

1D Columnar stacking structures in the single crystals of 5,10-diarylporphyrin metal complexes

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ABSTRACT: A general design of a *meso*-aryl porphyrin for the formation of a 1D columnar stacking structure in the single crystal state is proposed. We found that 5,10-diphenyl- and 5,10-bis(pentafluorophenyl)porphyrin metal complexes (M = Zn, Ni) can stack in a complementary manner to form a 1D columnar stacking structure in the single crystals, while the corresponding freebase porphyrins displayed herringbone or dimeric orthogonal packing forms. The structural details of the obtained 1D columnar packing structures are discussed in comparison with precedented examples including 5,10-diphenylporphyrin Cu(II) and Ag(II) complexes, 5,10-diphenyl *N*-confused porphyrin Ag(III) complex and 5,10-bis(pentafluorophenyl)corrole.

KEYWORDS: porphyrin, metal complex, X-ray diffraction analysis, packing structure, polymorph.

INTRODUCTION

Molecular assembly in the solid state plays a vital role for electronics applications such as OFET and OPV [1]. A variety of π -conjugated molecules have been studied to exploit effective conducting properties through overlap of π -orbitals. Among them, porphyrins have been regarded as a good motif because of their square-planar structure, effective π -conjugation, strong visible light absorption, and rich metal coordination ability. By virtue of these advantages, discotic columnar liquid crystalline molecules based on porphyrin scaffolds have been developed to exhibit a promising conductive character [2, 3]. In addition, it is well known that a 1D columnar stacking structure in the single crystal state also offers an effective conducting pathway with significant isotropic character (Fig. 1) [4]. Since the solid-state packing of porphyrins is often susceptible to peripheral substituents (*i.e.* β -alkyl and *meso*-aryl substituents) [5], a design principle for columnar packing in the solid-state is essentially useful for applications in materials science. Herein, we show an interesting tendency of 5,10-diarylsubstituted porphyrins to stack in a 1D columnar fashion in the single crystal.

RESULTS AND DISCUSSION

Synthesis of 5,10-diphenylporphyrin **1H** has been previously reported by several groups [6]. In our own right, we found better reaction conditions for acidcatalyzed condensation of 5,10-diphenyltripyrrane (**3a**) [7] and 2,5-di(hydroxymethyl)pyrrole (**4**) (Scheme 1) [8]. To a mixture of **3a** and **4** in chloroform was added a catalytic amount of BF₃·OEt₂, and the resulting mixture was stirred for 1 h at room temperature, followed by oxidation conducted with 5 equivalents of chloranil. After the usual work-up, the residual solids were subjected to separation by column chromatography. Notably, a troublesome contamination with 5,15-diphenylporphyrin or 5-phenylporphyrin was somehow suppressed, and **1H** was obtained in 12% yield [9]. In a similar but

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Fig. 1. Schematic representations for packing structures of porphyrins

slightly modified manner, a condensation reaction of 5,10-bis(pentafluorophenyl)tripyrrane (**3b**) [10] with **4** followed by oxidation with chloranil gave 5,10-bis(pentafluorophenyl)porphyrin **2H** in 17% yield. **2H** would be a useful building-block for the construction of designed porphyrin arrays [11]. Metal complexes of **1H** and **2H** were prepared according to the usual procedures (see the experimental section). Thus, Ni(II) complexes **1Ni** and **2Ni**, and Zn(II) complexes **1Zn** and **2Zn** were prepared.

In a recent report by Senge *et al.*, the crystal structure of **1H** has been shown in detail [12]. In the solid-state of **1H**, porphyrins are stacked in a so-called herringbone manner with an interplanar distance of 3.681Å. The two phenyl groups are tilted against the porphyrin plane by 55–62°. As long as we re-investigated the solid-state

structure of **1H** by ourselves, no polymorphs were found, likely because this packing structure does not include void spaces occupied by solvent molecules. In the meantime, we have successfully grown single crystals of 2H by slow-vapor diffusion of *n*-heptane into a chlorobenzene solution of 2H. X-ray diffraction (XRD) analysis revealed that two porphyrins are $\pi - \pi$ stacked in a complementary manner with an interplanar distance of 3.395Å (Fig. 2). A set of two stacked porphyrins is packed perpendicular to the neighboring set in a closest (β -H)–(porphyrin π plane) distance of 2.639Å. Since the unit cell included chlorobenzene molecules, other solvent systems were examined. Although single crystals were also obtained from a 1,2-dichlorobenzene/n-octane system, the packing structure was almost the same (see Supporting information).

