ELECTRONIC SUPPLEMENTARY INFORMATION
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Flexible porphyrin tetracarboxylic acids for crystal engineering

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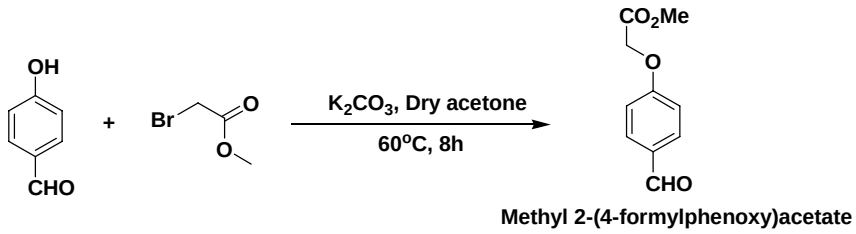
Materials preparation

Synthesis of tetrakis[4-(carboxymethyleneoxy)phenyl]porphyrin

The title compound, tetrakis[4-(carboxymethyleneoxy)phenyl]porphyrin was prepared by a three step procedure. The first step involves synthesis of Methyl-2-(4-formylphenoxy) acetate. Then, in the second step we synthesized the methyl ester of tetrakis[4-(carboxymethyleneoxy)phenyl]porphyrin, and finally the third step is the conversion of methyl ester into the carboxyporphyrine by alkaline hydrolysis.

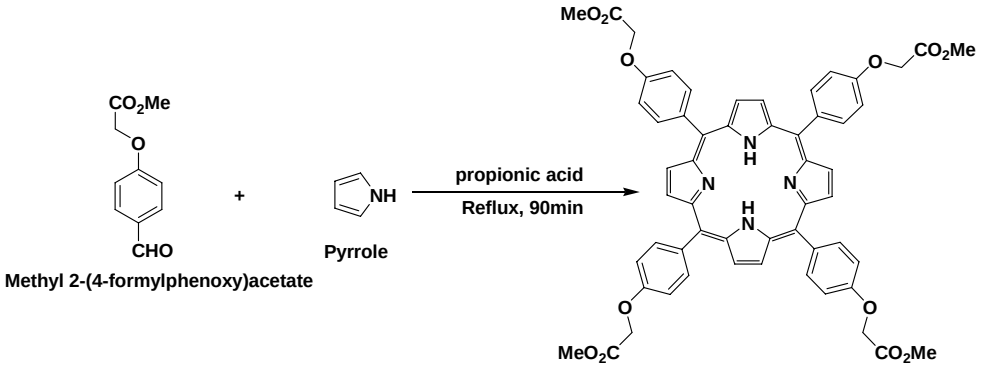
STEP 1: Synthesis of Methyl-2-(4-formylphenoxy) acetate:



Methyl 2-(4-formylphenoxy)acetate

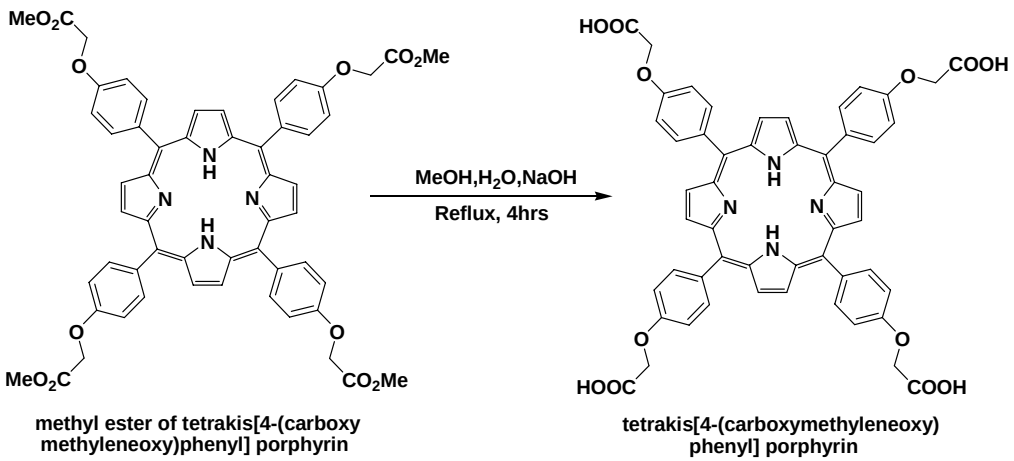
4-Hydroxybenzaldehyde (2.44 g, 20 mmol), methyl bromoacetate (3.34 g, 22 mmol) and anhydrous K_2CO_3 (1.65 g, 12 mmol) were placed in a round bottom flask and then added dry acetone (20ml). The reaction mixture was stirred for 8h at 60ºC (the reaction progress being monitored at regular intervals by TLC). After completion of the reaction, it was filtered off (to remove unreacted K_2CO_3) .The solvent was removed under reduced pressure and yellow liquid was obtained. The isolated product was washed with NaOH (5%) solution in water and then extracted with dichloromethane. The organic extracts were collected over anhydrous sodium sulphate; subsequent removal of the solvent gave the methyl-2-(4-formylphenoxy) acetate. Yield: 64%.

