Supplementary data

Reversible caterpillar-motion-like isomerization in a \(N,N'\)-dimethyl hexaphyrin(1.1.1.1.1.1) induced by two-electron oxidation or reduction

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1. Compound Data

- **15,30-bis(2,4,6-trifluorophenyl)-5,10,20,25-tetrakis(pentafluorophenyl)[26]hexaphyrin 3**

  1H NMR (600 MHz, CDCl3): δ = -2.55 (s, 4H, inner βCH), -2.16 (br, NH), 7.80 (m, 4H, phenyl), 9.15 (d, J = 4.6 Hz, 4H, outer βCH), and 9.41 (d, J = 4.4 Hz, 4H, outer βCH) ppm; UV/Vis(CH2Cl2): λmax = 1022, 894, 772, 715, and 568 nm; ESI-TOF-MS (positive-mode) (%intensity): C66H19F26N6 [M+H]: calcd.: 1389.13, found: 1389.11 (100).

- **5,20-bis(2,4,6-trifluorophenyl)-10,15,25,30-tetrakis(pentafluorophenyl)[26]hexaphyrin 4**

  4 was not obtained as a pure form. 1H NMR (600 MHz, CDCl3): δ = -2.60 (d, J = 4.1 Hz, 2H, inner βCH), -2.54 (d, J = 3.8 Hz, 2H, inner βCH), -2.16 (br, NH), 7.20-7.90 (phenyl), 9.08 (d, J = 4.6 Hz, 2H, outer βCH), 9.11 (d, J = 5.0 Hz, 2H, outer βCH), 9.42 (not clear, outer βCH), and 9.52 (d, J = 4.6 Hz, 2H, outer βCH) ppm.

- **5,20-bis(2,4,6-trifluorophenyl)-10,15,25,30-tetrakis(pentafluorophenyl)[28]hexaphyrin 6**

  1H NMR (600 MHz, CDCl3): δ = 2.31 (s, 2H, inner βCH), 2.44 (s, 2H, inner βCH), 3.98 (s, 2H, outer NH), 6.71 (t, J = 7.8 Hz, phenyl), 7.65 (d, J = 4.6 Hz, 2H, outer βCH), 7.68 (d, J = 5.0 Hz, 2H, outer βCH), 7.70 (d, J = 4.6 Hz, 2H, outer βCH), and 7.80 (d, J = 4.6 Hz, 2H, outer βCH) ppm; UV/Vis(CH2Cl2): λmax = 763, 591, 445, and 389 nm; ESI-TOF-MS (positive-mode) (%intensity): C66H19F26N6 [M+H]: calcd.: 1391.14, found: 1391.17 (100).

- **meso-pentafluorophenyl N-methyl[26]hexaphyrin 7**

  ![Diagram of meso-pentafluorophenyl N-methyl[26]hexaphyrin 7](image)

Hexaphyrin 1 (50 mg, 0.0342 mmol) was added to a solution of TBAF·3H2O (100 mg, large excess) and CH3I (11 µl, 0.171 mmol) in CH2Cl2 (22 ml) and the resulting mixture was refluxed overnight. The solution was washed with water and evaporated. The reaction mixture was separated by silica gel
column chromatography with a 1:1 mixture of CH$_2$Cl$_2$ and hexane as an eluent. After recrystallization from a mixture of CH$_2$Cl$_2$ and hexane, N-methyl hexaphyrin 7 was obtained as green solids (21.5 mg, 43 %) together with the recovery of 1 (19 mg, 38%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta = -3.31$ (s, 3H, methyl), -1.70 (d, $J = 4.1$ Hz, 1H, inner $\beta$CH), -1.08 (d, $J = 4.1$ Hz, 1H, inner $\beta$CH), -0.96 (d, $J = 4.5$ Hz, 1H, inner $\beta$CH), -0.78 (br, NH), -0.61 (d, $J = 4.5$ Hz, 1H, inner $\beta$CH), 7.80 (d, $J = 4.6$ Hz, 1H, outer $\beta$CH), 8.15 (d, $J = 4.6$ Hz, 1H, outer $\beta$CH), 8.62 (d, $J = 4.8$ Hz, 1H, outer $\beta$CH), 8.71 (d, $J = 4.8$ Hz, 1H, outer $\beta$CH), 8.72 (d, $J = 4.8$ Hz, 1H, outer $\beta$CH), 8.77 (d, $J = 4.8$ Hz, 1H, outer $\beta$CH), 9.06 (d, $J = 4.8$ Hz, 1H, outer $\beta$CH), and 9.14 (d, $J = 4.8$ Hz, 1H, outer $\beta$CH) ppm; UV/Vis(CH$_2$Cl$_2$): $\lambda_{\text{max}}(\varepsilon) = 1041$ (1800), 896 (4100), 774 (11000), 717 (19000), 570 (190000), and 406 (23000) nm; ESI-TOF-MS (positive-mode) (%intensity) : C$_{67}$H$_{17}$F$_{30}$N$_6$ [M+H]: calcd. : 1475.1030, found : 1475.0851 (100).