In the course of our study, we found different types of single crystals of 2Ni depending on the solvent system used to grow them. A single crystal grown from a mixture of toluene and *n*-heptane looks like a rhombic plate. The XRD analysis of the crystal showed a dimeric stacking form similarly to the case of 2H (Fig. 3a). On the other hand, thin fiber-like crystals were obtained by slow vapor diffusion of *n*-octane into a solution of **2Ni** in 1,2-dichlorobenzene. Interestingly, the XRD analysis of the crystal revealed a 1D columnar stacking structure (Fig. 3b), in which each porphyrin unit is stacked in a complementary manner to avoid the steric congestion between the pentafluorophenyl groups at the *meso*-positions. The interplanar distances $(d^1 \text{ and } d^2)$ are calculated to be 3.399 and 3.531Å and the Ni-Ni distances are 4.418 and 3.970Å, respectively. From these



Scheme 1. Synthesis of 5,10-diarylporphyrins



Fig. 2. Solid-state packing structure of **2H**. Single crystals were grown from chlorobenzene/*n*-heptane. Solvent molecules included in the crystal lattice were omitted for clarity

values, the horizontal offset distances are calculated to be 2.822 and 1.815Å. Despite our continuous attempts, the crystal structure of **1Ni** was not obtained, mainly due to the poor solubility.

Fiber-like crystals of **1Zn** and **2Zn** suitable for XRD analysis were obtained by slow-vapor diffusion

of *n*-heptane and *n*-octane into the 1,2-dichlorobenzene solutions, respectively. The XRD analyses revealed 1D columnar stacking structures in both cases. 1Zn crystallizes in the triclinic space group with one molecule in the asymmetric unit (Fig. 4a). The interplanar distances are calculated to be 3.270 and 3.324Å. On the other hand, **2Zn** crystallizes in the monoclinic space group with two independent molecules in the asymmetric unit. Although the structural details about the packing structure of 2Zn become complicated, the interplanar distances are calculated to be 3.090, 3.195, 3.371, and 3.411A, being in the range of typical π - π stacking distance (Fig. 4b). The horizontal offset distances are calculated; 1.858 and 1.808Å for 1Zn, and 4.274, 2.367, 1.525 and 2.043Å for 2Zn. Relatively larger offset distances in 2Zn are notable, which is partly ascribed to the disordering of the solvate molecules in the crystal lattice.

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Regarding the trend to form 1D columnar packing structures in the single crystals of 5,10-disubstituted porphyrins, let us consider the generality of this phenomenon. Very recently, Senge *et al.* reported a copper(II) complex of 5,10-diphenylporphyrin (**1Cu**) which showed columnar packing similar to the case of **1Zn** [12]. 5,10-Diphenyl-substituted silver(II) porphyrin **1Ag** and silver(III) *N*-confused porphyrin **5Ag** both were reported to display 1D columnar stacking structures in the single crystal state [13]. In another case, 5,10-bis(pentafluorophenyl)corrole (**6H**) has been recently reported to form a 1D columnar packing structure, and this is likely the only example of freebase 5,10-disubstituted porphyrinoid that forms columnar stacking in the single crystal [14]. In contrast,



Fig. 3. Solid-state packing structures of 2Ni in different packing modes. The single crystals were grown from (a) toluene/*n*-heptane and (b) 1.2-dichlorobenzene/*n*-octane. The solvent molecules included in the crystal lattice were omitted for clarity



Fig. 4. X-ray crystal structures of (a) **1Zn** and (b) **2Zn**. Single crystals were grown from (a) 1,2-dichlorobenzene/*n*-heptane and (b) 1,2-dichlorobenzene/*n*-octane. The solvent molecules included in the crystal lattice were omitted for clarity

Compd.	Interplane distance [Å]	Horizontal offset distance [Å] ^a	e [Å] ^a MPD [Å] ^b	
1Zn	3.324, 3.270	1.808, 1.858	0.028	
$1Cu^{[12]}$	3.292, 3.285	1.698, 1.711	0.018	
1Ag ^[13]	3.322, 3.299	1.641, 1.686	0.020	
2Zn	3.090, 3.195, 3.371, 3.411	4.274, 2.367, 1.525, 2.043	0.055, 0.047	
2Ni	3.531, 3.399	1.815, 2.822	0.126	
5 Ag ^[13]	3.307, 3.319	1.642, 1.699	0.026	
6H ^[14]	3.400, 3.431, 3.304, 3.368	2.550, 2.117, 2.481, 2.148	0.046, 0.053	

Table 1. Summary of structural details for columnar stacked porphyrinoids

^a The horizontal offset distances are calculated by [(metal-metal distance)²–(interplane distance)²]^{1/2}. For a freebase, an empty metal center was defined as the gravity center of four nitrogens. ^b The mean-plane was defined by core 24 atoms in the case of porphyrins and by core 23 atoms in the case of corrole.

cobalt(III) and gallium(III) complexes of **6H** did not form 1D stacking structures due to the axially metal-coordinated pyridines [15].

