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Dome-distortion and fluorine-lined channels: synthesis, and molecular and crystal structure of a metal- and C–H bonds-free fluorophthalocyanine†

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The first perfluorinated metal-free phthalocyanine exhibits a dome-like molecular distortion usually induced by large metal ions. Fluorine-lined channels account for ~ 39% of the unit cell volume. The intermolecular interlocking of peripheral iso-perfluoroalkyl short-chains contributes to these features, which could be used in the rational design of robust materials.

Phthalocyanines (Pcs) are important as pigments and dyes, sensors, in photodynamic therapy, optical recording, photovoltaics, catalysis, *etc.*[1] Unlike porphyrins,[2] Pcs exhibit a low degree of distortion from planarity, a feature that combined with their aromaticity ensures chemical robustness while favoring solid-state aggregation. Ring substituents, metals, if any, and axial ligands, are additional parameters that tune Pcs' properties. The dihydrogen parent compounds, PcH_2s, share many properties with the metallated Pcs, PcMs, for example conductivity,[3] but have specific attributes as well. The N–H protons, bonded to opposite pairs of N atoms, form two tautomers. They may have different spectroscopic properties in anisotropic environments, created by matrices, or even by crystal packing. Thus, the quasi-symmetric potential in α-PcH_2 becomes less degenerate in β-PcH_2.[4] Spectroscopic hole burning in such materials may allow information storage with densities up to 10^{11} bit cm^{-2},[5] or femtosecond holographic imaging.[6]

Molecular and packing information regarding PcH_2s, however, is extremely rare: since the first 1935 X-ray structure of PcH_2,[7] only 5 additional species had atomic coordinates determined.[8] Tetrakis, non-peripherally substituted[9] PcH_2s retain both the planarity and herringbone stacking of α and β PcH_2s phases.[10] Octakis, non-peripheral R_8PcH_2s progressively distort toward a saddle shape, forced by increasing intramolecular congestion of R = n- and iso-alkyl,[11,12] iso-alkoxy,[13] and phenyl[14] groups. While n-alkyl and iso-alkoxy groups induce brick stone packing, n-alkoxy substituted PcH_2s form progressively crystalline, columnar and isotropic (liquid) phases upon heating.[15] Hexadecakis substituted PcH_2s have not been reported.[8]

The above R substituents are all C–H based. Halogen substitution has consequences for Pcs' electronic structures, reactivity and applications. While perhalogen, $X_{16}PcH_2$s (X = Cl, Br, I) form from phthalic anhydrides using Co^{2+} templates,[16] the fluorinated material, X = F, could not be prepared.[16*b*] X-Ray structural details of *any* perhalogenated Pc are not available,[17] with the exception of $F_{64}PcZn$ and Co.[18]

We report here the synthesis of the first perfluorinated PcH_2, 29*H*,31*H*,1,4,8,11,15,18,22,25-octafluoro-2,3,9,10,16,17,23,24-octaperfluoro(isopropyl)phthalocyanine, $F_{64}PcH_2$, **1**, obtained from the corresponding phthalonitrile.[19]‡ Its molecular structure and solid-state packing are shown in Fig. 1.[20] The two Hs are disordered over the four N isoindole positions, which define the 4N plane, consistent with the "half-hydrogens" model derived *via* neutron diffraction for unsubstituted PcH_2.[21] The bond lengths in **1** are similar to those found in other PcH_2s. The ring of $F_{64}PcH_2$, however, exhibits a dome-like distortion, unknown for protonated phthalocyanines.[8] In contrast to saddle distortions, in which the isoindole units are alternatively above and below the 4N-plane, in the dome, C_{4v}, distortion they are on the same side. An estimation of the distortion is given by the dihedral angle between the opposite isoindole units, which for **1** is ~ 20°.

