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meso,meso′-Bis(5-azaindol-2-yl)-Appended *meso*−*meso*-Linked Zn(II) Diporphyrin: A Discrete Fluorescent Assembly

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ABSTRACT

Cu(II)-catalyzed intramolecular cyclization of *meso*-(4-aminopyrid-3-yl)ethynyl Zn(II) porphyrin provided *meso*-(5-azaindol-2-yl)-substituted Zn(II) porphyrin. *meso,meso′*-Bis(5-azaindol-2-yl)-substituted diporphyrin 7 was similarly prepared and was found to form a fluorescent trimeric prismatic assembly consisting of single atropisomer 7_{in-in}.

Since the structure of the light-harvesting complex LH2 of the purple bacterium was determined to be a circular chromophoric architecture, cyclic porphyrin arrays have attracted considerable interest in view of photosynthetic antenna models.[1,2] Toward the construction of such arrays, both covalent[3] and noncovalent approaches[4] have been attempted. Most of covalent approaches need time-consuming and many tedious synthetic steps,[5,6] while in some cases template synthesis facilitates the formation of cyclic arrays.[7] As a promising noncovalent method, metalloporphyrins having coordinating substituents have been often used for the construction of cyclic porphyrin arrays via metal−ligand coordination interactions. Among these, we have explored

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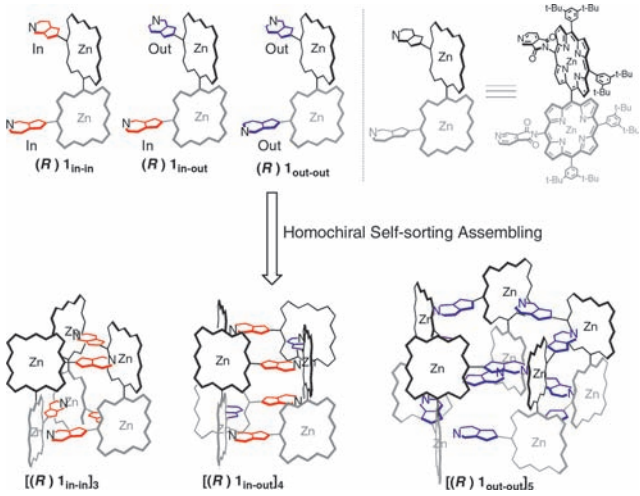
self-sorting assembly of *meso*-pyridyl-appended Zn(II) diporphyrins, where the angle of coordinating direction with regard to the porphyrin plane controls the size and structures of assemblies.[8] Interestingly, *meso*-cinchomeronimide-appended Zn(II) diporphyrins **1** exhibit high fidelity self-sorting assembly to form cyclic trimer $(\mathbf{1}_{\mathbf{in-in}})_3$, tetramer $(\mathbf{1}_{\mathbf{in-out}})_4$, and pentamer $(\mathbf{1}_{\mathbf{out-out}})_5$ through a rigorous self-sorting process (Scheme 1).[8c] However, these assemblies have a serious drawback of the strong fluorescence quenching by intramolecular electron transfer to the appended electron-deficient imide moieties.

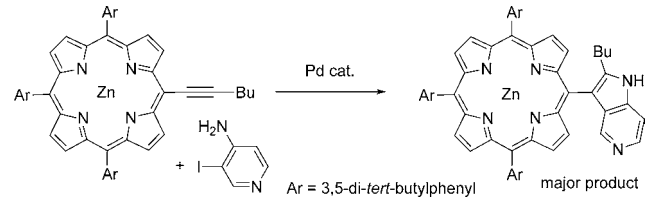
Scheme 1. Homochiral Self-Sorting Assembly of *meso*-Cinchomeronimide-Appended Zn(II) *meso*−*meso* Linked Diporphyrins[a]



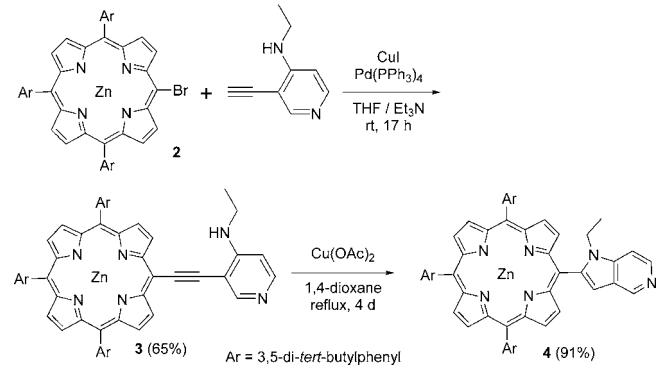
[a] The same self-sorting assembling occurs for (*S*)-enantiomers.

