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Selective Formation of a Single Atropisomer of *meso-meso*-Linked Zn^{II} Diporphyrin through Supramolecular Self-Assembly

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Atropisomerism is an intrinsic property of *meso*-aryl substituted porphyrins, which is thermally accessible and difficult to control, because there is usually no particular energy gain for rotation of the *meso*-aryl group in either direction.^[1] The ¹H NMR spectrum of 4-butoxypyrid-3-yl-substituted Zn^{II} porphyrin **1** in CDCl₃ exhibited a single set of signals both for the pyridyl protons and the butoxy protons in a shielded region (Figure 1), indicating the formation of a

But judicious control of porphyrin atropisomerization could be quite useful for the realization of orientationally ordered, functional molecular systems.^[2] Despite this expectation, only limited examples have been known for one-way atropisomerization, in which the atropisomerization control is driven by favorable enthalpic interactions between the host and guest.^[3]

Metalloporphyrins that have coordinating side arms can be

used for the construction of well-defined supramolecular architectures.^[4] By using this strategy, we have explored selfsorting, self-assembly of *meso*-pyridine appended *mesomeso*-linked Zn^{II} diporphyrins.^[5] Here we examined the selfassembling behavior of *meso*-3-pyridyl-substituted Zn^{II} porphyrin and *meso-meso*-linked Zn^{II} diporphyrins. In this study, a moderately bulky butoxy group was introduced at the 4-pyridyl position to set a considerable rotational barrier at room temperature. Herein, we report self-sorting, self-assembling, and entropically driven one-way atropisomerization.



Figure 1. ¹H NMR spectrum of 1 in CDCl₃.

symmetric and complementarily coordinating discrete assembly. The aggregated structure has been determined by single-crystal X-ray diffraction analysis to be a cyclic hexameric wheel (Figure 2)^[6a] in which all the porphyrin units are identical and connected through a complementary coordination network. In accordance with the observed upfield shifts, each butoxy group is located over each porphyrin ring as a result of the pyridyl coordination. The dihedral angle between neighboring porphyrin rings is 65.7° and the centerto-center distances are 8.8 and 9.4 Å for an adjacent pair and a neighboring pair, respectively, to give a unique zigzag wheel structure. This assembly can be also detected by absorption spectroscopy (Figure 3). At low concentration, the absorption spectrum of 1 showed a typical feature of a monomeric Zn^{II} porphyrin with a Soret band peak at 413 nm, whereas the Soret band is split into two peaks at 413 and 422 nm at high concentration, indicating notable excitation interactions between constituent porphyrins. In contrast, the ¹H NMR and absorption spectra of **1** in pyridine indicate that 1 exists as a monomer (see the Supporting Information). This formation of a hexameric structure is different



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Figure 2. X-ray crystal structure of $(1)_6$. a) Top view and b) side view. The *meso*-aryl groups and hydrogen atoms are omitted for clarity. The thermal ellipsoids were at the 50 % probability level.



Figure 3. UV/Vis absorption spectra of 1 at $10^{-4} \sim 10^{-5}$ m in CHCl₃. Inset shows the concentration-dependent absorption coefficient change at 542 nm and a theoretical curve fitting analysis for hexamer formation with $k_6 = 2.0 \times 10^{24}$ m⁻⁵.

from the previously reported tetrametric zigzag-shaped assemblies formed from Zn^{II} porphyrins that contain a *meso*-3-pyridyl substituent.^[7] The tetrameric zigzag assembly is likely to be the possible smallest structure formed from *meso*-3-pyridyl substituted Zn^{II} porphyrin. Note that the 4-butoxy-substituent introduced at the pyridyl group prevents the formation of such a tetrameric assembly by steric hindrance and drives **1** to form the hexameric assembly.

