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Extremely large cavity assembled by self-interlocking of distorted biconcave porphyrins†

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Received 26th August 2004, Accepted 6th December 2004
First published as an Advance Article on the web 6th January 2005

X-Ray analyses of free base, zinc, and nickel complexes of 2,3;7,8;12,13;17,18-tetrakis(6,13-dihydro-6,13-pentaceno)-21*H*,23*H*-porphine revealed that the porphyrin chromophores adopted a heavily-saddled conformation by interlocking of the biconcave porphyrins in the crystals containing halobenzenes as crystalline solvents, while the ring was almost flat in the crystals obtained from benzene or from chlorobenzene and isopropanol.

Introduction

Porphyrins with well-defined cavities have attracted great attention as enzyme and biological system mimics,[1] size- and chemo-selective catalysts,[2] and recognition tools.[3] The chromophores containing metal centres are usually surrounded by large groups at peripheral positions, which are designed to prevent undesired oxidative self-decomposition or self-quenching, or to create a certain space for the catalytic reactions. Design of the cavity space in such compounds is very important and many structural studies have been reported.[4] The external perturbations such as the size of substituents, central metals and axial ligands are known to cause nonplanar distortion of the porphyrin rings to adopt saddle, waved, ruffled or domed conformations.[5] We have been interested in the properties of porphyrins with rigid and bulky substituents at β-positions and revealed that even a dodecasubstituted porphyrin with four bicyclo[2.2.2]octene-fused frameworks adopted a slightly waved, planar conformation.[6] In this case, the cavities were shallow and included no molecules. In the cases of porphyrins with two deeper cavities created by four 9,10-dihydro-9,10-anthraceno[7] and larger moieties[8] at the β-positions, their crystals always contained solvent or co-crystallizing molecules. Kräutler and co-workers reported an interesting co-crystal structure of such porphyrins with [60]fullerene.[9] In all reported crystal structures of these biconcave porphyrins, the porphyrin chromophore was almost flat and shows only slight out-of-plane distortion. If the cavity size and shape on one side are forced to change, those on the other side must be affected *via* the distortion of the porphyrin ring, and thus allosteric recognition by these cavities can be expected. For this purpose, porphyrins with large rigid wings would be advantageous because only a small force at the edges of the wings can distort the central porphyrin ring. Based on this idea, we planned to prepare porphyrins surrounded by four pentacene moieties and found interesting structural differences which depend on the crystal packing

Results and discussion

Preparation of the biconcave porphyrins

The targeted 2,3;7,8;12,13;17,18-tetrakis(6,13-dihydro-6,13-pentaceno)porphyrins **12–14** were prepared as illustrated in Scheme 1. According to the literature, 6,13-dihydro-6,13-ethenopentacene (**8**) was prepared from commercially available bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (**1**) *via* tetraethyl esters.[10] During this preparation sequence, we encountered difficulty in crystallization of **5** from a mixture with other isomers especially in the first trial. Crystallization of **5** took from one day to one month depending on the purity of **5** and the presence of seed crystals. To avoid this problem, the anhydride was converted to tetramethyl ester **2b** and then isomerized to give a mixture of **3b** and **4b**. From this mixture, almost all of **4b** crystallized easily and the all-*trans* tetraester **3b** was obtained in 83% yield as a viscous oil. Reduction of **3b** gave **5** in 98% yield as white solids. The tetraol **5** was converted to the corresponding tetrachloro derivative **6** and then tetramethylidene compound **7** in good yields. The Diels–Alder reaction of **7** with benzyne followed by oxidation with DDQ gave **8** in 60% yield. The etheno bridge of **8** was converted to a pyrrole ring by successive treatment of PhSCl, mCPBA and ethyl isocyanoacetate with *t*-BuOK,[11] and the pyrrolecarboxylate **11** was obtained in 30% yield. The targeted porphyrin **12** was obtained in 30% yield by acid-catalyzed tetrameric cyclization of the hydroxymethylpyrrole derived from the reduction of **11** with $LiAlH_4$. Metallation of the porphyrin with zinc acetate and nickel acetate gave the corresponding porphyrins **12** and **13** in quantitative yields. The porphyrins **12**, **13** and **14** are readily soluble in common organic solvents such as chloroform, toluene, ethyl acetate, and so on. Introduction of phenyl groups at the *meso* positions of the porphyrins was attempted by using the reaction of benzaldehyde with α-free pyrrole derived from **11** under Lindsey conditions. No porphyrin product, however, was obtained probably due to steric reasons.

