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A non-fused mono-*meso*-free pentaphyrin and its rhodium(I) complex†

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5,10,15,20-Tetrakis(pentafluorophenyl) [22]pentaphyrin(1.1.1.1.1) 7 was synthesised and its bis-rhodium(I) complex 12 has been revealed to be a non-fused, yet planar pentaphyrin with an inverted pyrrole. Both 7 and 12 are aromatic, showing sharp Soret-like bands and diatropic ring currents.

A recent surge in the chemistry of expanded porphyrins is due largely to their attractive optical, electrochemical, and coordination properties arising from their large π-conjugation frameworks.[1] Structures of expanded porphyrins depend on many factors such as the number of pyrrole units, the bridges, the *β*- or *meso*-substituents, the coordinated metals, the availability of hydrogen bonding interactions, and the degree of protonation. Among these, pentaphyrins(1.1.1.1.1) that bear five pyrroles regularly connected through *meso*-carbons, should contain structural frustration because of the addition of a pyrrole and a *meso*-carbon to the planar porphyrin skeleton. While *β*-alkylated pentaphyrins **1**[2] and **2**,[3] and doubly *N*-confused mono-oxygenated pentaphyrin **3**[4] were shown to be non-fused macrocycles, *meso*-aryl-substituted pentaphyrin **4**, formed from our modified Rothemund–Lindsey protocol,[5] was forced to take an *N*-fused conformation with two inverted pyrroles, because of severe steric congestion (Chart 1).[6] This *N*-fused pentaphyrin provided a Möbius aromatic molecule as the minimum size of expanded porphyrins[7] and multiply fused molecules upon phosphorus insertion.[8] Beside these, conformational studies of the regular pentaphyrins(1.1.1.1.1) should be a useful step in better understanding the structure–conformation relationship of expanded porphyrins. Recently, we revealed that the removal of two *meso*-pentafluorophenyl substituents from regular [26]hexaphyrin **5** to 5,10,20,25-tetrakis(pentafluorophenyl) substituted hexaphyrin **6** led to a drastic conformational change from a rectangular to a spectacle shape owing to the substantial steric relief and favorable intramolecular hydrogen bonding interactions.[9] We thought that the similar removal of the *meso*-pentafluorophenyl substituent would cause large conformational and stability changes of pentaphyrins. In this paper, we report the synthesis of mono-*meso*-free pentaphyrin **7** that takes a non-fused and planar conformation with an inverted pyrrole.

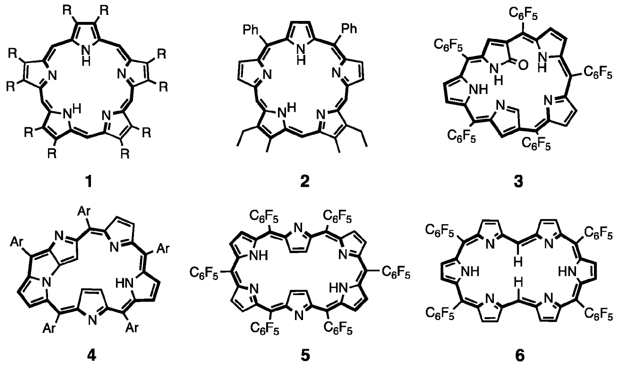
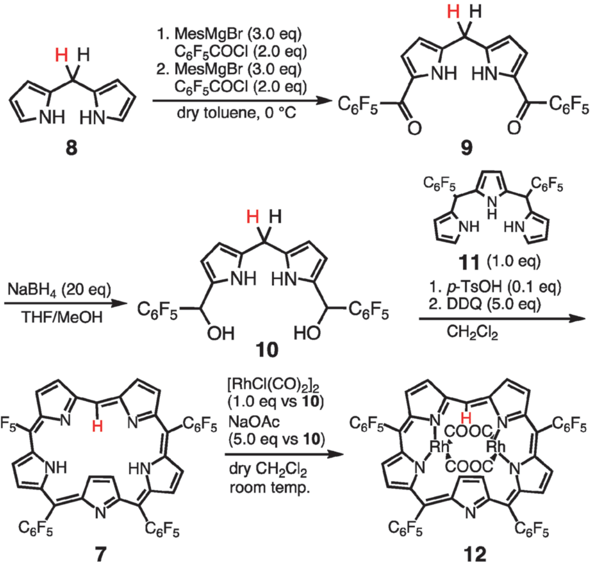


Chart 1 Various conformations of pentaphyrins and *meso*-free expanded porphyrins.

We planned to synthesise mono-*meso*-free pentaphyrin **7** by the cross-condensation of tripyrrane **11**[10] and the *meso*-free dipyrromethane dicarbinol **10** (Scheme 1). Along with this plan, stepwise diacylation[11] of dipyrromethane **8** produced **9**



Scheme 1 Synthesis of mono-*meso*-free pentaphyrin **7** and its bis-rhodium(I) complex **12**.

