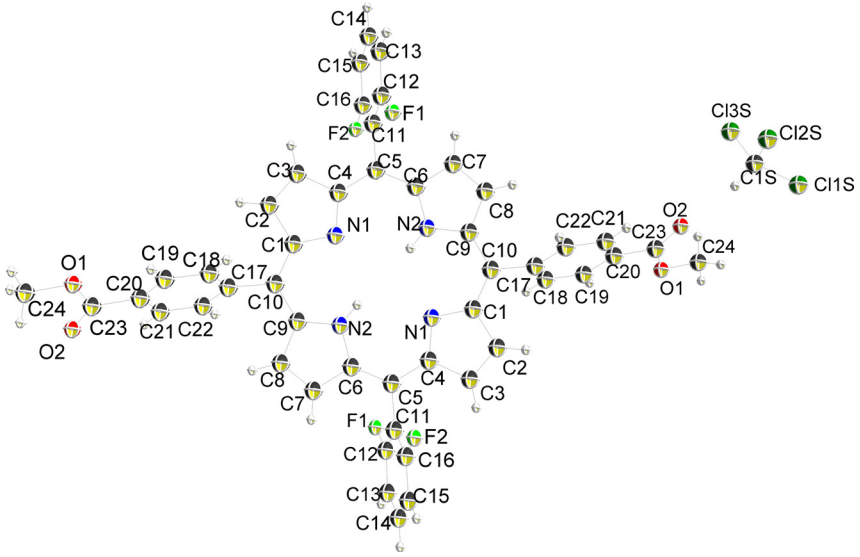
Bingcui Yang, Yuzhou Wang and Hao Cui*

The crystal structure of dimethyl 4,4′-[10,20-bis(2,6-difluorophenyl) porphyrin-5,15-diyl]dibenzoate chloroform solvate, $C_{50}H_{32}Cl_6F_4N_4O_4$



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Abstract

$C_{50}H_{32}Cl_6F_4N_4O_4$, triclinic, $P\bar{1}$ (no. 2), a = 6.6447(6) Å, b = 12.5839(11) Å, c = 14.3335(11) Å, α = 85.845(7)°, β = 85.679(7)°, γ = 85.679(7)°, V = 1188.89(18) Å^3, Z = 1, $R_{gt}(F)$ = 0.0605, $wR_{ref}(F^2)$ = 0.1740, T = 200 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Hao Cui**, School of Pharmaceutical Sciences, Guangxi University of Chinese Medicine, Nanning 530200, P.R. China, E-mail: ch008szx6@163.com. https://orcid.org/0000-0002-8378-7309
Bingcui Yang and Yuzhou Wang, School of Pharmaceutical Sciences, Guangxi University of Chinese Medicine, Nanning 530200, P.R. China

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.10 × 0.05 × 0.05 mm
Wavelength:	CuKα radiation (1.54184 Å)
μ:	3.86 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	66.0°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6205, 4076, 0.043
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3205
$N(param)_{refined}$:	308
Programs:	CrysAlis^{Pro} [1], Olex2 [2], Shelx [3, 4]

1 Source of materials

All chemicals were purchased from commercial sources and used as received without further purification. Procedures for the preperation of trimethyl dimethyl4,4′-[10,20- bis(2,6-difluorophenyl)porphyrin-5,15-diyl]dibenzoate were adapted from the reported papers [5, 6]. Under N_2 atmosphere, trifluoroacetic acid (0.3 ml) was added to a stirred solution of 20 g (122 mmol)methyl p-formylbenzoate and 100 ml pyrrole under nitrogen gas atmosphere. The reaction mixture was