STEP 2: Synthesis of methyl ester of tetrakis[4-(carboxymethyleneoxy)phenyl] porphyrin



3.88 g (20mmol) of Methyl-2-(4-formylphenoxy) acetate was dissolved in 50ml of propionic acid and heated to 100°C. To this, 1.34g (20mmol) of distilled pyrrole was added. The resulting mixture was heated to refluxing for 90mins. Then, the mixture was cooled to RT and neutralized with K_2CO_3. The mixture was extracted with chloroform and the organic extracts were collected over anhydrous sodium sulphate; subsequent removal of the solvent gave black solid product. This product was dissolved in ethyl acetate and kept at RT for over night. The solid was filtered off and washed properly with ethyl acetate. The methyl ester of tetrakis[4-(carboxy methyleneoxy)phenyl]porphyrin was obtained as a purple solid. Yield = 11% (according to pyrrole). FT-IR (cm^{-1}): 3371(b), 2946(w, ν_{C-H}), 1751(s, $\nu_{C=O}$ asymmetric), 1602(s, $\nu_{C=C}$), 1506(s, $\nu_{C=C}$), 1431(m, $\nu_{C=O}$ symmetric), 1295(m), 1214(m, ν_{C-O}), 1177(s), 1075(m), 974(w), 801(s), 710(w), 604(w). ^{1}H-NMR ($CDCl_3$): 8.78 (8H, s), 8.07 (8H, d, J=8.6Hz), 7.23 (8H, d, J=8.6Hz), 4.88 (8H, s), 3.89 (12H, s).

STEP 3: Deesertification procedure



0.20 g (0.207mmol) of the porphyrin ester was dissolved in 20ml of methanol. To this, 0.067 g (1.65mmol) of NaOH in 2ml of water was added and heated at 75°C for 4 hours. The course of the reaction was monitored by thin layer chromatography (TLC). At the end of the reaction solvent was removed by rotary evaporation. The crude porphyrin was treated with 0.5 N HCl solution, yielding green precipitate which was filtered and washed with water several times and dried. Protonated porphyrin was neutralized by adding 5ml of pyridine. Solvent was removed by vacuum distillation. The bluish green solid was washed with water several times and dried under vacuum. Yield = 75%. FT-IR (cm^{-1}): 3384(b), 2895(w, ν_{C-H}), 1729(s, $\nu_{C=O}$ asymmetric), 1598(s, $\nu_{C=C}$), 1491(s, $\nu_{C=C}$), 1421(m, $\nu_{C=O}$ symmetric), 1222(bm, ν_{C-O}), 1173(m), 1065(s), 820(s), 687(m), 598(w), 520(w). ^{1}H-NMR (DMSO-d^{6}): 8.85 (8H, s), 8.13 (8H, d, J=8.6Hz), 7.36 (8H, d, J=8.6Hz), 4.98 (8H, s).

Crystallization procedures.

1; 10 mg of porphyrin ester was dissolved in 10 ml of 4:1 ethyl acetate/ hexane mixture (v/v) and kept it for slow evaporation. After 5 days purple plate type of crystals appeared.

2'; 5 mg of tetrakis[4-(carboxymethyleneoxy)phenyl] porphyrin was dissolved in 3 ml of DMF and placed in a 8 ml capped glass vessel. This mixture was heated at 100°C for 2days. After cooling the sample to room temperature, it was kept for crystallization. After 2 months purple plate type crystals appeared.