X-Ray structures of the biconcave porphyrins

Single crystals for X-ray analysis were prepared either by slow diffusion of isopropanol into a solution of the porphyrin in an aromatic solvent (**12**·8PhCl·4*i*-PrOH and **14**·8PhCl·4*i*-PrOH) or by slow evaporation of solvents from a solution of the porphyrin in a dichloromethane and aromatic solvent mixture

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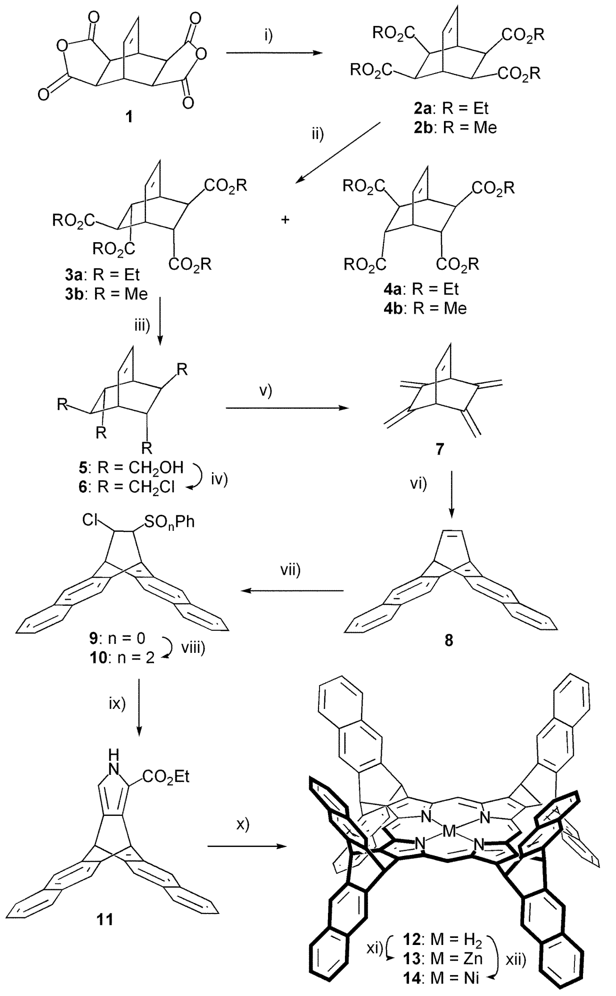
† Electronic Supplementary Information (ESI) available: Crystal packing diagrams and X-ray data of **12**·12PhH, **12**·8PhCl·4*i*-PrOH, **12**·9PhBr, **12**·$7CH_2Cl_2$·2PhH, **13**·12PhH, **13**·10PhCl, **14**·12PhH, **14**·8PhCl·4*i*-PrOH and **16**·7PhMe in CIF format. See http://www.rsc.org/suppdata/ob/b4/b413082k/

DOI: 10.1039/b413082k



Scheme 1 *Reagents, conditions and yields:* i) EtOH, pTSA, PhMe, reflux, **2a**: 95%; MeOH, $CH(OMe)_3$, reflux, **2b**: 85%. ii) ROH, RONa, reflux, **3a** + **4a**: quant; **3b**: 83%. iii) LAH, THF, rt, from **3a** + **4a**: 75%; from **3b**: 98%. iv) $SOCl_2$, pyridine, rt, 94%. v) *t*-BuOK, THF, reflux. vi) *o*-$NH_2C_6H_4CO_2H$, ONO-amyl, THF; DDQ, toluene, 60% (from **6**). vii) PhSCl, CH_2Cl_2, rt; 99%. viii) mCPBA, CH_2Cl_2, 0 °C; 82%. ix) $CNCH_2CO_2Et$, *t*-BuOK, THF, −20 °C to rt; 37%. x) $LiAlH_4$, THF, 0 °C; pTSA, $CHCl_3$, rt; *p*-chloranil, $CHCl_3$, rt; 30%. xi) $Zn(OAc)_2$, MeOH, $CHCl_3$, rt; quant. xii) $Ni(OAc)_2$, MeOH, $CHCl_3$, rt; quant.

(**12**·12PhH, **12**·7CH_2Cl_2·2PhH, **12**·9PhBr, **13**·12PhH, **13**·10PhCl and **14**·12PhH), and the crystals listed in the parentheses are successfully obtained. Their crystallographical data are shown in Table 1.[12] When the solvent molecules were not properly modeled, the structures were refined without such solvent molecules by the SQUEEZE method.[13] All values given in this text are calculated based on the SQUEEZED structures, when both structures with or without solvents are refined. Regardless of the central metals, three space groups were observed in the structures of the porphyrins: $P4_2/n$ for **12**·9PhBr and **13**·10PhCl; $I4_1/a$ for **12**·12PhH, **12**·8PhCl·4*i*-PrOH, **13**·12PhH, **14**·12PhH and **14**·8PhCl·4*i*-PrOH; and $P\bar{1}$ for **12**·7CH_2Cl_2·2PhH.