Dome-type distortions are common in PcMs, induced by metals too large to fit in the 4N plane.[8] The maximum distortion for non-substituted PcMs, 20° for M = Pb,[22] matches the value observed for **1**. Since there are no metals in **1**, the source of this large distortion needs to be revealed. Firstly, we note that convex-stacked Pc rings, Fig. 1d, exhibit the classical slipped-stacked arrangements, in which one ring is translated with respect to the other along the meso-N vector. The 3.46 Å shift is longer than but comparable with the 3.32 and 3.42 Å values for the α and β PcH_2s, respectively. The ~ 3.047 Å 4N–4N interplanar distance, on the other hand, with the exception of a sandwich Sm complex,[23] appears to be the shortest of *any* Pc. Short distances are generally observed in oxidized PcMs.[8] The

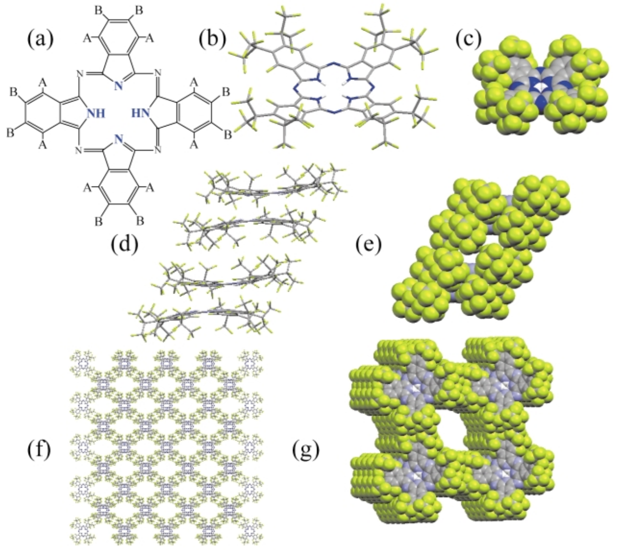

Fig. 1 Skeletal and CPK representations of **1**. Color code: C: gray; H: white; N: blue; F: green. (a) Non-peripheral, A, and peripheral, B, positions; in **1** A = F, B = *i*-C_3F_7; the central protons are in one of the tautomeric forms. (b, c) Molecular structure, showing the protons disordered over the four nitrogen atoms of the 4N plane. (d, e) Biconvex-biconcave assembly viewed perpendicular to the *c* axis. (f) Packing diagram viewed along the *c* axis. (g) Perspective view of a fluorine-lined channel.

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† Electronic supplementary information (ESI) available: ORTEP representation and packing diagrams of **1**; details of data collection, structure solution and refinement; crystallographic tables; plot of the average dihedral angles of opposite isoindole rings of **1** as a function of the average opposite N–N distance. See http://www.rsc.org/suppdata/cc/b3/b303035k/

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interplanar distance between the meso N planes is longer, ~ 3.2 Å, due to the curving of the molecule. Notably, the interlayer distance in graphite is longer, 3.354 Å, which increases to 3.47 Å for the graphene sheets of carbon nanotubes.[24] Short interplanar distances in Pcs are also attributed, at least in part, to π–π interactions. In the case of **1**, however, we postulate that the strong electron withdrawing effect of the fluorinated substituents and the non-planar polyene system do not preclude, or may even favor, tighter stacking. This issue, however, remains to be fully clarified.