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† Electronic supplementary information (ESI) available: General experimental methods, HR-ESI-TOF mass spectra, UV/vis absorption spectra, NMR spectra, X-ray crystal structures, results of DFT calculations and TPA spectra. CCDC 864560. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc32054a

in 67% yield, which was reduced with $NaBH_4$ to afford **10** quantitatively (Scheme 1). A solution of **10** and **11** in CH_2Cl_2 was treated with 0.1 equiv. *p*-toluenesulfonic acid for 30 min and the resulting solution was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for 30 min. After usual work-up, we identified a spot corresponding to mono-*meso*-free pentaphyrin **7** on TLC of the reaction mixture. We attempted to purify this compound by repeated chromatography over gel permeation and silica gel columns but a particular chemical instability of **7** hampered its complete purification. Nevertheless, almost pure **7** gave the parent negative ion peak at m/z = 1050.0775 (calcd for $C_{49}H_{13}N_5F_{20}$ = 1050.0768 $[M–H]^-$) in the high-resolution electrospray ionisation time-of-flight mass spectroscopy (HR-ESI-TOF MS), and exhibited highly upfield shifted singlets for the *meso*-proton at −6.14 ppm and for the inner β-protons at −1.82 ppm, and downfield shifted signals due to the outer protons at 8.91, 9.09, and 9.66 ppm (ESI†). These data indicate a symmetric non-fused aromatic pentaphyrin structure with an inverted pyrrole. The UV/vis absorption spectrum of **7** exhibits a sharp Soret band at 509 nm and Q bands at 645, 694, 754, and 831 nm as a typical feature of aromatic expanded porphyrins (ESI†).

In next step, the crude mixture that contained **7** was reacted with $[RhCl(CO)_2]_2$ in CH_2Cl_2 in the presence of sodium acetate to produce bis-rhodium(I) complex **12** in 10% yield (three steps from **9**).[6b] The chemical stability of **12** was considerably improved, allowing its full characterisation even under the aerobic conditions. The HR-ESI-TOF MS indicated the parent positive ion peak of **12** at m/z = 1367.8656 (calcd for $C_{53}H_{12}N_5F_{20}O_4Rh_2$ = 1367.8675 $[M + H]^+$). The ^{1}H NMR spectrum again indicated a highly symmetric feature, exhibiting a singlet due to the *meso*-proton at −5.11 ppm, a singlet due to the inner β-protons at −2.84 ppm, signals due to the outer β-protons at 6.53, 7.98, 8.27, and 8.89 ppm. The chemical shift difference between the inner and outer β-protons is large, 11.7 ppm. The structure of **12** was unambiguously determined by single crystal X-ray diffraction analysis‡ to be a non-fused mono-*meso*-free symmetric pentaphyrin with an inverted pyrrole (Fig. 1). The two rhodium ions are coordinated over the inward-pointing two pyrroles with bond distances of Rh(1)—N(4), Rh(1)—N(5), Rh(2)—N(1), and Rh(2)—N(2) of 2.054(5), 2.052(5), 2.040(5), and 2.056(5) Å, respectively. The pentaphyrin skeleton is roughly planar with the mean-plane deviation of 0.330 Å. Importantly, the rhodium coordination nicely shields the reactive *meso*-free position, hence improving the distinct chemical stability of **12**. The harmonic oscillator model of aromaticity (HOMA)[12] of **12** was calculated to be 0.56. The UV/vis absorption spectrum of **12** is similar to that of **7**, exhibiting a strong Soret band at 539 nm and Q bands at 683, 722, and 794 nm (Fig. 2).

We have already reported the TPA properties of various porphyrin derivatives including expanded porphyrins which exhibit relatively large TPA cross section values due to their enlarged π-conjugation pathways.[13] In this report, we have measured the TPA values of **12** by photoexcitation using a wavelength-scanning open-aperture Z-scan method in the wavelength range of 1200–1500 nm at which one-photon absorption contribution is negligible. While the maximum TPA cross-section value of porphyrin monomer is known to be less than 100 GM at the Q-band region, the maximum TPA cross-section value of **12** was estimated to be 1200 GM at 1300 nm which is similar to *N*-fused [22]pentaphyrin **4** (see Fig. S12†).[6] These results are thought to reflect their planar structures, elongated π-conjugation length and strong aromaticities.[14]

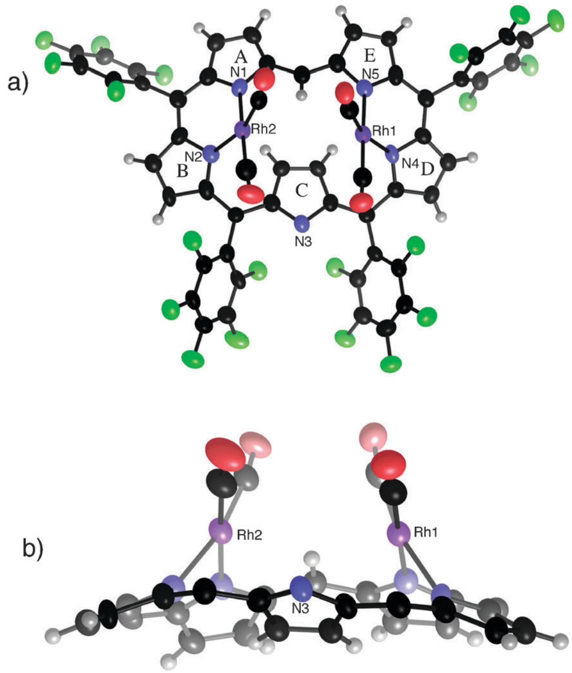

Fig. 1 X-Ray crystal structure of **12**: (a) top view and (b) side view. Thermal ellipsoids represent 50% probability and *meso*-aryl substituents are omitted for clarity in side view.