All the columnar stacking structures discussed in this paper are compared in Table 1. For **1Zn**, **1Cu**, **1Ag** and **5Ag**, the interplanar distances fall within the range of 3.27–3.32Å, and the horizontal offset distances are shorter (1.64–1.86Å). In these molecules, smaller mean plane deviation (MPD) values (less than 0.03Å) are

favorable for the formation of the π -stacked structures. On the other hand, π - π overlapping was somewhat hampered for a less planar porphyrin such as **2Ni** (MPD: 0.126Å) that displays larger interplanar and horizontal offset distances. **2Zn** and **6H** displayed relatively large interplanar and horizontal offset distances despite their relatively smaller MPD values. Both single crystals contained two independent molecules in their assymetric units, making the unit cell larger and the void space



Fig. 5. Examples of 5,10-disubstituted porphyrinoids reported previously

expanded. As a result, the columnar packing structure became less suitable to form rigid packing. Thus, the choice of solvent molecules that could be included between columnars is crucial, so that polymorphic crystals can be easily expected as seen in **2Ni**. This work may invoke further investigation on porphyrinic crystal engineering in light of numerous intriguing applications such as guest encapsulation, spin array and isotropic conductivity [16].

EXPERIMENTAL

General

Commercially available solvents and reagents were used without further purification unless otherwise noted. Spectroscopic grade solvents were used for all the spectroscopic studies. Silica gel column chromatography was performed on a Wakogel C-300. Alumina column chromatography was performed on a Sumitomo y-Alumina KCG-1525W (Blockmann grade II). Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F254 (Merck 5554). UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5300PC spectrometer. Absolute fluorescence quantum yields were determined on a HAMAMATSU C9920-02S. ¹H and ¹⁹F NMR spectra were recorded on a JEOL ECA-600 spectrometer (operating at 600.17 MHz for ¹H and 564.73 MHz for ¹⁹F) using the residual solvent as the internal reference for ¹H $(\delta = 7.26 \text{ ppm in CDCl}_3)$ and hexafluorobenzene as an external reference for ¹⁹F (δ = 162.9 ppm). High-resolution atmospheric-pressure-chemical-ionization time-of-flight mass-spectroscopy (HR-APCI-TOF-MS) was performed on a BRUKER micrOTOF model using positive mode.

Crystal data

Single-crystal X-ray diffraction analysis data for **2H**, **2Ni**, **1Zn**, and **2Zn** were collected at -180 °C with a Rigaku XtaLAB P200 using graphite monochromated Cu-K_{α} radiation ($\lambda = 1.54187$ Å) (Table 2). The structures were solved by direct methods (SHELXS-97)

and refined with the full-matrix least square technique (SHELXL-97).

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5,10-Diphenylporphyrin (1H)

5,10-Diphenyltripyrrane (**3a**) (1.5 g, 4.0 mmol) was dissolved in degassed chloroform (500 mL), to which a solution of 2,5-dihydroxymethylpyrrole (**4**) (505 mg, 4.0 mmol) in methanol was added. After the mixture was stirred for 10 min, borontrifluoride diethyletherate (0.10 mL, 20 mol%) was added and the solution was stirred for 1 h at room temperature in the dark. Chloranil (4.9 g, 5 equiv) was added to the reaction mixture and the mixture was further stirred for 40 min. Then the solution was passed through an alumina column and a silica-gel column. The solution was purified by recrystallization from dichloromethane/methanol to afford **1H** (221 mg, 0.48 mmol, 12%). The spectroscopic data have been reported previously [6].

5,10-Bis(2,3,4,5,6-pentafluorophenyl)porphyrin (2H)

5,10-Bis(2,3,4,5,6-pentafluorophenyl)tripyrrane (**3b**) (2.5 g, 4.5 mmol) was dissolved in degassed dichloromethane (2.0 L), to which a solution of 2,5-dihydroxymethylpyrrole (**4**) (570 mg, 4.5 mmol) in methanol was added. After the mixture was stirred for several minutes, *p*-toluene sulfonic acid monohydrate (120 mg, 16 mol%) was added and the solution was stirred for 16 h at room temperature in the dark. Chloranil (3.3 g, 3.1 equiv) was added to the reaction mixture and the mixture was further stirred for 30 min. Then the solution was passed through an alumina column and a silica-gel column. The solution was purified by recrystallization from dichloromethane/methanol to afford **2H** (480 mg, 0.75 mmol, 17%).