Secondly, the F_{64}Pc ring appears more expandable relative to the unsubstituted Pc ring, *while retaining its planarity*, as evidenced by the *longer* opposite N**---**N distances within the 4N set of F_{64}PcZn, 4.012 ± 0.004(3) Å, *vs.* the 3.960 ± 0.004(2) Å values for PcZn.[25] For $F_{64}PcH_2$, this parameter, 3.942(4) Å, is within the 3.91–4.04 Å range observed for *planar* PcH_2.[8] In a hypothetically planar $F_{64}PcH_2$ molecule, the N**---**N distance is estimated to remain below the upper limit for PcH_2s.[26] Thirdly, in PcH_2s, dihedral angles above 5° are induced only by bulky non-peripheral substituents.[27] In **1**, F_{64}PcZn,[18a] and F_{64}PcCo (two examples),[18b] both the peripheral iso-C_3F_7 and non-peripheral F substituents adopt similar conformations, *viz.* one set of eight CF_3 groups above, and one below the 4N plane (Fig. 1a). However, the metal complexes are planar, while the dome distortion, unlike the saddle one, actually *shortens* the distance between the CF_3 groups located on the concave face of the dome. Taken together, the above data suggest that intramolecular effects, including steric congestion (hydrogens and/or substituents), are insufficient to explain the observed distortion. The formation of dimeric, bis-biconvex units is attributed to intermolecular interactions as well: the 3.52 Å shift allows the perfluoroisopropyl groups of the two molecules to interlock. Intermolecular H-bonding interactions are not observed. The bis-biconvex assemblies interact further *via* their "exterior" CF_3 groups located on the concave faces of the domes, Fig. 1b, forming biconvex-biconcave units, the basis of the slipped-stack columnar arrangement of Fig. 1b. The substituent-induced packing and distortion in **1** are somewhat surprising considering the above-mentioned propensity of the Pc ring for planarity, violated thus far only by severe intramolecular steric congestion of adjacent non-peripheral groups.[12,14]

The packing, Figs. 1c and 1d, leaves voids of ~ 3658 Å^3, a surprisingly large ~ 39% proportion of the 9362.0 Å^3 total unit cell volume. The channels, if filled, may contain 45–50 acetone molecules; only about 8 are present in **1**.[26]

In summary, we have prepared the first perfluorinated PcH_2 and uncovered its unprecedented, dome-like structural deformation in the solid state. We suggest that intermolecular interlocks favor the formation of fluorine-lined solid-state channels while imposing a metal-induced type molecular distortion. The combination of electronic and steric factors results in the second shortest stacking distance of any phthalocyanine. Complex **1** could be a convenient starting point for the synthesis of new Pc metal complexes. The observation that perfluoroalkyl short-chains[27] may induce these features, may help in the rational design of robust materials exhibiting interesting electronic and chemical properties.

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Notes and references

‡ Synthetic procedure and selected spectroscopic data for 29*H*,31*H*,1,4,8,11,15,18,22,25-octafluoro-2,3,9,10,16,17,23,24-octaperfluoro(isopropyl)phthalocyanine, **1**: Perfluoro-(4,5-di-isopropyl)phthalonitrile[19] (1.020 g, 2.04 mmol) and $Fe(OAc)_2$ (0.139 g, 0.799 mmol) were placed in a pressure vessel, evacuated, and then heated to 210 °C for 6 hours. The greenish-blue mixture was allowed to cool, washed with toluene and sublimed at 100 °C to remove the unreacted phthalonitrile. The crude material was purified chromatographically (silica-gel, 20–30% acetone–hexane). Overall yield: ~ 73% (50.2% $\mathbf{F_{64}PcFe}$ and 22.4% **1**). ^{19}F NMR (376 MHz, d_6-acetone, $CFCl_3$ std.) δ: −71.4 (CF_3, 48F), −105.9 (aromatic F, 8F), −164.8 (aliphatic F, 8F); TOF MS ES- [*m/e*] 1999.5; IR (KBr, cm^{-1}): 3436, 1288, 1250, 1170, 1189, 1183, 967, 750, 731, 713; UV/Vis (acetone), λ_{max} (lg ε) 690 (5.15).

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20 Crystallographic data for **1**: solvated single crystals were obtained from acetone. $C_{56}H_2F_{64}N_8$, monoclinic, *C*2/*m*; unit-cell dimensions: a = 27.029(6) Å, b = 27.391(6) Å, c = 12.749(3) Å, β = 97.311(4)°, V = 9362(4) Å^3, Z = 4, D_{calc} = 1.421 g cm^{-3}. Intensity data were collected at 173(2) K using Mo Kα radiation. The structure was solved by direct methods and expanded using Fourier techniques; 38240 reflections were measured, of which 8482 were independent. Final R_1 = 0.0626, R_w = 0.1645 ($I > 2.0\ \sigma(I)$). CCDC 201428. See http://www.rsc.org/suppdata/cc/b3/b303035k/ for crystallographic data in .cif or other electronic format.

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