3: A mixture of tetrakis[4-(carboxymethyleneoxy)phenyl]porphyrin (5.0 mg, 0.005 mmol), and $Cu(NO_3)_2{\cdot}2½H_2O$ (3.5 mg, 0.015 mmol) was dissolved in 4 ml of MeOH/NH_4OH (2:1) mixture, placed in a capped glass vessel and heated at 85°C for 48h. After cooling the sample to room temperature, block-shaped red crystals appeared, which were washed with water and dried in air. Yield: 10% (based on Cu). FT-IR (cm^{-1}): 3448(bm), 3343(bs), 2922(w, ν_{C-H}), 1602(s, $\nu_{C=O}$ asymmetric), 1504(m), 1415(m, $\nu_{C=C}$), 1388(s, $\nu_{C=O}$ symmetric), 1340(w), 1229(s, ν_{C-O}), 1177(w), 1066(m), 1001(m), 803(s), 720(m), 610(w).

4: 9.1 mg (0.01 mmol) of tetrakis[4-(carboxymethyleneoxy)phenyl] porphyrin and 8.2 mg (0.03 mmol) of $Zn(NO_3)_2{\cdot}6H_2O$ was dissolved in 2 ml of 3:1 DMF/EtOH mixture (v/v). To this, 0.05 ml of 1 N HNO_3 was added. The green reaction mixture was placed in a sealed reactor and heated at 80°C for 24 hrs. Crystals suitable for X-ray

analysis were obtained upon cooling the reactor to ambient temperature. Yield: 24% (based on Zn). FT-IR (cm^{-1}): 2925(w, ν_{C-H}), 1654(s, $\nu_{C=O}$ asymmetric), 1506(m), 1421(m, $\nu_{C=C}$), 1333(m, $\nu_{C=O}$ symmetric), 1219(s, ν_{C-O}), 1174(m), 1104(w), 1064(m), 993(m), 848(m), 802(w), 719(w), 610(w).

Crystal Structure Determinations:

The X-ray measurements (Nonius KappaCCD diffractometer, MoKα radiation) were carried out at 110(2) K on crystals coated with a thin layer of amorphous oil to minimize crystal deterioration, possible structural disorder and related thermal motion effects, and to optimize the precision of the structural results. These structures were solved by direct methods (SIR-97) and refined by full-matrix least-squares (SHELXL-97). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon were located in idealized/calculated positions and were refined using a riding model, with $U_{iso} = 1.2\ U_{eq}$ of the parent atom. Those attached to O and N atoms, which are involved in hydrogen bonding were located in difference-Fourier maps; then their O-H and N-H distances were restrained to common values. Crystallographic refinements of all the structures converged to acceptable R-values, representing precisely determined structural models of compounds **1, 3** and **4** (and partly of **2'**), and allowing reliable characterizations of the molecular structures and supramolecular binding motifs.

Crystallographic data for compound 2'.

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3).