2H; ¹H NMR (600.17 MHz; CDCl₃): δ , ppm 10.36 (s, 2H, por-*meso*), 9.50 (s, 2H, por- β), 9.46 (d, *J* = 4.8 Hz, 2H, por- β), 8.97 (d, *J* = 4.8 Hz, 2H, por- β), 8.95 (s, 2H, por- β) and -3.44 (s, 2H, NH); ¹⁹F NMR (564.73 MHz; CDCl₃) δ (ppm): -137.86 (d, *J* = 17.5 Hz, 4F, *o*-F), -152.15 (t, *J* = 21.9 Hz, 2F, *p*-F) and -161.79 (d, *J* =

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Compound	2H	2Ni	2Ni	1Zn	2Zn	
Empirical formula	$\begin{array}{c} 2(C_{32}H_{12}F_{10}N_4)\cdot\\ C_6H_4Cl \end{array}$	$\frac{2(C_{32}H_{10}F_{10}N_4Ni)\cdot}{C_7H_8}$	$\begin{array}{c} C_{32}H_{10}F_{10}N_4Ni \\ 1.5(C_6H_{14}Cl_2) \end{array}$	$\begin{array}{c} C_{32}H_{20}N_4Zn \cdot \\ C_6H_4Cl_2 \end{array}$	$\begin{array}{c} 2(C_{32}H_{10}F_{10}N_4Zn)\cdot\\ C_6H_4Cl_2.0.5(C_6Cl_2)\end{array}$	
$M_{\scriptscriptstyle W}$	1397.46	1490.39	919.64	672.9	3260.26	
<i>T</i> [K]	93 (2)	93 (2)	93 (2)	93 (2)	93 (2)	
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic	
Space group	$P 2_1/a$ (No. 14)	<i>P can</i> (No. 60)	$P 2_1/c$ (No. 14)	P -1 (No. 2)	<i>C</i> 2/ <i>m</i> (No. 15)	
a [Å]	12.258 (4)	12.5641 (12)	7.440 (2)	6.6099 (18)	19.530 (5)	
<i>b</i> [Å]	14.505 (5)	14.3019 (13)	19.583 (4)	12.212 (5)	25.401 (6)	
<i>c</i> [Å]	16.184 (5)	31.686 (3)	24.048 (6)	18.562 (5)	13.044 (3)	
α [deg]	90	90	90	103.027 (1)	90	
β [deg]	94.7115 (6)	90	97.203 (6)	95.391 (3)	97.034 (9)	
γ[deg]	90	90	90	96.693 (19)	90	
Volume [Å ³]	2870.1 (16)	5693.7 (9)	3476.1 (15)	1438.6 (8)	3211 (3)	
Ζ	2	4	4	2	4	
Density [Mg/m ³]	1.617	1.739	1.757	1.682	1.686	
Crystal size [mm ³]	$0.07 \times 0.05 \times 0.01$	$0.16 \times 0.09 \times 0.03$	$0.06 \times 0.03 \times 0.02$	$0.56 \times 0.06 \times 0.02$	$0.03 \times 0.02 \times 0.01$	
Completeness	0.991	0.986	0.99	0.96	0.99	
Reflections collected/ unique	18699/5065	20060/5000	23105/6125	16950/4403	19786/5269	
Goodness-of-fit	1.016	1.053	1.069	1.015	1.008	
$R_1 \left[I > 2\sigma \left(I \right) \right]$	0.0688	0.0286	0.0461	0.0307	0.0645	
$wR_2 \left[I > 2\sigma \left(I \right) \right]$	0.1814	0.0786	0.1106	0.0812	0.182	
R_1 (all data)	0.1162	0.0341	0.0727	0.0338	0.0786	
wR_2 (all data)	0.2057	0.0806	0.1221	0.0827	0.1968	
CCDC	1582878	1582880	1582879	1582877	1582881	
Solvent systems	C ₆ H ₅ Cl/heptane	toluene/heptane	C ₆ H ₄ Cl ₂ /octane	C ₆ H ₄ Cl ₂ /heptane	C ₆ H ₄ Cl ₂ /octane	

Table 2. Crystal data structure refinements for 2H, 2Ni, 1 Zn and 2Zn

 $R_1 = \Sigma(||F_0| - |F_c||) / \Sigma |F_0|, \ wR_2 = \Sigma w(|F_0|^2 - |Fc|^2)^2 / \Sigma w(|F_0|^2)^2]^{1/2}.$

17.5 Hz, 4F, *m*-F); HR-APCI-TOF-MS: *m/z* 642.0891, calcd. for $C_{32}H_{12}F_{10}N_4$ 642.0897 [*M*]⁺. UV-vis (CH₂Cl₂): λ_{max} , nm (ϵ [M⁻¹cm⁻¹]) = 404 (184000), 498 (12200) and 571 (4200); fluorescence (CH₂Cl₂, λ_{ex} = 571 nm): λ_{max} , nm = 624 and 688, Φ_F = 0.030.

