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## COMMUNICATION

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## Control of higher-order structures of zinc chlorophyll coordination polymers

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We describe the control of the higher-order structures of supramolecular coordination polymers of zinc chlorophyll derivatives by rational design of molecular structure; positional isomers differing in the location of the coordination site leads to staircase-like or helical structures as revealed by X-ray crystallography.

Nature uses light-harvesting antenna to efficiently collect the sunlight as the initial step in the photosynthesis.<sup>1</sup> To mimic the natural antenna function, several artificial antenna models have been constructed.<sup>2</sup> Antenna models should consist of highly-ordered assemblies of a number of porphyrin or chlorophyll molecules. One of the major strategies to construct such assemblies is to use intermolecular coordination interactions.<sup>3,4</sup>

Recently, we reported on the self-assembly of the zinc chlorophyll derivatives appended by a *N*-hetero ring at the 3-position through the intermolecular axial coordination of the nitrogen atom in the *N*-hetero ring to the zinc centre in another chlorophyll molecule in the crystal.<sup>5</sup> The derivative with vinylpyridine at the 3-position formed double-helical coordination polymers in the crystal. It was suggested that the double-helical motif provides an efficient conduit for Förster-type energy transfer, which is sensitive to the interchromophore orientation and distance. Therefore, the tuning of higher-order structure of the zinc chlorophyll coordination polymer merits special attention for searching for motifs that enable more efficient light harvesting. Herein, we report the control of higher-order structures employing two zinc chlorophyll derivatives **Zn3Py** and **Zn4Py** appended by a phenylpyridine moiety. We have designed these compounds differing only in the position of the coordinatable nitrogen atom anticipating that altering the angle made between the chlorophyll plane and the

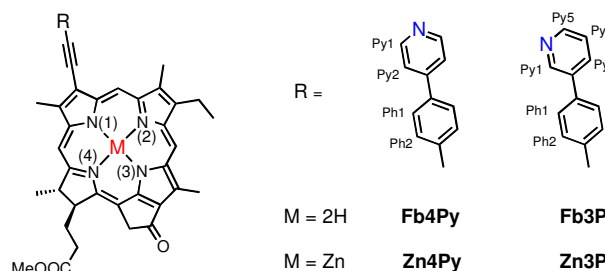


Chart 1. Chemical structures of the chlorophyll derivatives appended by a phenylpyridine moiety.

axis of the ligand would have a consequence in the higher-order structure (Chart 1).

**Zn3Py** and **Zn4Py** were synthesized following a reported procedure (see Supporting Information).<sup>6</sup>

The <sup>1</sup>H-NMR spectra for the zinc complex and free-base derivatives **Fb3Py**, **Zn3Py**, **Fb4Py**, and **Zn4Py** in CDCl<sub>3</sub> are shown in Figure S11. The signals for the phenylpyridine group appeared in the aromatic region for the free-base chlorophylls, while the corresponding signals for the zinc complexes appeared in significantly upfield regions. The upfield shifts were particularly large for the signals of the protons adjacent to the nitrogen in the pyridine ring (Py1 in **Zn4Py** and Py1 and Py5 in **Zn3Py**). The magnitude of the upfield shifts became smaller as the distance from the nitrogen in the pyridine ring was longer. This trend indicates the axial coordination of the pyridine moiety to the zinc centre in another chlorophyll molecule.

We obtained a needle-like single crystal of **Zn4Py** deposited from a THF/toluene solution exposed to methanol vapour and a rhombic-shaped single crystal of **Zn3Py** from a THF solution