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
O(1)	-951(4)	9412(4)	4021(3)	56(1)
C(2)	-809(6)	8600(6)	4319(4)	50(2)
O(3)	-1409(5)	8241(5)	4852(4)	84(2)
C(4)	165(6)	8006(5)	4017(4)	49(2)
O(5)	214(3)	8156(3)	3197(2)	43(1)
C(6)	941(5)	7612(4)	2779(4)	37(2)
C(7)	1801(5)	7042(4)	3100(4)	39(2)
C(8)	2513(5)	6555(4)	2606(4)	37(2)
C(9)	2381(5)	6615(4)	1801(4)	35(1)
C(10)	1495(5)	7171(5)	1504(4)	41(2)
C(11)	784(5)	7669(5)	1981(4)	39(2)
C(12)	3183(5)	6117(4)	1269(3)	33(1)
C(13)	6235(5)	3292(4)	-731(3)	33(1)
C(14)	6295(5)	2291(4)	-652(4)	35(1)
C(15)	5642(5)	2013(4)	-50(4)	36(1)
C(16)	5107(5)	2827(4)	250(4)	36(1)
N(17)	5479(4)	3606(4)	-175(3)	36(1)
C(18)	4298(5)	2843(4)	859(4)	37(2)
C(19)	3983(5)	1910(4)	1215(4)	35(1)
C(20)	4347(6)	1585(5)	1949(5)	53(2)
C(21)	4101(6)	715(5)	2271(4)	49(2)
C(22)	3422(5)	137(4)	1890(4)	36(2)
C(23)	3057(6)	449(5)	1159(4)	56(2)
C(24)	3322(6)	1304(5)	834(4)	54(2)
O(25)	3113(4)	-728(3)	2164(3)	42(1)
C(26)	3754(6)	-1169(5)	2781(4)	44(2)
C(27)	3443(6)	-881(5)	3591(4)	47(2)
O(28)	2565(4)	-421(3)	3716(3)	51(1)
O(29)	4104(5)	-1157(4)	4112(3)	74(2)
C(30)	3763(5)	3656(4)	1127(4)	37(2)
C(31)	2854(5)	3641(5)	1690(4)	42(2)
C(32)	2547(5)	4544(4)	1800(4)	40(2)
C(33)	3234(5)	5138(4)	1318(4)	36(2)
N(34)	3962(4)	4566(4)	906(3)	36(1)
O(35)	7805(4)	5162(4)	3632(3)	62(2)
C(36)	8607(6)	5648(5)	3443(4)	46(2)
O(37)	9331(5)	5878(4)	3900(3)	76(2)
C(38)	8745(6)	6021(5)	2603(4)	42(2)
O(39)	8040(4)	5632(3)	2062(3)	44(1)
C(40)	8367(5)	4766(4)	1785(4)	38(2)
C(41)	9244(6)	4209(5)	2069(4)	45(2)
C(42)	9483(5)	3344(5)	1742(4)	44(2)
C(43)	8883(5)	3029(4)	1151(4)	35(1)
C(44)	7981(5)	3599(5)	878(4)	44(2)
C(45)	7750(5)	4461(5)	1177(4)	43(2)
C(46)	9183(5)	2105(4)	789(4)	36(2)
C(47)	8584(5)	1310(4)	995(4)	37(2)

C(48)	7633(5)	1318(5)	1521(4)	41(2)
C(49)	7316(5)	429(5)	1622(4)	40(2)
C(50)	8058(5)	-150(4)	1156(3)	33(1)
N(51)	8803(4)	415(4)	765(3)	36(1)
C(52)	8007(4)	-1132(4)	1141(3)	31(1)
C(53)	7288(5)	-1635(4)	1727(3)	33(1)
C(54)	6459(5)	-2224(5)	1534(3)	36(2)
C(55)	5862(5)	-2727(5)	2091(4)	37(2)
C(56)	6083(5)	-2641(5)	2884(4)	37(2)
C(57)	6901(5)	-2062(4)	3096(3)	36(2)
C(58)	7489(5)	-1563(4)	2525(4)	37(2)
O(59)	5434(4)	-3161(3)	3390(3)	46(1)
C(60)	5595(6)	-3031(5)	4193(4)	50(2)
C(61)	4720(7)	-3499(6)	4693(5)	60(2)
O(62)	3984(5)	-3917(5)	4399(3)	79(2)
O(63)	4830(5)	-3376(5)	5429(3)	76(2)
C(64)	8657(4)	-1699(4)	640(3)	30(1)
C(65)	8609(5)	-2696(4)	589(3)	33(1)
C(66)	9362(5)	-2946(5)	22(4)	38(2)
C(67)	10102(5)	2133(4)	274(4)	36(2)
N(68)	9428(4)	-1375(4)	112(3)	34(1)
C(69)	2225(9)	4501(8)	4315(7)	99(3)
N(70)	1416(8)	3882(9)	4577(6)	130(4)
C(71)	516(8)	3655(8)	4113(5)	84(3)
C(72)	622(8)	1220(6)	3368(6)	82(3)
N(73)	656(5)	255(4)	3087(3)	53(2)
C(74)	421(8)	247(6)	2252(5)	70(2)
C(75)	7426(7)	1358(6)	4281(5)	68(2)
N(76)	7225(6)	415(5)	4578(4)	67(2)
C(77)	6243(7)	-16(8)	4297(7)	94(3)
C(78)	5041(7)	4646(6)	2868(5)	66(2)
N(79)	6016(5)	4231(4)	3283(3)	47(1)
C(80)	6483(7)	3372(6)	2927(5)	66(2)
C(81)	4297(7)	1863(6)	4163(6)	72(3)
N(82)	3324(12)	1846(12)	3891(9)	194(7)
C(83)	2878(8)	2614(7)	3608(6)	75(3)
O(84)	2049(5)	6455(5)	5336(4)	98(2)