General procedure for the synthesis of zinc(II) porphyrins

A saturated solution of $Zn(OAc)_2$ in methanol was added to a solution of **1H** or **2H** in chloroform and the resulting mixture was stirred for 2–3 h at 40–50 °C. The reaction mixture was quenched with water and extracted with chloroform. The organic layer was dried with anhydrous Na₂SO₄, passed through a short plug of silica gel, and evaporated to remove the solvent. Purification was carried out by silica gel column chromatography and recrystallization. The spectroscopic data of 1Zn have been reported previously (Fig. 5) [6a].

2Zn; ¹H NMR (600.17 MHz; acetone-*d*₆): δ, ppm 10.55 (s, 2H, por-*meso*), 9.67 (s, 2H, por-β), 9.63 (d, *J* = 4.6 Hz, 2H, por-β), 9.24 (d, *J* = 4.6 Hz, 2H, por-β), and 9.22 (s, 2H, por-β); ¹⁹F NMR (564.73 MHz; acetone-*d*₆): δ ppm -139.83 (d, *J* = 17.7 Hz, 4F, *o*-F), -156.80 (t, *J* = 17.5 Hz, 2F, *p*-F) and -165.36 (t, *J* = 17.5 Hz, 4F, *m*-F); HR-APCI-TOF-MS: *m/z* 704.0029, calcd. for C₃₂H₁₀F₁₀N₄⁶⁴Zn704.0032[*M*]⁺. UV-vis (CH₂Cl₂): λ_{max}, nm (ε [M⁻¹cm⁻¹]) = 404 (303000), 534 (7900) and 568 (3000); fluorescence (CH₂Cl₂, λ_{ex} = 534 nm): λ_{max}, nm 572 and 621, Φ_F = 0.015.

General procedure for the synthesis of nickel(II) porphyrins

An excess amount of Ni(acac)₂,xH₂O was added to a solution of **1H** or **2H** in toluene and the resulting mixture was stirred overnight under reflux. The reaction mixture was quenched with water and extracted with dichloromethane. The organic layer was dried with anhydrous Na₂SO₄, passed through a short plug of silica gel, and evaporated to remove the solvent. Purification was carried out by silica gel column chromatography and recrystallization. The spectroscopic data of **1Ni** have been reported previously [6a].

2Ni; ¹H NMR (600.17 MHz; CDCl₃): δ, ppm 10.02 (s, 2H, por-*meso*), 9.31 (s, 2H, por-β), 9.30 (d, J = 4.6 Hz, 2H, cor-β), 8.85 (d, J = 4.6 Hz, 2H, por-β), and 8.82 (s, 2H, por-β); ¹⁹F NMR (564.73 MHz; CDCl₃): δ, ppm -137.86 (d, J = 17.5 Hz, 4F, *o*-F), -153.42 (t, J = 21.9 Hz, 2F, *p*-F) and -162.92 (t, J = 17.5 Hz, 4F, *m*-F); HR-APCI-TOF-MS: *m/z* 698.0099, calcd. for C₃₂H₁₀F₁₀N₄⁵⁸Ni 698.0094 [*M*]⁺. UV-vis (CH₂Cl₂): λ_{max} , nm (ε [M⁻¹cm⁻¹]): 394 (231000), 515 (13700) and 548 (15500).

CONCLUSION

In summary, we revealed that 5,10-diarylporphyrin Zn(II) and Ni(II) complexes showed 1D columnar stacking structures in the single crystal state, while such a packing mode has never been found in free-base porphyrins. Ni(II) 5,10-diphenylporphyrin **2Ni** showed polymorphs depending on the solvents used for recrystallization. Taking the 1D columnar packing of **5Ag** and **6H** into consideration together, we conclude that 5,10-diarylporphyrinoids are promising candidates to form a 1D columnar packing structure in the single-crystal state.

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Supporting information

Figures of NMR spectra, mass spectra, and crystallographic data are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under numbers CCDC-1582878 (**2H**), 1582879-1582880 (**2Ni**), 1582877 (**1Zn**) and 1582881 (**2Zn**). Copies can be obtained on request, free of charge, *via* http://www.ccdc.cam.ac.uk/ data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: deposit@ccdc.cam. ac.uk).

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