With this background, we embarked on the exploration of *meso*,*meso*-linked Zn(II) diporphyrin bearing a 5-azaindole ring, which has a shape similar to that of a cinchomeronimide but does not quench the fluorescence of a Zn(II) porphyrin. We thus attempted to prepare an azaindole-appended porphyrin by the conventional acid-catalyzed reaction using formyl-substituted azaindoles or the metal-catalyzed cross coupling using iodinated azaindoles. However, all these attempts ended in failure. Recently, instead, we developed the efficient synthesis of *meso*-5-azaindolyl porphyrins via Pd-catalyzed intermolecular annulation reaction of *meso*-ethynyl Zn(II) porphyrin and 4-amino-3-iodopyridine (Scheme 2).[9] This method allowed for the synthesis of *meso*-(5-aza-indol-3-yl)porphyrin but not for a *meso*-(5-aza-indol-2-yl)-substituted one. Here we wish to report the synthesis of *meso*-(5-azaindol-2-yl)porphyrins via Sonogashira coupling of *meso*-bromoporphyrin with (4-aminopyrid-3-yl)acetylene and subsequent Cu(II)-catalyzed *intra*molecular cyclization.[10]

Scheme 2. Synthesis of 5-Azaindolyl Zn(II) Porphyrin via Pd-Catalyzed Annulation Reaction



Scheme 3. Synthesis of **4**



A synthetic route to 5-azaindol-2-ylporphyrin **4** is shown in Scheme 3. Sonogashira coupling reaction of *meso*-brominated porphyrin **2** with 4-ethylamino-3-ethynylpyridine provided (4-ethylaminopyrid-3-yl)ethynylporphyrin **3** in 65% yield. Then, we examined the Cu(II)-catalyzed intramolecular cyclization reaction reported by Hiroya et al.[10a] for porphyrin substrate **3**. The cyclization reaction was not completed in 1,2-dichloroethane or toluene even after refluxing for 4 days, but we found that the use of 1,4-dioxane at reflux allowed full conversion of **3** to provide **4** in 91% yield in 4 days. The structure of **4** has been confirmed by the spectroscopic data and single-crystal X-ray diffraction analysis. High-resolution electrospray ionization time-of-flight mass spectrum detected the parent ion peak of **4** at $m/z = 1081.5831$ (calcd for $C_{71}H_{81}N_6Zn$ $(M + H)^+ = 1081.5809$). The ^1H NMR spectrum of **4** in coordinating pyridine-d_5 is fully

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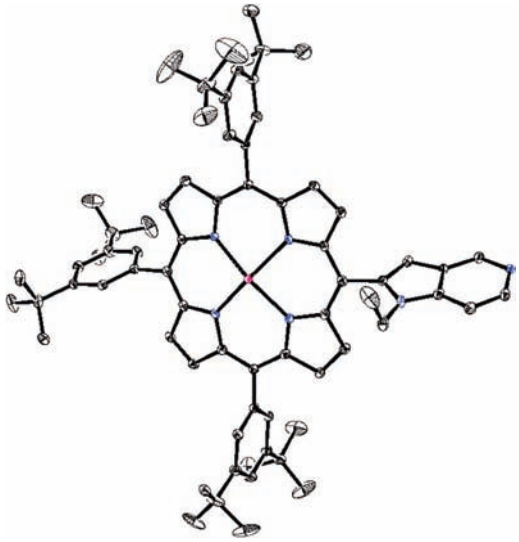


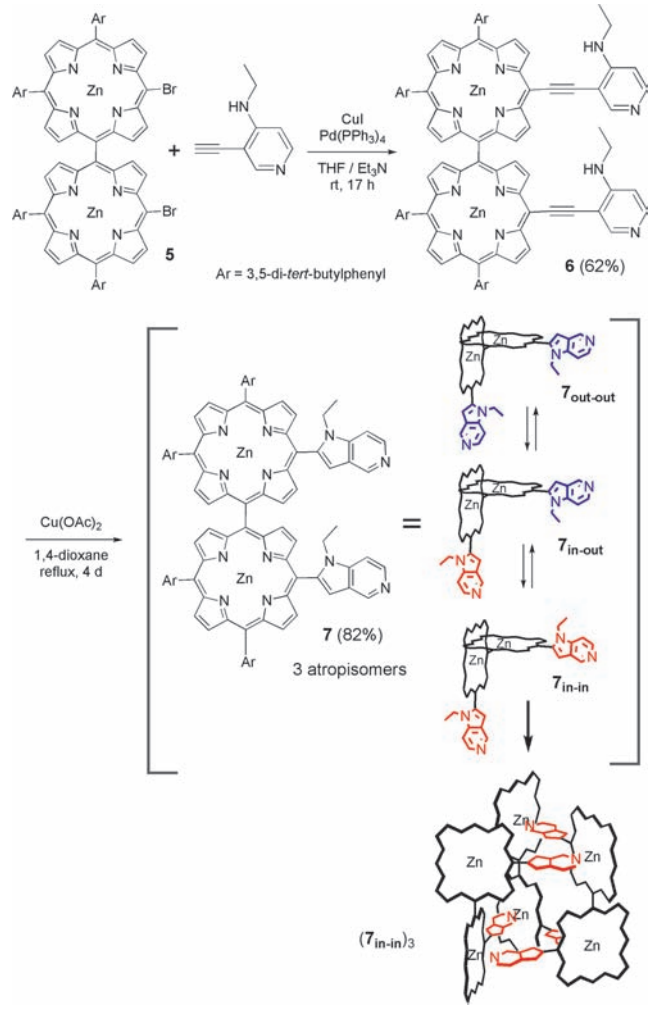
Figure 1. X-ray crystal structure of **4**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids were at 50% probability level.