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.3442 (4)	0.3524 (2)	0.05240 (19)	0.0254 (6)
C1S	1.4212 (7)	0.9357 (4)	0.3317 (3)	0.0616 (10)
H1S	1.343549	0.927057	0.277662	0.074*
C2	−0.4452 (4)	0.2958 (2)	0.1329 (2)	0.0318 (6)
H2A	−0.555455	0.254554	0.132063	0.038*
C3	−0.3487 (4)	0.3144 (2)	0.2085 (2)	0.0321 (6)
H3	−0.380183	0.289548	0.270166	0.039*
C4	−0.1856 (4)	0.3808 (2)	0.17473 (19)	0.0247 (5)
C5	−0.0438 (4)	0.4141 (2)	0.23223 (18)	0.0254 (6)
C6	0.1139 (4)	0.4784 (2)	0.20376 (18)	0.0259 (6)
C7	0.2443 (4)	0.5209 (2)	0.2642 (2)	0.0322 (6)
H7	0.244723	0.505999	0.328732	0.039*
C8	0.3678 (4)	0.5869 (2)	0.2116 (2)	0.0315 (6)
H8	0.465833	0.625575	0.233778	0.038*
C9	0.3204 (4)	0.5862 (2)	0.11598 (19)	0.0247 (5)
C10	0.4038 (4)	0.6469 (2)	0.0393 (2)	0.0248 (6)
C11	−0.0628 (4)	0.3789 (2)	0.33453 (19)	0.0291 (6)
C12	0.0653 (5)	0.2986 (3)	0.3724 (2)	0.0376 (7)
C13	0.0558 (6)	0.2646 (3)	0.4663 (2)	0.0518 (9)
H13	0.146584	0.210811	0.489029	0.062*
C14	−0.0919 (6)	0.3125 (4)	0.5256 (2)	0.0575 (10)
H14	−0.101712	0.290211	0.588984	0.069*
C15	−0.2244 (6)	0.3925 (4)	0.4920 (2)	0.0580 (11)
H15	−0.324219	0.424608	0.531937	0.070*
C16	−0.2063 (5)	0.4242 (3)	0.3976 (2)	0.0439 (8)
C17	0.5556 (4)	0.7224 (2)	0.06003 (19)	0.0262 (6)
C18	0.5063 (4)	0.8320 (2)	0.0507 (2)	0.0302 (6)
H18	0.383290	0.857421	0.027781	0.036*
C19	0.6380 (4)	0.9035 (2)	0.0753 (2)	0.0322 (6)
H19	0.603267	0.976493	0.069042	0.039*
C20	0.8220 (4)	0.8663 (2)	0.1091 (2)	0.0300 (6)
C21	0.8721 (4)	0.7572 (2)	0.1191 (2)	0.0340 (7)
H21	0.994457	0.732004	0.142749	0.041*
C22	0.7406 (4)	0.6860 (2)	0.0939 (2)	0.0341 (7)
H22	0.776252	0.613033	0.099701	0.041*
C23	0.9665 (4)	0.9407 (3)	0.1392 (2)	0.0373 (7)
C24	1.0484 (5)	1.1182 (3)	0.1414 (3)	0.0504 (9)
H24A	1.020229	1.186677	0.109154	0.076*
H24B	1.188083	1.095033	0.128417	0.076*
H24C	1.021009	1.123777	0.207632	0.076*
Cl1S	1.5749 (2)	1.04093 (11)	0.30153 (11)	0.0888 (5)
Cl2S	1.5640 (2)	0.81582 (11)	0.35393 (10)	0.0836 (4)
Cl3S	1.2493 (3)	0.96599 (15)	0.42467 (16)	0.1309 (8)
F1	0.2097 (3)	0.25112 (18)	0.31402 (15)	0.0544 (6)
F2	−0.3335 (4)	0.5046 (2)	0.36539 (15)	0.0695 (8)
N1	−0.1869 (3)	0.40386 (18)	0.07987 (16)	0.0244 (5)
N2	0.1683 (3)	0.51828 (18)	0.11461 (15)	0.0237 (5)
H2	0.114938	0.502963	0.064918	0.028*
O1	0.9218 (3)	1.04173 (17)	0.10955 (17)	0.0403 (5)
O2	1.1075 (4)	0.9118 (2)	0.1845 (2)	0.0600 (8)