$P4_2/n$ structures

The porphyrin rings occupy a $\bar{4}$ special position and adopt a saddle conformation; the maximum displacements of β-pyrrole and *meso* carbons from the mean planes are 0.338(4) Å and 0.074(4) Å for **12**·9PhBr, and 0.319(3) Å and 0.104(3) Å for **13**·10PhCl, respectively (Fig. 1). The tilting angles of pyrrole units toward the porphyrin mean plane are 8.58(11)° for **12**·9PhBr and 7.11(8)° for **13**·10PhCl. The angles between the naphthalene moieties and the porphyrin mean planes are 46.47(6)° and 80.36(6)° for **12**·9PhBr, and 48.02(4)° and 79.31(5)° for **13**·10PhCl (Fig. 2). The most interesting feature

Table 1 Crystallographic summary of tetrakis(dihydropentaceno)porphyrins[a]

Crystals	**12**·12PhH	**12**·8PhCl·4*i*-PrOH	**12**·9PhBr	**12**·7CH_2Cl_2·2PhH	**13**·12PhH	**13**·10PhCl	**14**·12PhH	**14**·8PhCl·4*i*-PrOH
FW	2353.1	2556.6	2828.8	2166.5	2416.4	2602.5	2409.8	2613.2
System	Tetragonal	Tetragonal	Tetragonal	Triclinic	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	$I4_1/a$	$I4_1/a$	$P4_2/n$	$P\bar{1}$	$I4_1/a$	$P4_2/n$	$I4_1/a$	$I4_1/a$
a/Å	19.390(1)	19.720(1)	22.627(1)	16.235(2)	19.612(3)	22.4739(8)	19.2176(8)	19.650(1)
b/Å	19.390(1)	19.720(1)	22.627(1)	18.758(3)	19.612(3)	22.4739(8)	19.2176(8)	19.650(1)
c/Å	36.077(2)	35.239(4)	12.7634(8)	19.279(2)	36.445(8)	12.8564(3)	36.142(2)	35.387(3)
α/°	90	90	90	78.364(9)	90	90	90	90
β/°	90	90	90	63.381(6)	90	90	90	90
γ/°	90	90	90	88.39(1)	90	90	90	90
V/Å^3	13564(1)	13703(1)	6534.6(7)	5128(1)	14017(4)	6493.5(4)	13348(1)	13663(1)
Z	4	4	2	2	4	2	4	4
μ/mm^{-1}	0.066	0.357	2.824	0.432	0.231	0.453	0.204	0.357
Unique	7742	7853	7465	22806	7994	6886	7623	7821
R_{int}	0.067	0.093	0.066	0.066	0.060	0.027	0.057	0.093
Obs.	4343 [4993][b]	2457	[4697][c]	[10520][d]	4242	[3535][e]	5261 [6282][f]	[3152][g]
Param.	419 [253][b]	361	[316][c]	[1063][d]	418	[255][e]	352 [309][f]	[255][g]
R_1	0.065 [0.066][b]	0.097	[0.089][c]	[0.084][d]	0.059	[0.068][e]	0.070 [0.061][f]	[0.075][g]
$_wR^2$ (all)	0.159 [0.198][b]	0.241	[0.238][c]	[0.201][d]	0.159	[0.199][e]	0.173 [0.170][f]	[0.204][g]
GOF	1.117 [1.001][b]	1.214	[1.242][c]	[0.999][d]	1.005	[0.999][e]	1.412 [1.100][f]	[1.000][g]
T/°C	−100	−100	−100	−150	25	−150	−150	−100
CCDC No.	248908, 248909	248910	248906	248915	248911	248907	248912, 248914	248913

[a] Values in brackets are obtained by removal of some solvent molecules using the PLATON–SQUEEZE program. The refined structures are [b] **12**, [c] **12**·4PhBr, [d] **12**·PhH, [e] **13**, [f] **14**·4PhH and [g] **14**, respectively.

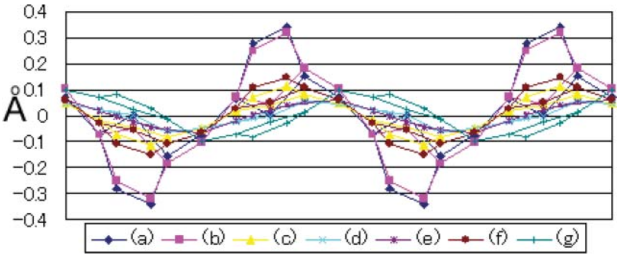


Fig. 1 Deviation from the mean porphyrin plane: (a) **12**·9PhBr (refined as **12**·4PhBr), (b) **13**·10PhCl (refined as **13**), (c) **12**·12PhH, (d) **12**·8PhCl·4*i*-PrOH, (e) **13**·12PhH, (f) **14**·12PhH (refined as **14**·4PhH) and (g) **14**·8PhCl·4*i*-PrOH (refined as **14**).