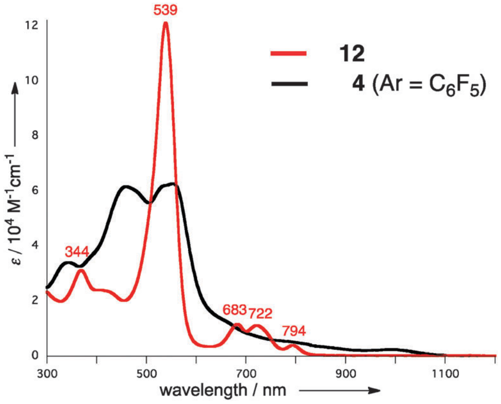

Fig. 2 UV/vis absorption spectra of **12** and **4** (Ar = C_6F_5).

To explore the excited-state dynamics of **12**, femtosecond transient absorption measurements were carried out (Fig. S13†). In the TA spectrum of **12**, intense ground-state bleach signals around 500–570 nm are observed that are accompanied by an excited-state absorption band in the 570–670 nm spectral region. The excited state lifetime of **12** was estimated to be 21 ps with a residual long-lived component. Such a long-lived component of **12** is similar to those of other transition metal complexes like rhodium complexes, which arises from facile intersystem crossing process to populate the triplet state giving rise to a lack of fluorescence.[15] As a result of the transition metal effect, we could not detect any fluorescence from **12**.

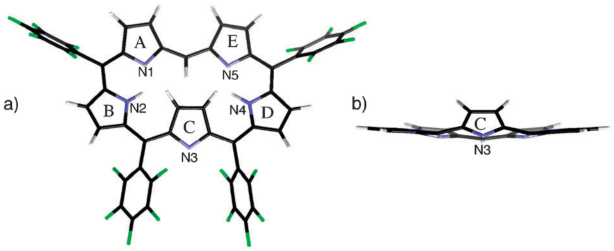

Fig. 3 Optimized structure of **7** (a) top view and (b) side view. *meso*-Aryl substituents are omitted for clarity in side view.

To obtain further insight into the stable conformations and aromatic properties of **7** and **12**, we performed DFT calculations (B3LYP/6-31G(d)/LANL2DZ).[16] The optimized structure of **7** thus calculated has four inward-pointing pyrroles and one outward-pointing pyrrole, which is essentially the same as that of **12** except the large bending of the pyrrole C (Fig. 3). Importantly, this conformation is exceedingly more stable than other conformers (ESI†). This structure well explains the ^{1}H NMR spectral data of **7**, and is reminiscent of the similar conformation of 5,10,15,20-tetraphenylsapphyrin.[17] In sharp contrast, the optimized structure of non-fused *meso*-pentakis(pentafluorophenyl) substituted pentaphyrin(1.1.1.1.1) was calculated to be a conformer with two-inverted pyrrole rings, which is prone to undergo an *N*-fusion reaction (ESI†). These calculations also revealed nearly degenerate HOMO/HOMO–1 and LUMO/LUMO + 1, and large HOMO–LUMO gaps of 2.01 and 2.15 eV for **7** and **12**, respectively. The nucleus-independent chemical shift (NICS) values[18] at the centre of the macrocycles were calculated to be −17.4 and −21.8 ppm for **7** and **12**. These results are in line with the strong aromaticity of **7** and **12** (ESI†).

In summary, we synthesised mono-*meso*-free pentaphyrin **7** and its rhodium(I) complex **12** as the first example of a *β*-unsubstituted non-fused pentaphyrin, which showed aromaticity arising from 22π-electronic circuit along the relatively planar skeleton with an inverted pyrrole ring. The free base **7** is susceptible to oxidative damages because of the free *meso*-position but the chemical stability of **12** is considerably improved by the shielding of the free *meso*-position by the coordinated rhodium metals. The large TPA value of **12** (1200 GM) has been ascribed to its planar structure, elongated π-conjugation length and strong aromaticity.

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Notes and references

‡ Crystal data for **12**·CH_2Cl_2; $C_{54}H_{13}Cl_2F_{20}N_5O_4Rh_2$ M = 1452.41, monoclinic, space group $C2/c$ (No. 15), Z = 8, a = 26.9166(5), b = 14.9711(3), c = 24.9775(4) Å, β = 90.1129(8)°, V = 10065.2(3) Å, λ(Cu-Kα) = 7.470 mm^{-1}, r = 1.917 Mg m^{-3}, T = −180(2) °C, Total reflections 8531, unique 5726 (R_{int} = 0.1217). R_1 = 0.0675 [$I > 2\sigma(I)$] and wR_2 = 0.1754 (all data) GOF = 1.022.

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