl in benzonitrile at 200 ºC for an hour. Highly polar blue fraction in silica gel column was collected. The axial ligands at this stage were carbonyl, which was replaced by a pyridyl group during crystallization. MALDI-TOF-MS (m/z): 1207.3892 (calcd for C$_{71}$N$_7$H$_{60}$F$_5$Ru = 1207.3874 [M+2CO]); UV/vis (CHCl$_3$): $\lambda_{\text{max}}$ [nm] (ε) = 367 (62700), 564 (29300), 637 (43700).

**ii. X-ray crystal structure of 1**

*Figure S1.* X-ray crystal structure of 1. The thermal ellipsoids were scaled to the 50% probability level.

Crystallographic data for 1: C$_{13}$H$_{5}$N$_2$Br$_2$F$_5$, $M_w$ = 468.03, monoclinic, space group C2/c (no. 13), $a = 13.432(6)$, $b = 15.534(7)$, $c = 7.285(3)$ Å, $\beta = 93.759(6)^\circ$, $V = 1516.6(12)$ Å$^3$, $Z = 4$, $\rho_{\text{calcld}} = 2.050$ g/cm$^3$, $T = -173(2)$ ºC, 5116 measured reflections, 1332 unique reflections ($R_{int} = 0.0508$), $R = 0.0455$ ($I > 2\sigma(I)$), $R_w = 0.1309$ (all data), GOF = 1.056, CCDC 862131.
iii. $^1$H NMR spectra of 3a, 3b, and 3c

![1H NMR spectra of 3a, 3b, and 3c](image)

Figure S2. $^1$H NMR spectra of 3a (top), 3b (middle), and 3c (bottom) in CDCl$_3$ for 3a and 3c and in toluene-$d_8$ for 3b. * indicates residual solvent peaks.

iv. Absorption and fluorescence spectra of 3a and 3b

![Absorption and fluorescence spectra of 3a and 3b](image)

Figure S3. Absorption (solid line) and fluorescence (dashed line) spectra of 3a (left) and 3b (right) in CHCl$_3$. 

Electronic Supplementary Material (ESI) for Chemical Communications

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v. DFT and TDDFT calculations of triazaporphyrins

Figure S4. Partial MO diagram of 3a (middle), 3b (right), and 3c (left). Peripheral p-tert-butyphenyl substituents are included in these calculations.
Table S1. Selected transition energies and wave functions of 3a, 3b, and 3c in the Q band region calculated by the TDDFT (B3LYP/6-31G(d)) method. Peripheral \textit{p}-tert-butylphenyl substituents are included in these calculations.

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<th>wave function$^\text{[b]}$</th>
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[a] Oscillator strength. [b] Wave functions based on the eigenvectors predicted by TDDFT. H and L represent the HOMO and LUMO, respectively.
Figure S5. Partial MO diagram of 3a (middle), 3b (right), and 3c (left). Peripheral $p$-tert-butylphenyl substituents are not included in these calculations.
Table S2. Selected transition energies and wave functions of 3a, 3b, and 3c in the Q band region calculated by the TDDFT (B3LYP/6-31G(d)) method. Peripheral p-tert-butylphenyl substituents are not included in these calculations.

<table>
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[a] Oscillator strength. [b] Wave functions based on the eigenvectors predicted by TDDFT. H and L represent the HOMO and LUMO, respectively.

vi. References