consistent with its structure (Supporting Information). Slow vapor diffusion of methanol to a THF solution of **4** provided nice crystals for X-ray diffraction analysis. The X-ray crystal structure elucidated the structure of **4** unambiguously, revealing the *meso*-appended 5-azaindol-2-yl moiety (Figure 1).[11] In line with this structural change, the UV/vis absorption spectrum changes radically from a strongly perturbed one with peaks at 450, 583, and 636 nm for the *meso*-ethynylated porphyrin **3** to a normal one with peaks at 434, 564, and 607 nm for **4** (Supporting Information). Importantly, the fluorescence of **4** is observed at 614 and 664 nm with a certainly high fluorescence quantum yield ($\Phi_F = 0.055$).

With an efficient protocol for azaindole formation, *meso*,*meso*′-bis(5-azaindol-2-yl)-substituted *meso*−*meso*-linked Zn(II) diporphyrin **7** was prepared as shown in Scheme 4. Sonogashira coupling of *meso*,*meso*′-dibrominated diporphyrin **5** with 4-ethylamino-3-ethynylpyridine provided *meso*,*meso*′-diethynylated diporphyrin **6** in 62% yield, which was converted to diporphyrin **7** in 82% yield via the Cu(II)-catalyzed intramolecular cyclization. Interestingly, the ^{1}H NMR spectrum of **7** in $CDCl_3$ shows only a single set of peaks with large upfield shifts for the azaindolyl protons (H^a: 6.38, H^b: 3.10, H^c: 2.60, H^d: 5.14 ppm), suggesting the formation of a single assembling entity, in which the 5-nitrogen atom of the azaindol-2-yl group coordinates to the Zn(II) center of the other porphyrin in a complementary manner (Figure 2). By comparing the retention time of this assembly in the analytical GPC-HPLC with those of cinchomeronimide-appended *meso*−*meso*-linked diporphyrins, this assembly has been assigned to a trimer of **7** (Supporting

(11) Crystallographic data for **4**: formula: $C_{71}H_{80}N_6Zn{\cdot}4C_4H_8O$, M_w = 1371.22, monoclinic, space group $P2_1/c$, a = 16.5956(13) Å, b = 34.837(3) Å, c = 14.5206(11) Å, β = 115.729(2)°, V = 7562.7(11) Å^3, Z = 4, $\theta^{\sim}_{calcd}$ = 1.204 g cm^{-3}, T = −183 °C, 38986 measured reflections, 13314 unique reflections (R_{int} = 0.0623), R_1 = 0.0937 ($I > 2\sigma(I)$), wR_2 = 0.2320 (all data), GOF = 1.046.

Scheme 4. Synthesis of $(\mathbf{7}_{\mathbf{in-in}})_3$



Information). The fact that only a single assembling entity was formed from **7** is different from the assembling behaviors of cinchomeronimide-appended *meso*−*meso*-linked diporphyrins **1**. In the latter case, the rotational barrier of the *meso*-substituted cinchomeronimide group is rather high, not allowing free atropisomerism at room temperature and hence realizing self-sorting assembling to form $(\mathbf{1}_{\mathbf{in-in}})_3$, $(\mathbf{1}_{\mathbf{in-out}})_4$, and $(\mathbf{1}_{\mathbf{out-out}})_5$ from $\mathbf{1}_{\mathbf{in-in}}$, $\mathbf{1}_{\mathbf{in-out}}$, and $\mathbf{1}_{\mathbf{out-out}}$, respectively. In the present system, the corresponding rotational barrier seems smaller, allowing facile atropisomerism to provide three atropisomers ($\mathbf{7}_{\mathbf{in-in}}$, $\mathbf{7}_{\mathbf{in-out}}$, and $\mathbf{7}_{\mathbf{out-out}}$), among which