In the next step, Zn^{II} porphyrin **1** was coupled with AgPF₆ in CHCl₃ at reflux to provide the *meso-meso*-linked Zn^{II} diporphyrins **3** (Scheme 1).^[8] After demetallation, the free



Scheme 1. Synthesis of meso-meso-linked diporphyrins.

base diporphyrin **2** was obtained by gel permeation chromatography (GPC) analysis in 41 % yield, which consisted of three atropisomers $2_{out-out}$, 2_{in-out} , and 2_{in-in} . These atropisomers, which are different in the orientation of the pyridyl substitutents with respect to the *meso-meso* connection, were separated over a silica-gel column.^[9] But these isomers underwent slow atropisomerism to reach a 1:2:1 mixture at room temperature (see Figure S10 in the Supporting Information). Respective Zn^{II} metallation provided the Zn^{II} complexes $3_{out-out}$, 3_{in-out} , and 3_{in-in} , respectively, which exhibited ¹H NMR spectra in [D₅]pyridine that was indicative of their dissociation as a monomeric diporphyrin (see the Supporting Information).^[10] These complexes showed similar atropisomerism to their free-base counterparts in pyridine.

In noncoordinating CHCl₃, however, $\mathbf{3}_{out-out}$, $\mathbf{3}_{in-out}$, and $\mathbf{3}_{in-in}$ self-assembled to form different aggregates **A**, **B**, and **C**, respectively, which showed no interconversions at room temperature, and Zn^{II} metallation of the pristine mixture of **2** led to a roughly 1:2:1 mixture of **A**, **B**, **C**, indicating high self-sorting self-assembly.^[5] As found from the GPC retention times (Figure 4 a), the size of the aggregates becomes larger in the order of **C** (22.6 min; 2-mer) < **A** (19.7 min; 10–12-mer) < **B** (18.2 min; 24–28-mer).^[11] Although the ¹H NMR spectra of **A** and **B** are considerably broad owing to their large sizes, the smallest aggregate **C** shows a rela-



Figure 4. a) Analytical GPC-HPLC chromatograms (eluent: CHCl₃; —==the pristine mixture of 3; …==2; —==A, B, and, C. The band intensities of A, B, and C were adjusted to simulate the pristine mixture). b) Thermal conversion of the pristine mixture to C in toluene at 110 °C for 24 h.

tively simple and sharp ¹H NMR spectrum in which the signals due to the H^a, H^b, and H^c protons are observed at 1.93, 3.14, and 5.53 ppm, respectively, indicating the coordination of pyridyl groups to zinc ions.

The aggregates A, B, and C are considered to be all racemic. Although the optical resolutions of A and B were unsuccessful, C was actually separated through a chiral HPLC column (SUMICHIRAL OA-3100) into two fractions C1 and C2 in the order of elution. These two fractions are mirror images of each other in the circular dichromism (CD) spectra (see Figure S12 in the Supporting Information). The structure of C1 was determined by single-crystal X-ray diffraction analysis (Figure 5),^[6b] indicating that C consists of two molecules of $\mathbf{3}_{in-in}$ that are complementarily coordinated in a face-to-face fashion. The meso-substituted pyridine rings are inclined by 17.8° towards the coordinating direction, the central zinc atoms are displaced by 0.4 Å from the porphyrin mean plane, the dihedral angle of the mesomeso-linked diporphyrin is 83.4°, and the interplanar distance of the two porphyrin planes is 4.8 Å. This X-ray structure revealed that C1 consists of two R isomers.

The aggregates, **A**, **B**, and **C** were stable at room temperature, but upon heating at 110°C in toluene, the large aggregates **A** and **B** were converted into the small aggregate **C** as monitored by analytical GPC-HPLC (Figure 4 b) and ¹H NMR spectroscopic measurements (see the Supporting Information), whereas **C** was quite stable under the heating conditions.^[12] This thermal conversion to **C** can be rationalized in terms of the entropy increase associated with the fragmentary reconstitution of the larger aggregates **A** and **B** to the small one **C**. Considering the dynamic supramolecular nature of these aggregates, the most probable mechanism is the dissociation of the aggregates to the respective monomers and subsequent random atropisomerization to give **3**_{out-out}, **3**_{in-out}, and **3**_{in-in}, which all form respective aggregates COMMUNICATION