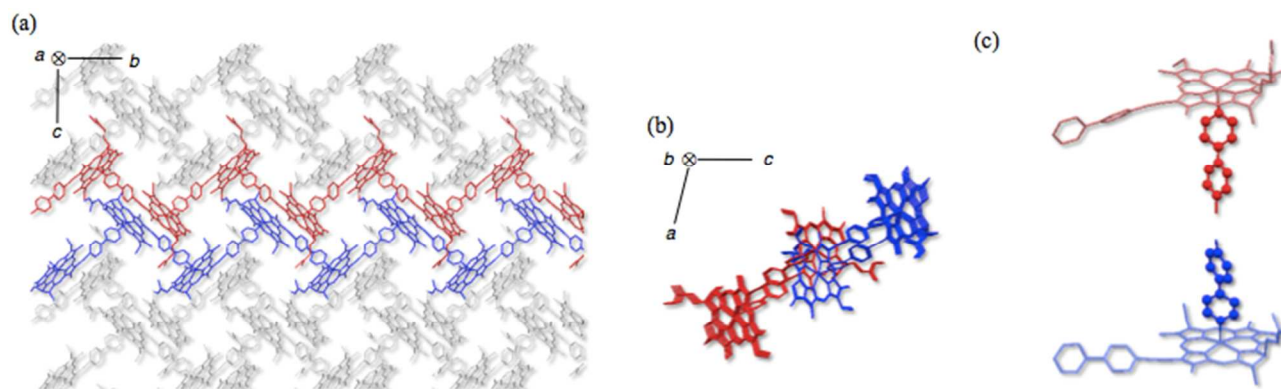


Figure 1. Crystal structure of **Zn4Py**. Hydrogen atoms and solvent molecules are omitted for clarity. (a) View along the *a*-axis showing the staircase-like coordination polymers. (b) View along the *b*-axis. (c) Inequivalent **Zn4Py** molecules.

exposed to diethyl ether vapour. The X-ray crystal structure analysis of the crystals clarified the assembled structures of these compounds in the solid state. Disorder was found in the methyl propionate residue and solvent molecules, part of which might have been lost, resulting in relatively large *R* values (**Zn4Py**:  $R_1 = 0.11$ ,  $wR_2 = 0.24$ ; **Zn3Py**:  $R_1 = 0.08$ ,  $wR_2 = 0.20$ ). The quality of the crystals was, nevertheless, sufficient for the present purpose of investigating the assembled structures.

**Zn4Py** molecules crystallized into space group  $P2_1$ . Wide channels are observed along the *a*-axis, which are probably occupied by solvent molecules, whose positions could not be determined (Figure 1). There are two inequivalent molecules in the unit cell, each forming a coordination polymer through the intermolecular axial coordination of the pyridine moiety to the zinc atom in another chlorophyll molecule, as shown in red or blue in Figures 1a and 1b. The polymer chains form staircase-like structure,<sup>7</sup> as the pyridine group coordinates to the chlorophyll plane nearly perpendicularly. The axial coordination angles between the  $N_{py}$ -Zn bond and the chlorophyll  $N_4$  plane are  $85^\circ$  (red) and  $87^\circ$  (blue), respectively. These polymers are antiparallel in the sense that the directions of pyridine $\rightarrow$ Zn coordination are in the  $-b$  and  $+b$  directions for the red and blue polymers, respectively. The chlorophyll molecules in a polymer stack with molecules in the adjacent antiparallel polymers with interplanar separation being  $\sim 3.4$  Å. It is noted that the pyridyl group coordinates to the zinc ion from the  $\alpha$ -face, which is anti to the propionate residue in the chlorophyll, in one polymer (red), while it coordinates from the  $\beta$ -face, which is *syn* to the propionate residue, in the other polymer (blue) as shown in Figure 1c.<sup>8</sup>

**Zn3Py** molecules also crystallized into space group  $P2_1$ . This crystal also contains disordered solvent molecules. Similar to **Zn4Py**, there are two inequivalent molecules in the unit cell, each forming a coordination polymer through the intermolecular axial coordination. Interestingly, the polymers are helical as shown in red or blue in Figures 2a and 2b. The axial coordination angles between the  $N_{py}$ -Zn bond and the chlorophyll  $N_4$  plane are  $88^\circ$  in both red and blue polymers. One polymer (red) extends in the  $-b$  direction with the coordination from the  $\beta$ -face (Figure 2c), forming a right-

handed helix, while the other polymer (blue) extends in the  $+b$  direction with the coordination from the  $\alpha$ -face forming a left-handed helix. A helical polymer is surrounded by four helical polymers with the opposite helicity, two of them being stacked with the central polymer as shown in Figure 2b with an interchlorophyll separation of  $\sim 3.3$  Å.

The two different motifs of the polymer structure derive from the different molecular structures. The axial coordination angle between the bond  $N_{py}$ -Zn and the chlorophyll  $N_4$  plane are almost vertical in both cases:  $\sim 86^\circ$  for the staircase and  $88^\circ$  for the helix, but the intramolecular angles  $N_{py}$ -Ct $_{py}$ -Ct( $N_4$ ) are respectively  $\sim 170^\circ$  and  $\sim 110^\circ$  due to the different position of the nitrogen atom in the pyridine ring, where Ct indicates centroid. The nearly linear arrangement of  $N_{py}$ -Ct $_{py}$ -Ct( $N_4$ ) in **Zn4Py** leads to nearly perpendicular interchlorophyll angles ( $N_4$  plane vs  $N_4$  plane:  $77^\circ$  for red;  $85^\circ$  for blue), resulting in the staircase-like motif, whereas the bent arrangement of  $N_{py}$ -Ct $_{py}$ -Ct( $N_4$ ) in **Zn3Py** leads to nearly parallel interchlorophyll angles ( $3^\circ$  for red;  $6^\circ$  for blue), resulting in the helical motif.