stirred at room temperature for 0.5 h. After that, TLC analysis (dichloromethane/hexane 3:1) showed the complete consumption of methy-lp-formylbenzoate. The excessive pyrrole was removed to afford the crude product. Then, the crude product was purified by column chromatography on silica gel eluted with (CH_2Cl_2/PE 3:1) to give the corresponding compound (15.62 g, 78 %) as a white solid. ^{1}H NMR (400 MHz, $DCCl_3$) δ 10.62 (s, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 6.63 (s, 2H), 5.91 (s, 2H), 5.66 (s, 2H), 5.44 (s, 3H). Under N_2 atmosphere, 4-(di(1*H*-pyrrole-2-yl)methyl)benzoate (1.12 g, 4 mmol) and 2,6-difluorobenzaldehyde (4 mmol) were dissolved in 500 ml dichloromethane, and then boron (tri) fluoride etherate (50 μL) was added. Subsequently, the reaction was stirred at room temperature for 1 h. After that, DDQ (2,3–dichloro-5,6- dicyano-p-benzoquinone) (4 mmol, 908 mg) was added, and the mixture was stirred at room temperature 2 h. The reaction mixture was evaporated to dryness, and the crude product was purified by chromatography (silica gel) with dichloromethane, dichloromethane/PE (3:1, by vol.) and dichloromethane successively, finally with pure green product obtained (140 mg, 20.6 % yield). ^{1}H NMR (400 MHz, $DCCl_3$) δ 8.84 (8H, d, *J* = 5.6), 8.43 (4H, d, *J* = 8.0), 8.29 (4H, d, *J* = 8.0), 7.78 (2 H, s), 7.37 (4 H, m), 4.10 (6 H, s), −2.80 (2 H, s). **MALDI–TOF–MS** (*m*/*z*): $[M]^+$ calcd. for $C_{48}H_{30}F_4N_4O_4$, 803.2237; found, 803.2275. Single crystals were obtained from solution of the title compound in $DCCl_3$ at room temperature for two days.

2 Experimental details

Single-crystal X-ray diffraction data for the title structure was collected on SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer by 'CrysAlisPro 1.171.39.46' [2]. A suitable crystal was selected and mounted on the diffractometer and the data was collected. The structure was solved with the Shelxt [3] structure solution program and refined with the xl [4] refinement package. The positions of the hydrogen atoms were generated geometrically. The cif-file of the title compound can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif (2265016).

3 Comment

Fluorine, with the strong electrophilic properties and the unique properties of fluorine, can cause many interesting changes in the porphyrin ring when it is introduced. Fluoro-porphyrins are widely used in the fields of biology, biochemistry [7], catalysis [8], medicine [9] and materials [8] due to their unique structural characteristics. It is of great significance to design fluoro-porphyrin-containing compounds or porous materials. We have synthesized a

fluoro-porphyrin-containing compound, which can be used for the synthesis of fluoro-porphyrin-containing metal-organic frameworks after hydrolysis. The crystal structure of the complex is shown in the figure. The symmetric unit contains the half porphyrin and one $CHCl_3$ molecule. The substituent at the substitution positions of porphyrin 10,20 is 2,6-difluorophenyl and the substituent at position 5,10 is phenyl. The bond lengths and angles within molecule are in the expected ranges [10]. The distance of N1–C1, N1–C4, N2–C6, N2–C9 is 1.367(3), 1.370(4), 1.371(4), 1.374(3) Å, the distance of C1s–Clsl, C1s–Cls2, C1s–Cls3 is 1.743(4), 1.743(5), 1.732(5) Å, the distance of F1–C12, F2–C16 is 1.356(4), 1.347(4) Å. Void between porphyrin molecules in the structure are occupied by $CHCl_3$ molecules.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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