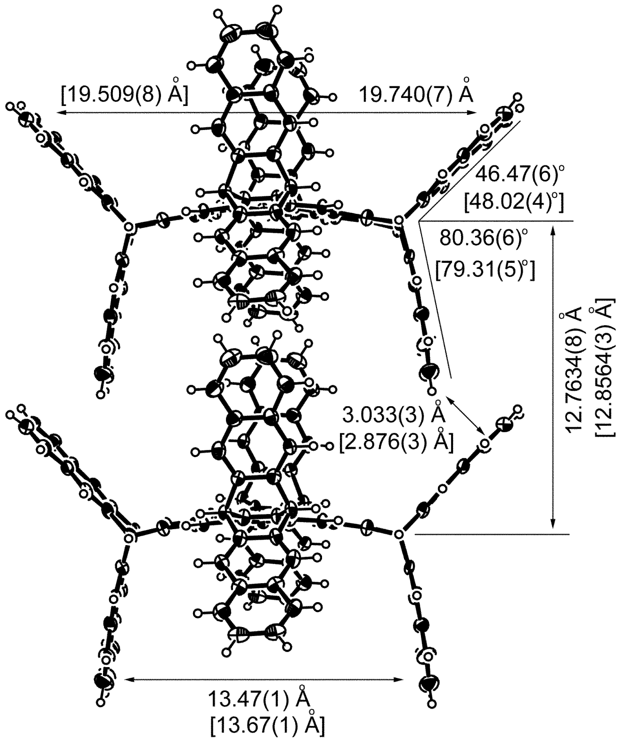


Fig. 2 ORTEP stacking diagram of the porphyrin molecules in **12**·9PhBr (refined as **12**·4PhBr) and **13**·10PhCl (refined as **13**, in the brackets).

in these structures is the molecular packing. The porphyrin molecules linearly stack by alternate in-and-out distortion of the dihydropentacene wings along the ***c*** axis, and thus there are large cavities centred at other $\bar{4}$ special positions between the porphyrin molecules. The cavity volumes are 726 Å^3 for **3**·9PhBr and 718 Å^3 for **13**·10PhCl calculated by PLATON,[13] and four molecules of the corresponding halobenzenes are caged in the cavity in a heavily disordered fashion. The minimum distances between the stacking porphyrins are 3.033(3) Å for**12**·9PhBr and 2.876(3) Å for **13**·10PhCl.

$I4_1/a$ structures

The porphyrin rings also occupy a $\bar{4}$ special position. In contrast to the $P4_2/n$ structures, the porphyrin rings are more planar and adopt a variety of out-of-plane conformations: saddling (**12**·12PhH and **14**·12PhH), propellering (**13**·12PhH and **14**·8PhCl·4*i*-PrOH) and ruffling (**12**·8PhCl·4*i*-PrOH). The maximum displacements of the ring carbons are in a range between 0.148(2) for **14**·12PhH and 0.056(4) Å for**12**·8PhCl·4*i*-PrOH (Fig. 1 and Table 2) and the tilting angles of pyrroles toward the porphyrin mean planes are from 1.74(8)° to 2.92 (5)° (Table 2). Therefore, the angles between the naphthalene moieties and the porphyrin mean planes are around 60° [from 56.06(6)° to 62.62(3)°]. In the crystal packing, four of the naphthalene units of a porphyrin molecule are in each of four

Table 2 Distortion of $I4_1/a$-type structures

Crystals	Out-of-plane	Displacement from porphyrin mean plane/Å						Angles *vs.* porphyrin mean plane		
		N	C^1	C^2	C^3	C^4	C^{meso}	Naphthalene		Pyrrole
12·12PhH^a	Saddling	0.041(1)	0.082(1)	0.112(1)	0.075(1)	0.017(1)	−0.050(1)	62.58(2)°	58.65(2)°	2.18(4)°
12·8PhCl·4*i*-PrOH	Ruffling	−0.011(4)	0.056(4)	0.042(4)	−0.008(4)	−0.023(4)	−0.048(5)	60.42(7)°	56.30(7)°	2.14(14)°
13·12PhH	Propellering	0.021(2)	−0.016(2)	0.003(2)	0.042(2)	0.051(2)	0.063(2)	61.52(4)°	57.74(4)°	1.74(8)°
14·12PhH^b	Saddling	0.051(2)	0.109(2)	0.148(2)	0.109(2)	0.026(2)	−0.065(2)	62.62(3)°	58.81(3)°	2.92(5)°
14·8PhCl·4*i*-PrOH^c	Propellering	0.022(4)	−0.012(4)	0.029(4)	0.084(4)	0.071(4)	0.100(4)	60.71(6)°	56.06(6)°	2.37(13)°

The refined structures are ^{a} **12**, ^{b} **14**·4PhH and ^{c} **14**, respectively.

neighbouring porphyrin cavities forming a three-dimensional network (Fig. 3). The aromatic solvent molecules prevent the direct staking of the naphthalene units of these molecules. In the packing of **12**·8PhCl·4*i*-PrOH and **14**·8PhCl·4*i*-PrOH, the four isopropanol molecules are arranged around another $\bar{4}$ special position with hydrogen bonding.