The relative efficiency of Förster-type energy transfer within the coordination polymers were estimated by use of the factor  $\kappa^2 r^{-6} \times 10^9 / \text{Å}^6$ , which is proportional to the efficiency, where  $\kappa^2$  and  $r$  are the orientation factor and the centre-to-centre distance between the transition moments, respectively (Figure S12). It was assumed that the  $Q_y(0,0)$  transition moment lies at the centre of the chlorophyll in the direction of the N(1)-N(3) axis.<sup>9</sup> The values of  $\kappa^2 r^{-6} \times 10^9 / \text{Å}^6$  for the staircase-like polymers of **Zn4Py** are quite small due to the unfavourable, mutually vertical orientation of the transition moments between the neighbouring chlorophyll molecules related by coordination (0.7 for red;  $2 \times 10^{-3}$  for blue). The next neighbours are parallel, but the molecules are already far apart (0.03 for red; 0.4 for blue). On the other hand, the helical polymers of **Zn3Py** provide favourable values for the energy transfer. The transition moments in the polymers are either nearly parallel or antiparallel between any chlorophyll pairs ( $176^\circ$  between the neighbours and  $0^\circ$  between the next neighbours for red;  $167^\circ$  between the neighbours and  $0^\circ$  between the next neighbours for blue). Furthermore, the intermolecular distances for the helical polymers of **Zn3Py** are smaller (15 Å between the direct

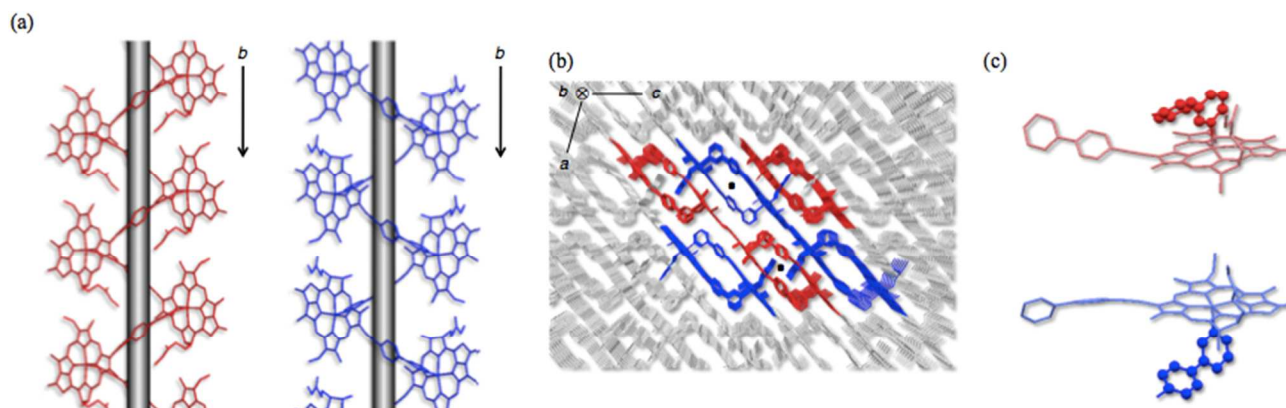


Figure 2. Crystal structure of **Zn3Py**. Hydrogen atoms and solvent molecules are omitted for clarity. (a) Views perpendicular to the *b*-axis showing the helical coordination polymers. Red and blue polymers have right and left-handed helicities, respectively. (b) View along the *b*-axis showing the packing of the coordination polymers. (c) Inequivalent **Zn3Py** molecules.

neighbours; 14  $\square$  between the next neighbours) than those for the staircase-like **Zn4Py** polymers (18  $\square$ ; 23  $\square$ ). Therefore, the helical structure is a promising motif as light-harvesting model.

In summary, we have demonstrated that the control of higher-order structures of zinc chlorophyll coordination polymers formed by the intermolecular axial coordination may be possible by rational positioning of the coordination site and consequent alteration of the interchlorophyll angle. We also suggest that helical structures of the coordination polymer can offer favourable arrangements of chlorophyll molecules for light-harvesting applications. In preliminary experiments, we have confirmed that these crystals emit fluorescence (Figure S13), from which we could probe the excited-state processes occurring in the crystals. Work is ongoing on the photophysical aspects of the semi-synthetic chlorophyll assemblies.