- meso-pentafluorophenyl NN’-dimethyl [26]hexaphyrin 8

A solution of TBAF in THF (10 mM, 11 ml, 0.00684 mmol) was added into a solution of 1 (50 mg 0.0342 mmol) and CH$_3$I (2 ml, large excess) in THF (60ml) and ther resulting mixture was refluxed for 1 day under nitrogen. The solution was washed with water and evaporated. The reaction mixture was separated by silica gel column chromatography with a 1:1 mixture of CH$_2$Cl$_2$ and hexane to give N,N’-dimethyl hexaphyrin 8 as green solids (24 mg, 50 %). $^1$H NMR (600 MHz, CDCl$_3$): $\delta = -2.93$ (s, 6H, methyl), -0.95 (s, 2H, inner $\beta$CH), -0.07 (s, 2H, inner $\beta$CH), 7.68(s, 2H, outer $\beta$CH), 8.03 (s, 2H, outer $\beta$CH), 8.38 (s, 2H, outer $\beta$CH), and 8.57 (s, 2H, outer $\beta$CH) ppm; UV/Vis(CH$_2$Cl$_2$): $\lambda_{\text{max}}(\varepsilon [M^{-1}cm^{-1}]) = 919$ (1900), 872 (1600), 787 (12000), 722 (14000), 578 (160000), and 406 (22000) nm; ESI-TOF-MS (positive-mode) (%intensity) : C$_{68}$H$_{19}$F$_{30}$N$_6$ [M+H]: calcd. : 1489.1197, found : 1489.1170 (100).

- N,N’-dimethyl [28]hexaphyrin 9

$N,N'$-Dimethyl [26]hexaphyrin 8 was dissolved in CH$_2$Cl$_2$, to which NaBH$_4$ and methanol were added carefully. The resulting mixture was stirred for 1 h and quenched with water. $N,N'$-Dimethyl [28]hexaphyrin 9 was obtained as green solids by recrystallization from a mixture of CH$_2$Cl$_2$ and...
methanol. $^1$H NMR (600 MHz, CDCl3): $\delta$ = 2.49 (s, 6H, methyl), 4.37 (s, 4H, inner $\beta$CH), 7.17 (s, 8H, outer $\beta$CH) and 7.48 (br, inner NH) ppm; UV/Vis(CH$_2$Cl$_2$): $\lambda$$_{\text{max}}$($\epsilon$ [M$^{-1}$cm$^{-1}$]) = 769 (9800), 606 (140000), and 434 (32000) nm.; ESI-TOF-MS (negative-mode) (%intensity) : C$_{68}$H$_{19}$F$_{30}$N$_6$ [M−H]: calcd.: 1489.1198, found : 1489.0729 (100).

- meso-hexakis(pentafluorophenyl) [26]hexaphyrin dianion

Dianion of 1 was prepared by addition of excess amounts of TBAF or TBAT. $^1$H NMR (600 MHz, CDCl3): $\delta$ = -4.33 (s, 4H, inner $\beta$CH), 9.21 (s, 4H, outer $\beta$CH) and 9.51 (s, 4H, outer $\beta$CH) ppm; UV/Vis(CH$_2$Cl$_2$): $\lambda$$_{\text{max}}$($\epsilon$) = 975 (16000), 880 (22000), 823 (20000), 617 (370000), and 601 (570000) nm.

2. $^1$H-NMR Spectra.

![Fig. S1 $^1$H NMR spectrum of 3 in CDCl$_3$.](image-url)
Fig. S2 $^1$H NMR spectrum of 3 and 4 in equilibrium state in CDCl₃.
Fig. S3 $^1$H NMR spectrum of 5 and 6 in equilibrium state in CDCl$_3$. The ethyl quartet at 4.12 ppm was due to contaminated ethyl acetate.
**Fig. S4** $^1$H NMR spectrum of 7 in CDCl$_3$.

**Fig. S5** $^1$H NMR spectrum of 8 in CDCl$_3$. 
Fig. S6 $^1$H NMR spectrum of 9 in CDCl$_3$.

Fig. S7 $^1$H NMR spectrum of dianion of 1 in CDCl$_3$.

3. UV-visible Absorption Spectra.

Fig. S8 UV/visible absorption spectrum of 3 in CH$_2$Cl$_2$. 
Fig. S9 UV/visible absorption spectrum of 5 in CH$_2$Cl$_2$.

Fig. S10 UV/visible absorption spectrum of 7 in CH$_2$Cl$_2$. 
Fig. S11 UV/visible absorption spectrum of 8 in CH$_2$Cl$_2$.

Fig. 12 UV/visible absorption spectrum of 9 in CH$_2$Cl$_2$.

Fig. S13 ESI-TOF mass spectrum of 3 (4). Upper: observed; lower: calculated.

Fig. S14 ESI-TOF mass spectrum of 5 (6). Upper: observed; lower: calculated.
Fig. S15 ESI-TOF mass spectrum of 7. Upper: observed; lower: calculated.

Fig. S16 ESI-TOF mass spectrum of 8. Upper: observed; lower: calculated.
5. Determination of the activation barrier for isomerization.

\[-E_a/R = -11789\]
\[E_a = 11789/8.3 = 1420 \text{ [J/mol]} = 1.42 \text{ [KJ/mol]}\]

Fig. S19 Comparison of mean plane deviation diagrams of 8 and 9.

7. Structural comparison of 1 and ist dianion.

Fig. S20 Structure of 1.
Fig. S21 Structure of dianion of 1.