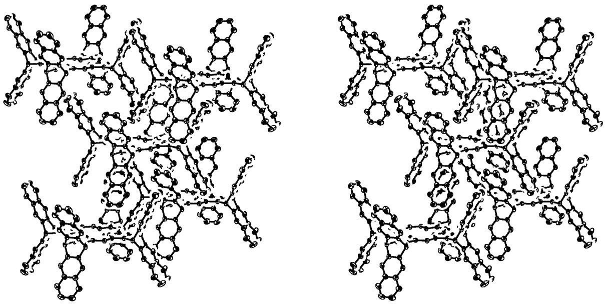


Fig. 3 Stereo view of $I4_1/a$ structure (**12**·12PhH). The solvent molecules and protons are omitted for clarity.

$P\bar{1}$ structures

Two independent porphyrin molecules α and β exist in **12**·7CH$_2$Cl$_2$·2PhH (Fig. 4), at special positions with $\bar{1}$ symmetry, and show waved out-of-plane distortion of porphyrin rings. The tilting angles of pyrrole moieties are 3.91(11) and 3.55(10) Å for structure α, and 2.33(11) and 2.08(10) Å for structure β. The angles between the naphthalene moieties and the porphyrin mean planes are in a wide range from 51.42° to 79.20° [57.01(5)° (A), 57.27(5)° (B), 52.03(5)° (C), 67.62(6)° (D), 51.42(5)° (E), 79.20(5)° (F), 61.57(5)° (G) and 65.03(5)° (H)]. This fact clearly shows that the dihydropentacene wings are forced to tilt by the crystal packing. In this crystal structure, naphthalene units of one porphyrin molecule α insert into the space between the neighbouring dihydropentacene wings of the other molecule β, and thus these porphyrin molecules show obvious in-plane distortions (Fig. 5). The angles of C$^{\alpha}$–C^{meso}–C$^{\alpha}$ inserted with the wings are widened to be 127.7(3)° and 127.4(3)°, while the others are narrowed to be 126.2(3)° and 125.7(3)°, respectively.

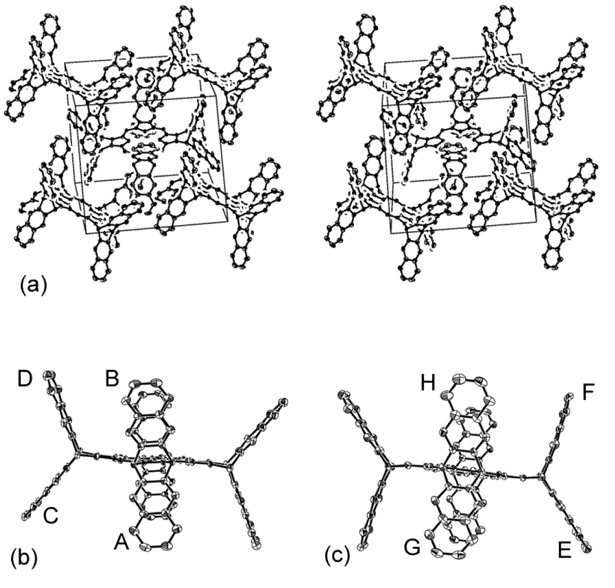


Fig. 4 (a) Stereo view of **12**·7CH$_2$Cl$_2$·2PhH. One molecule of structure α is surrounded by four molecules of structure β. (b) Structure α. (c) Structure β. The solvent molecules and protons are omitted for clarity.

Comparison of tetrakis(dihydropentaceno) and tetrakis(didydroanthraceno)porphyrins

From MOPAC calculations[14] of **12** and 2,3;7,8;12,13;17,18-tetrakis(9,10-dihydro-9,10-anthraceno)-21*H*,23*H*-porphine (**15**, Chart 1) as saddle and planar conformations, the energy difference between the two conformers of **12** is smaller than that of **15**; the planar conformation of **12** is more stable than the saddle one only by 2.1 kcal mol^{-1} (AM1) and 1.0 kcal mol^{-1} (PM3), while the difference of **15** is 4.0 kcal mol^{-1} (AM1) and 3.2 kcal mol^{-1} (PM3). This considerably low energy barrier of **12** would be a reason for a variety of conformations being observed in crystalline states.

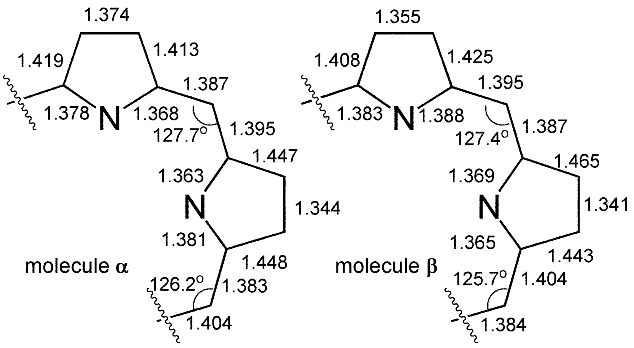
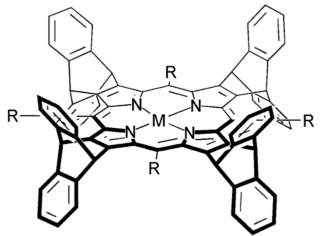


Fig. 5 Bond lengths (Å) and angles of **12**·7CH$_2$Cl$_2$·2PhH.