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## Notes and references

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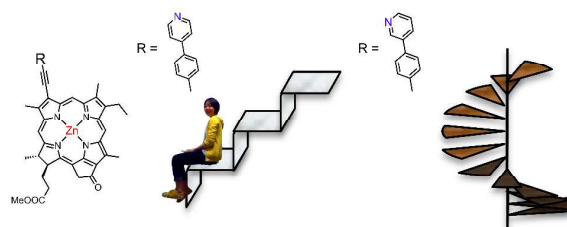
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<sup>†</sup> Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data for new compounds, the crystallographic data, and the relative efficiencies for energy transfer. See DOI: 10.1039/b000000x/

<sup>§</sup> Crystal data for **Zn4Py** (CCDC 995012):  $C_{45}H_{39}N_5O_3Zn$ ,  $M_r = 763.18$  g mol<sup>-1</sup>, Monoclinic,  $P2_1$ ,  $a = 10.372(7)$   $\square$ ,  $b = 22.684(14)$   $\square$ ,  $c =$

$18.375(11)$   $\square$ ,  $V = 4187.5(5)$   $\square^3$ ,  $T = 93$  K, 29029 reflections measured, 14538 unique ( $R_{int} = 0.1169$ ),  $R_1 = 0.1136$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.2384$  (all data), Flack parameter = 0.10(2),  $S = 1.046$ . Crystal data for **Zn3Py** (CCDC 995011):  $C_{102}H_{106}N_{10}O_9Zn_2$ ,  $M_r = 1746.70$  g mol<sup>-1</sup>, Monoclinic,  $P2_1$ ,  $a = 14.904(4)$   $\square$ ,  $b = 14.159(3)$   $\square$ ,  $c = 21.949(5)$   $\square$ ,  $V = 4563.1(19)$   $\square^3$ ,  $T = 93$  K, 37583 reflections measured, 19583 unique ( $R_{int} = 0.0795$ ),  $R_1 = 0.0787$  ( $I > 2\sigma(I)$ ),  $wR_2 = 0.2032$  (all data), Flack parameter = 0.061(11),  $S = 1.021$ .

- G. D. Scholes, G. R. Fleming, A. Olaya-Castro, R. van Grondelle, *Nat. Chem.*, 2011, **3**, 763.
- (a) J. Otsuki, *J. Porphyrin Phthalocyanines*, 2009, **13**, 1069. (b) J. Otsuki, in *Multiporphyrin Arrays*, ed. D. Kim, Pan Stanford, USA, 2012, ch. 12, pp. 587-628.
- (a) T. Jochum, C. M. Reddy, A. Eichhöfer, G. Buth, J. Szymtkowski, H. Kalt, D. Moss, T. S. Balaban, *Proc. Natl. Acad. Sci.*, 2008, **105**, 12736. (b) S. Sengupta, F. Würthner, *Acc. Chem. Res.*, 2013, **46**, 2498.
- (a) Y. Kobuke, *Eur. J. Inorg. Chem.*, 2006, 2333. (b) H. Tamiaki, A. R. Holzwarth, K. Schaffner, *J. Photochem. Photobiol. B: Biol.*, 1992, **15**, 355.
- (a) Y. Shinozaki, G. Richards, K. Ogawa, A. Yamano, K. Ohara, K. Yamaguchi, S.-i. Kawano, K. Tanaka, Y. Araki, T. Wada, J. Otsuki, *J. Am. Chem. Soc.*, 2013, **135**, 5262. (b) Y. Shinozaki, I. Yoshikawa, K. Araki, K. Ohara, K. Yamaguchi, S.-i. Kawano, K. Tanaka, Y. Araki, T. Wada, J. Otsuki, *Chem. Lett.*, 2014, DOI: 10.1246/cl.140135.
- (a) K. M. Smith, D. A. Goff, D. J. Simpson, *J. Am. Chem. Soc.*, 1985, **107**, 4946. (b) H. Tamiaki, S. Miyata, Y. Kureishi, R. Tanikag, *Tetrahedron*, 1996, **52**, 12421. (c) S.-i. Sasaki, K. Mizutani, M. Kunieda, H. Tamiaki, *Tetrahedron*, 2011, **67**, 6065.
- E. B. Fleischer, A. M. Shachter, *Inorg. Chem.*, 1991, **30**, 3763.
- J. S. Kavakka, S. Heikkinen, I. Kilpeläinen, N. V. Tkachenkob, J. Helaja, *Chem. Commun.*, 2009, **7**, 758.
- M. Linke, A. Lauer, T. von Haimberger, A. Zacarias, K. Heyne, *J. Am. Chem. Soc.*, 2008, **130**, 14904.



The higher-order structures of the zinc chlorophyll coordination polymers were controlled by the regiochemistry of the coordination sites.