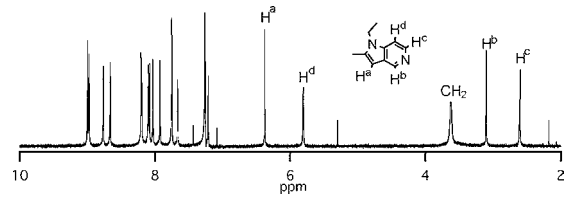


Figure 2. ^{1}H NMR spectrum of $\mathbf{7}_{\mathbf{in-in}}$ in $CDCl_3$.

only $\mathbf{7}_{in-in}$ assembles to form its trimer, since this is the most stable due to the least entropy cost for the assembling.[8d] Evaporation of a $CDCl_3$ solution of **7** left an assembly of $(\mathbf{7}_{in-in})_3$. When this was dissolved in pyridine-d_5, the ^{1}H NMR spectrum was just broad, not showing particular upfield shifts for the 5-azaindolyl protons, indicating that **7** exists as a monomer in pyridine. In addition, the ^{1}H NMR spectrum became slowly sharper to exhibit many peaks due to the presence of atropisomers by standing at room temperature for several days (Supporting Information). This change was accelerated upon heating at 110 °C.

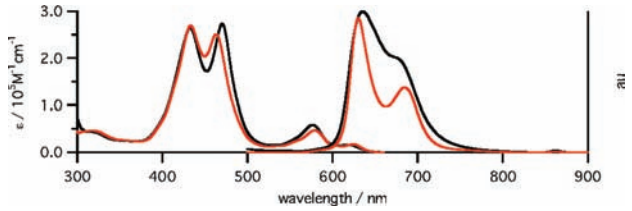


Figure 3. UV−vis absorption and fluorescence spectra of $\mathbf{7}_{in-in}$ (red line, in $CHCl_3$; black line, in pyridine).

The absorption spectrum of **7** in pyridine shows splitting of the Soret band (1820 cm^{-1}) typical for a *meso*−*meso*-linked diporphyrin, while $(\mathbf{7}_{in-in})_3$ in $CHCl_3$ shows a narrower splitting width (1500 cm^{-1}), indicating additional exciton coupling through self-assembling (Figure 3). Namely, transition dipole moments along with *meso*−*meso* linkage are strongly coupled as J-type interactions in the *meso*−*meso*-linked diporphyrin, while the three dipole moments in $(\mathbf{7}_{in-in})_3$ in $CHCl_3$ are coupled as additional intermolecular H-type interaction, giving rise to further blue shift. This splitting feature also supports the trimeric assembling of **7** in comparison to the assemblies of **1**.[12] The fluorescence spectrum of **7** in pyridine is broad with a peak at 636 nm and $\Phi_F = 0.061$. On the other hand, the fluorescence of **7** in $CHCl_3$ shows a clear vibronic structure with peaks at 630 an 685 nm and $\Phi_F = 0.039$.[13] The observed vibronic structure is consistent with the formation of a closely packed, rigid structure.

In summary, we synthesized *meso*-(5-azaindol-2-yl)-appended Zn(II) porphyrins **4** and **7** via Cu(II)-catalyzed intramolecular cyclization reaction. In noncoordinating $CHCl_3$, *meso*−*meso*-linked diporphyrin **7** predominantly forms a trimeric fluorescent assembly that consists of three single atropisomers $\mathbf{7}_{in-in}$ through facile rotation of the 5-azaindol-2-yl substituent and effective trapping via self-sorting assembling by complementary coordination. A 5-azaindol-2-yl substituent at *meso*-position does not quench the excited singlet state of Zn(II) porphyrin and allows a unique self-sorting assembly.

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Supporting Information Available: Experimental procedures, compound data, and crystallographic data for **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Splitting width of $\mathbf{7}_{in-in}$ in $CHCl_3$ is 1500 cm^{-1}, while those of the assemblies formed from **1** are 1540 cm^{-1} for $(\mathbf{1}_{in-in})_3$, 1390 cm^{-1} for $(\mathbf{1}_{in-out})_4$, and 1290 cm^{-1} for $(\mathbf{1}_{out-out})_5$, respectively.[8c]

(13) This is a substantial improvement in Φ_F, since the fluorescence quantum yields of $(\mathbf{1}_{in-in})_3$, $(\mathbf{1}_{in-out})_4$, and $(\mathbf{1}_{out-out})_5$ in $CHCl_3$ were less than 0.1%.