15: M = H$_2$, R = H
16: M = Zn, R = Ph

Chart 1

X-Ray analysis of *meso*-tetraphenyl derivative **16** revealed that even this sterically crowded porphyrin adopted the waved conformation (see ESI,† CCDC 248905), which was already reported for the similar tetrakis(9,10-dihydro-9,10-anthraceno)porphyrins by Kräutler *et al.*[7,9]

In conclusion, we prepared a porphyrin with four dihydropentacene wings, which had two large concave spaces on the porphyrin ring. The spaces combined in the crystals to form unique large cages by self-interlocking which induced the saddle distortion of the porphyrin. We showed that change of the size and shape of one cavity induced a change of the other side *via* distortion of the porphyrin, which had two cavities created by rigid substituents on both sites of the porphyrin plane.

Experimental

Melting points are uncorrected. Unless otherwise specified, NMR spectra were obtained with a JEOL GSX-270 or EX-400 spectrometer at ambient temperature by using CDCl$_3$ as a solvent, tetramethylsilane as an internal standard for ^{1}H and ^{13}C. Mass spectra were measured with a MStation spectrometer (JEOL MS-700). THF was distilled from sodium benzophenone ketyl and dichlorometane was distilled from CaH$_2$ prior to use. DMF was distilled under reduced pressure and then stored over MS 4 Å. Pyridine was distilled from CaH$_2$ and stored over MS 4 Å. Dry alcohols were purchased from Kanto Chemical Co. The tetraethyl ester route to 6,13-dihydro-6,13-ethenopentacene (**8**) was carried out according to the literature procedure[15,10] except for the isomerization process.

Isomerization of tetraethyl all-*endo*-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylate (2a)

Sodium (0.115 g) was added to dry ethanol (300 ml) under argon. After sodium disappeared, **2a** (40.0 g) was added and the mixture was refluxed for 30 h. Progress of the isomerization was monitored by ^{1}H NMR (DMSO-d_6; olefinic protons). The ratio of **3a** and **4a** (not determined in this case) reached *ca.* 20 : 1 and a rough estimation of the purity of **3a** was 90%. After removal of the solvent, the viscous oil was dissolved in chloroform (300 ml). The solution was washed with water (2 × 200 ml), dried over sodium sulfate and concentrated *in vacuo* to give tetraethyl all-*trans*-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylate (**3a**) in quantitative yield (purity *ca.* 90%) as a viscous oil. This material was used without further purification.

Tetramethyl all-*endo*-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylate (2b)

A suspension of all-*endo*-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic anhydride (**1**; 50.0 g, 0.20 mol), dry methanol (80 ml), trimethyl orthoacetate (76 ml) and TsOH·H$_2$O (0.10 g) was refluxed for 5 days under a dry atmosphere (protected by silica gel). The white suspension gradually became a pale brown solution. After checking by GC (absence of intermediate diester monoanhydride), the mixture was cooled and concentrated *in vacuo* to give a white solid, which was triturated with ether to give 57.8 g (85%) of the title compound as a white solid: mp 120 °C; δ_H (CDCl$_3$) 6.42 (2H, m), 3.42 (12H, s), 3.34 (2H, m) and 3.06 (4H, m); δ_C (CDCl$_3$) 171.92, 130.65, 51.92, 46.38 and 35.44; MS (EI) *m/z* 340 (M$^+$), 309, 249, 248 and 189; IR (KBr) 1739, 1439, 1215, 1195 and 1176 cm^{-1} (Found: C, 56.19; H, 5.92. C$_{16}$H$_{20}$O$_8$ requires C, 56.47; H, 5.92%).

Tetramethyl all-*trans*-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylate (3b)

To a solution of **2b** (59.5 g, 0.17 mol) in dry methanol (500 ml) was added a 28% methanol solution of sodium methoxide (1.0 ml) and the mixture was refluxed for 55 h. After checking completion of the isomerization by ^{1}H NMR (DMSO-d_6; olefinic protons), the mixture was cooled and acetic acid (1.0 ml) was added. The mixture was concentrated *in vacuo* to leave a viscous slurry. The slurry was triturated with ether (100 ml) and the white precipitates were filtered off. Concentration of the filtrate gave the title compound as a pale brown viscous oil: δ_H (CDCl$_3$) 6.31 (2H, m), 3.75 (6H, s), 3.68 (6H, s), 3.49 (2H, m), 3.18 (2H, m) and 2.96 (2H, m); δ_C (CDCl$_3$) 173.80, 172.85, 133.09, 52.45, 52.31, 45.14, 40.89 and 35.11; MS (EI) *m/z* 340 (M$^+$), 308, 248 and 137; IR (neat) 2954, 1732, 1437 and 1201 cm^{-1} (Found: C, 56.47; H, 5.99. C$_{16}$H$_{20}$O$_8$ requires C, 56.47; H, 5.92%).