A, B, and C, but the aggregates A and B are thermally more labile and tend to be fragmented, contributing to the accumulation of C. As a consequence, one-way atropisomerism to $\mathbf{3}_{in-in}$ is entropically driven. Note that the heating of $\mathbf{3}_{\text{out-out}}$, $\mathbf{3}_{in-out}$, and $\mathbf{3}_{in-in}$ in pyridine at 80°C for 5 h led to the nonselective statistical population of $\mathbf{3}_{\text{out-out}}, \mathbf{3}_{\text{in-out}}, \text{ and } \mathbf{3}_{\text{in-in}}$ in a 1:2:1 ratio. These results indicate a relatively low rotational barrier for a meso-butoxy-3-pyridyl substituent in nonaggregated dimers, whereas such barriers become higher in the aggregates.^[13] More importantly, the one-way atropisomerism to



Figure 5. X-ray crystal structure of C1. The *meso*-aryl groups and hydrogen atoms are omitted for clarity. The thermal ellipsoids were at the 50% probability level.

 $\mathbf{3}_{in-in}$ has been achieved only through thermal fragmentary reconstitutions of **A** and **B** to **C**. Another requirement for this process is that the aggregate **C** is thermodynamically more stable than its fragments at 110 °C. Finally, the synthetic merit of this process has been shown by isolation of $\mathbf{3}_{in-in}$ in more than 90% yield after full one-way atropisomerism.

In summary, *meso*-(4-butoxypyrid-3-yl)-substituted Zn^{II} porphyrins quantitatively assemble to form a discrete hexameric macroring and the *meso-meso*-linked Zn^{II} diporphyrins undergo self-sorting self-assembly to form the respective discrete aggregates dictated by the orientation of *meso-*pyrid-3-yl substituents with respect to *meso-meso* connec-

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tion. One-way atropisomerism has been achieved through the fragmentary reconstitution of the supramolecular aggregates to form the smallest assembly.

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- [6] Crystallographic data for (1)₆: formula $C_{258}H_{258}N_{30}O_6Zn_6$; $M_r =$ 4267.16; tricrinic; space group $P\bar{1}$; a=20.531(3), b=20.913(3), c=22.602(4) Å; $\alpha = 65.044(2)$, $\beta = 65.706(2)$, $\gamma = 64.760(2)^{\circ}$; V =7634(2) Å³; Z=1; ρ_{calcd} =1.217 g cm⁻³; T=-183 °C; 38 538 measured reflections; 26158 unique reflections ($R_{int} = 0.0545$); $R_1 = 0.0759$ (I > $2\sigma(I)$; $wR_2 = 0.2040$ (all data); GOF = 0.875. Crystallographic data for $(\mathbf{3}_{in-in})_2$: formula $C_{172}H_{168}N_{20}O_4Zn_4$; $M_r = 2840.74$; tetragonal; space group $P4_{3}2_{1}2$; a=25.440(4), b=25.440(4), c=62.575(13) Å; $V = 40\,497(11)$ Å³; Z = 2; $\rho_{\text{calcd}} = 0.982 \text{ g cm}^{-3}$; T = -170 °C; 346836 measured reflections; 37056 unique reflections ($R_{int} = 0.1103$); $R_1 =$ 0.0807 ($I > 2\sigma(I)$); $wR_2 = 0.2332$ (all data); GOF = 1.028. The contribution to the scattering arising from the presence of the disordered solvents in the crystals was removed by use of the utility SQUEEZE in the PLATON software package.^[14] CCDC-668107 (1)₆ and 668108 $(\mathbf{3}_{in-in})_2$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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- [9] R_f values were 0.6 (2_{out-out}), 0.3 (2_{in-out}), and 0.1 (2_{in-in}) on a TLC plate (Merck silica gel 60 F₂₅₄) with a 9:1 mixture of CHCl₃ and ethanol.
- [10] ¹H NMR spectra of $\mathbf{3}_{in-in}$ or $\mathbf{3}_{out-out}$ show single sets of signals, whereas that of $\mathbf{3}_{in-out}$ shows two sets of signals (see the Supporting Information).
- [11] Assembly sizes were estimated by comparison to the similar reference compounds (see Figure S13 in the Supporting Information).
- [12] The reverse process from **C** to **A** or **B** has not been observed even at high concentration up to 10^{-3} M.
- [13] The rotation about the central *meso-meso* link does not occur even at harder conditions (e.g., heating at reflux in pyridine for 12 h or in tetrachloroethane for 3 h; N. Yoshida, A. Osuka, *Tetrahedron Lett.* 2000, 41, 9287–9291).
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