Atom	x	y	z	U(eq)
H(4A)	861	8195	4248	58
H(4B)	64	7329	4159	58
H(7)	1896	6989	3649	46
H(8)	3104	6171	2822	44
H(10)	1379	7207	957	49
H(11)	190	8048	1765	46
H(14)	6727	1886	-972	42
H(15)	5553	1380	142	43
H(20)	4784	1982	2237	64
H(21)	4399	507	2761	58
H(23)	2610	54	878	67
H(24)	3049	1494	333	65
H(26A)	4540	-1029	2680	52
H(26B)	3690	-1862	2766	52
H(31)	2537	3097	1935	50
H(32)	1971	4754	2141	48
H(34)	4464	4758	562	43

H(38A)	8610	6714	2584	50
H(38B)	9522	5896	2434	50
H(41)	9677	4412	2480	54
H(42)	10086	2960	1938	53
H(44)	7528	3384	482	53
H(45)	7164	4855	968	52
H(48)	7297	1855	1751	49
H(49)	6715	216	1941	48
H(54)	6298	-2282	1000	44
H(55)	5304	-3130	1941	44
H(57)	7061	-2007	3631	43
H(58)	8046	-1159	2676	44
H(60A)	5576	-2347	4284	60
H(60B)	6333	-3298	4344	60
H(65)	8145	-3106	889	40
H(66)	9502	-3568	-145	46
H(68)	9601	-782	29	41
H(69A)	2632	4239	3871	148
H(69B)	2739	4588	4738	148
H(69C)	1874	5112	4153	148
H(70A)	1114	4117	5027	155
H(70B)	1780	3321	4720	155
H(71A)	47	4223	4003	126
H(71B)	80	3174	4395	126
H(71C)	799	3409	3621	126
H(72A)	1132	1608	3052	123
H(72B)	842	1199	3915	123
H(72C)	-132	1495	3324	123
H(73A)	1345	-22	3177	64
H(73B)	145	-96	3365	64
H(74A)	-344	474	2163	105
H(74B)	523	-398	2078	105
H(74C)	928	661	1957	105
H(75A)	7454	1375	3709	103
H(75B)	8133	1556	4475	103
H(75C)	6828	1788	4456	103
H(76A)	7171	419	5113	80
H(76B)	7833	35	4457	80
H(77A)	5590	394	4396	142
H(77B)	6154	-632	4571	142
H(77C)	6326	-100	3735	142
H(78A)	5261	4853	2336	99
H(78B)	4738	5188	3145	99
H(78C)	4477	4171	2848	99
H(79A)	6552	4673	3283	56
H(79B)	5817	4083	3793	56
H(80A)	5931	2884	2954	99
H(80B)	7143	3141	3211	99
H(80C)	6685	3522	2380	99
H(81A)	4761	2245	3806	108
H(81B)	4615	1218	4217	108
H(81C)	4260	2140	4675	108
H(82A)	2865	1618	4285	232
H(82B)	3341	1417	3507	232
H(83A)	3328	3145	3730	112
H(83B)	2133	2704	3836	112
H(83C)	2828	2585	3041	112

Table of hydrogen bonds (Å, º)**.**

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A [symmetry site] .
N70-H70A	0.920	1.909	158	2.782	O37 [-x+1, -y+1, -z+1]
N70-H70B	0.920	2.355	141	3.120	O3 [-x, -y+1, -z+1]
N73-H73A	0.920	1.813	158	2.690	O28
N73-H73B	0.920	1.856	169	2.764	O1 [x, y-1, z]
N73-H73B	0.920	2.510	117	3.043	O5 [x, y-1, z]
N76-H76A	0.920	2.041	167	2.945	O28 [-x+1, -y, -z+1]
N76-H76A	0.920	2.275	130	2.952	O29 [-x+1, -y, -z+1]
N76-H76B	0.920	1.851	168	2.758	O1 [x+1, y-1, z]
N79-H79A	0.920	1.815	154	2.673	O35
N79-H79B	0.920	1.811	155	2.671	O63 [-x+1, -y, -z+1]
N82-H82A	0.920	2.286	153	3.133	O3 [-x, -y+1, -z+1]
N82-H82B	0.920				

Powder diffraction diagrams for compound 4

Experimental (top) and structure-calculated (bottom) powder diffraction diagrams