The precipitates were revealed to consist of tetramethyl *trans-cis-trans*-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylate (**4b**) and **3b** in a ratio of 19 : 1: mp 145 °C; δ_H (CDCl$_3$) 6.54 (1H, t, J = 6.8 Hz), 6.09 (1H, dd, J = 7.3 and 6.8 Hz), 3.69 (6H, s), 3.66 (6H, s), 3.55 (2H, m), 3.28 (2H, m) and 2.88 (2H, m); δ_C (CDCl$_3$) 173.43, 173.02, 136.37, 130.28, 52.30, 52.19, 44.73, 44.42, 35.14 and 34.94; MS (EI) *m/z* 340 (M$^+$), 308, 248 and 221; IR (neat) 2956, 1730, 1261 and 1207 cm^{-1}. This dried compound is very hygroscopic and the weight increased during measurement of the elemental analysis (Found: C, 53.73; H, 5.66. C$_{16}$H$_{20}$O$_8$·H$_2$O requires C, 53.63; H, 6.19%).

trans-15-Chloro-16-phenylsulfanyl-6,13-dihydro-6,13-ethanopentacene (9)

To a solution of **8** (0.200 g, 0.657 mmol) in dry dichloromethane (15 ml) was added freshly prepared PhSCl[16] (0.093 ml, 0.788 mmol) at room temperature and the mixture was stirred for 3 days. After removal of the solvent, the residue was chromatographed on silica gel to give 0.291 g (99%) of the title compound as colourless crystals: mp 183 °C; δ_H (CDCl$_3$) 7.85 (1H, s), 7.84–7.74 (4H, m), 7.80 (1H, s), 7.78 (1H, s), 7.71 (1H, s), 7.51–7.41 (6H, m), 7.38–7.27 (3H, m), 4.68 (1H, d, J = 2.8 Hz), 4.53 (1H, d, J = 2.5 Hz), 4.26 (1H, dd, J = 3.9 and 2.8 Hz), 3.74 (1H, dd, J = 3.9 and 2.5 Hz); δ_C (CDCl$_3$) 138.70, 137.21, 136.03, 135.48, 134.16, 132.64, 132.63, 132.53, 132.04, 129.13, 127.73, 127.71, 127.70, 127.58, 127.50, 126.03, 125.88, 125.87, 125.83, 125.16, 124.69, 123.14, 122.08, 63.68, 57.90, 52.54, 49.23 and one carbon could not be found due to peak overlapping; MS (EI) *m/z* 448 (M$^+$), 412, 303, 278 and 247; IR (KBr) 3050, 3016, 2950 and 2865 cm^{-1} (Found: C, 80.33; H, 4.98. C$_{30}$H$_{21}$ClS requires C, 80.25; H, 4.71%).

trans-15-Chloro-16-phenylsulfonyl-6,13-dihydro-6,13-ethanopentacene (10)

To a solution of **9** (0.197 g, 0.439 mmol) in dry dichloromethane (30 ml) was added mCPBA (0.219 g, 1.27 mmol) at 0 °C and the mixture was stirred for 2 h. After precipitates were removed by filtration, the filtrate was washed with sat. NaHCO$_3$, water and brine, dried over Na$_2$SO$_4$ and concentrated. The residual solid was recrystallized from ethanol to give 0.173 g (82%) of the title compound as colourless crystals: mp 164 °C; δ_H (CDCl$_3$) 7.90 (1H, s), 7.90–7.70 (9H, m), 7.59 (1H, m), 7.55–7.40 (6H, m), 5.23 (1H, m), 4.70 (2H, m) and 3.67 (1H, m); δ_C (CDCl$_3$) 138.78, 137.38, 136.54, 135.43, 134.23, 134.00, 132.85, 132.59, 132.56, 132.52, 129.21, 128.50, 127.96, 127.68, 126.17, 126.15, 126.09, 126.03, 125.42, 124.60, 123.08, 122.17, 73.57, 56.62, 52.47 and 43.84 and two carbons could not be found due to peak overlapping; MS (EI) *m/z* 480 (M$^+$), 444, 339, 303 and 278; IR (KBr) 3058, 2946 and 2873 cm^{-1} (HRMS Found: 480.0951. C$_{30}$H$_{21}$ClO$_2$S requires 480.0950).

Ethyl 2,3-(6,13-dihydro-6,13-pentaceno)pyrrole-1-carboxylate (11)

To a stirred solution of **10** (0.100 g, 0.225 mmol) and ethyl isocyanoacetate (0.03 ml, 0.27 mmol) in dry THF (10 ml) was added a solution of potassium *tert*-butoxide in THF (1.0 M, 0.60 ml) at −20 °C. After removal of the cooling bath, the mixture was stirred. After 12 h, a dilute HCl solution was added and the mixture was extracted with ethyl acetate. The organic extract was washed with brine, dried over Na$_2$SO$_4$ and concentrated. The residue was chromatographed on silica gel (20% EtOAc–hexane) to give 36 mg of the title pyrrole as colourless crystals: mp 170 °C; δ_H (CDCl$_3$) 8.61 (1H, br), 8.23–7.34 (12H, m), 6.79 (1H, d, J = 2.4 Hz), 6.05 (1H, br-s), 5.57 (1H, br-s), 4.41 (2H, q, J = 7.3 Hz) and 1.49 (3H, t, J = 7.3 Hz); δ_C (CDCl$_3$) 170.01, 142.69, 142.03, 133.74, 131.91, 130.22, 129.80, 128.26, 127.48, 127.42, 125.70, 122.17, 121.58, 115.48, 114.48, 60.42, 47.23, 46.71 and 14.63; MS (EI) *m/z* 415 (M$^+$), 341 and 156; IR (KBr) 3317, 1670, 1415, 1323, 1288, 1126 and 760 cm^{-1} (HRMS Found: 415.1570. C$_{29}$H$_{21}$NO$_2$ requires 415.1572).

2,3;7,8;12,13;17,18-Tetrakis(6,13-dihydro-6,13-pentaceno)-21*H*,23*H*-porphine (12)

To a stirred solution of **11** (0.416 g, 1.00 mmol) in dry THF (15 ml) was added LiAlH$_4$ (0.14 g, 3.70 mmol) at 0 °C. After disappearance of **11** by TLC, water was added. The suspension was filtered through a Celite pad which was thoroughly washed with chloroform. The extract was dried over Na$_2$SO$_4$ and filtered. The volume was increased to 250 ml by addition of chloroform and *p*-TsOH (0.03 g) was added. After the mixture was stirred overnight at room temperature in the dark, *p*-chloranil (0.05 g) was added. The mixture was further stirred for 1 day. The mixture was washed with sat. NaHCO$_3$, water and brine, dried over Na$_2$SO$_4$ and concentrated. The residue was chromatographed on silica gel (40% EtOAc–hexane) and then recrystallized from dichloromethane–hexane to give 0.106 g (30%) of the title compound as a red powder: mp >300 °C; δ_H (CDCl$_3$) 10.75 (4H, s), 8.36 (16H, s), 7.81 (16H, m), 7.44, (8H, s), 7.38 (16H, m) and −4.75 (2H, br); δ_C (CDCl$_3$) 143.02, 131.68, 127.40, 125.79, 122.53, 98.74, 49.55 and α- and β-carbons of porphyrin ring could not be found due to tautomerisom of the inner pyrrolic protons; MS (MALDI-TOF) *m/z* 1417.8 ($M^+ + 3$), 1416.8 ($M^+ + 2$) and 1415.9 ($M^+ + 1$); λ_{max} (CH_2Cl_2) 400, 501, 532, 570 and 623 nm.

2,3;7,8;12,13;17,18-Tetrakis(6,13-dihydro-6,13-pentaceno)-21*H*,23*H*-porphyrinatozinc (13)

To a solution of **12** (10 mg) in chloroform (20 ml) was added a saturated solution of zinc(II) acetate in acetic acid (2 ml) at room temperature. After checking the conversion by UV, the mixture was washed with water and brine, dried over Na_2SO_4 and concentrated to give 10 mg of the title compound as pink powder: mp >300 °C; δ_H ($CDCl_3$) 10.81 (4H, s), 8.38 (16H, s), 7.82 (16H, m), 7.47 (8H, s) and 7.37 (16H, m); δ_C ($CDCl_3$) 152.16, 143.37, 142.35, 131.67, 127.39, 125.71, 122.45 and 99.60; MS (MALDI-TOF) *m/z* 1477 (M^+), 1478 ($M^+ + 1$) and 1479 ($M^+ + 2$); λ_{max} (CH_2Cl_2) 417, 538 and 570 nm (Found: C, 79.59; H, 4.30; N, 3.36. $C_{108}H_{60}N_4Zn\cdot 8H_2O$ requires C, 79.91; H, 4.72; N, 3.45%).

2,3;7,8;12,13;17,18-Tetrakis(6,13-dihydro-6,13-pentaceno)-21*H*,23*H*-porphyrinatonickel (14)

To a solution of **12** (10 mg) in chloroform (20 ml) was added a saturated solution of nickel(II) acetate in acetic acid (2 ml) at room temperature. After checking the conversion by UV, the mixture was washed with water and brine, dried over Na_2SO_4 and concentrated to give 10 mg of the title compound as red powder: mp >300 °C; δ_H ($CDCl_3$) 10.48 (4H, s), 8.29 (16H, s), 7.90 (16H, m), 7.36 (16H, m) and 6.80 (8H, s); δ_C ($CDCl_3$) 151.34, 142.96, 135.74, 131.64, 127.38, 125.74, 122.38 and 98.78; λ_{max} (CH_2Cl_2) 401, 515 and 549 nm.

Acknowledgements

We are grateful to the Research Center for Molecular-Scale Nanoscience, the Institute for Molecular Science for permission to carry out X-ray measurements (RAXIS-IV and AFC7R-Mercury CCD).

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