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Long rod-like array of bis(imidazolyl)porphyrinatocobalt(III) by successive complementary coordination†

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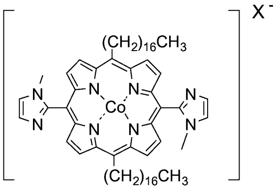
Simple bis(imidazolyl)porphyrin cobalt(III) complex was found to form a long polymeric array by complementary coordination of imidazole to cobalt ion. Formation of higher ordered assemblies was also observed.

Recently, multi-porphyrin systems have been paid considerable attention because of their structure-induced optical and electronic properties that may be applicable as molecular devices such as optical switches, conductive materials, and nonlinear optics.[1–4] Among them, a long linear porphyrin polymer system has been of particular interest and has been investigated using various methodologies. Though approaches leading to such a system are found in recent reports of covalently bonded porphyrin systems,[5] the preparation of supramolecular porphyrin polymers by self-assembly is also intriguing since it involves a relatively light synthetic burden and tunability for length by control of solvent or temperature. Based on these strategies, a number of non-covalently linked linear porphyrin polymers have been reported so far.[3a,3b,6] We have been interested in a porphyrin polymer system that shows strong electronic or photonic interactions between constituent monomer units throughout the polymer chain. Along the line, we reported a self-assembled dimer of zinc(II) imidazolylporphyrin and showed that the complementary coordination of imidazolyl to central Zn(II) was extremely stable, bringing strong interaction between porphyrin units.[7] In this context, we have focused our attention on the self-assembled porphyrin polymer system of bis(imidazolyl)porphyrin bearing hexa-coordinating metal ions. Such a structural motif should provide not only a rigid polymer backbone but also strong interaction among the monomer units and might show interesting properties such as conductivity.

Herein we report preparation of cobalt(III) bis(imidazolyl)porphyrin and its long, staircase shaped rod assemblies by strong coordination interaction with adjacent units and its higher ordered supramolecular assembly. In our earlier attempt towards this type of coordination assembly, we employed Mg(II) as the central metal ion as a mimic of photosynthetic antenna, which should avoid the use of metal ions to quench the fluorescence from porphyrin.[8] Liberated from such quenching limitations, we employed here cobalt(III) ion because cobalt(III) porphyrin is known to form very stable 6-coordinated complexes.[9] Another advantage of cobalt(III) ion is its redox properties that may produce an ion centred conducting pathway of electron through mixed-valence states.[3]

Cobalt(III) bis(imidazolyl)porphyrins **1a–c** were synthesized from 1-methylimidazol-2-carboxaldehyde and *meso*-(heptadecyl)dipyrromethane followed by cobalt introduction by using $CoCl_2$, $Co(BF_4)_2$, and $Co(ClO_4)_2$, respectively, and aerobic oxidation in the presence of acid. Co(III) mono(imidazolyl)porphyrins **2a–c** were also synthesized as the reference compounds. These species were confirmed by MALDI-TOF mass, UV/Vis, and ^{1}H-NMR spectroscopies. Imidazolyl substituted porphyrinatocobalt(III) complexes **1a–c** showed characteristic Soret absorption with split peak maxima at 404 and 474 nm (Fig. 1). In contrast, the reference dimers **2a–c** showed only broadened Soret bands without splitting in chloroform. This differs from the case of the Zn complex and suggests a smaller separation for the interaction between the dimeric porphyrin cobalt(III) complexes. Therefore, the large splitting of the Soret band observed in **1a–1c** is explained as a result of exciton interactions involving a large number of transition dipoles.[10] Here, the imidazolyl groups in one porphyrin unit are coordinated to cobalt(III) ions in two porphyrins to form a complementarily coordinated polymer. The red-shifted Soret peak at 474 nm should come from exciton couplings of transition dipoles along the imidazole groups with slipped face-to-face (J-type) interactions and the blue-shifted at 404 nm along the alkyl groups with face-to-face (H-type) interactions.[10] When pyridine was added to the chloroform solution, the split Soret band changed to a single sharp peak, indicating dissociation of the coordination structure into a monomer. Similar peak sharpening was observed on dilution with weakly coordinating methanol, but complete dissociation into the monomer was not observed even in chloroform/methanol (1 : 100) and the spectral pattern showed the dimer as the main species existing in the solution. Such dissociation behaviour agreed well with the fact that the binding constant of the 5th ligation for cobalt(III) porphyrin (that is related to dimer formation) is much larger than that of the 6th ligation.[9] The absorption spectra of cobalt porphyrins studied here did not show concentration dependencies over a wide concentration range (10^{-8} to 10^{-5} M in $CHCl_3$), indicating complete coordination even at such a low concentration as 10^{-8} M.



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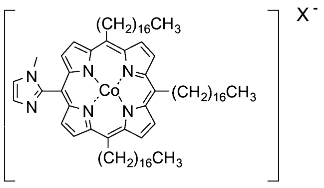

2

a; X = Cl^-, **b**; X = BF_4^-, **c**; X = ClO_4^-

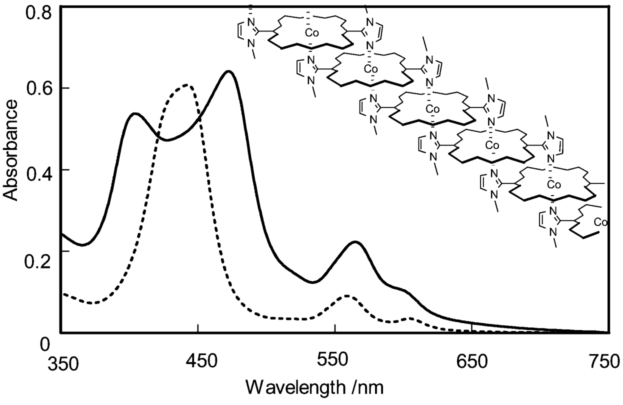

Fig. 1 Absorption spectrum of **1a** (solid line) and **2a** (broken line) recorded in chloroform with the schematic representation of the polymer structure of **1a**.

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† Electronic supplementary information (ESI) available: general procedures. See http://www.rsc.org/suppdata/cc/b2/b211434h/

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Interestingly, **1a**–**1c** showed a time dependent variation of the absorption spectrum on standing the chloroform solution after cobalt insertion. The rate was much affected by the choice of counter ion and became slower in the order **1c**, **1b** and **1a**. The organization process of **1c** was almost completed within 1 day from a 2 mM chloroform solution, while **1a** showed a residual dimer peak at 434 nm even after 1 week. This behaviour is compatible with the organization mechanism, where the 2nd axial imidazole coordination must replace the counter anions and follows the order of hardness of the counter ion ($Cl^- > BF_4^- \cong ClO_4^-$).‡ This propagation process can easily be suppressed by adding weakly coordinating solvent (*e.g.* methanol) or accelerated by eliminating methanol from tetrachloroethane–methanol simply by heating at 70 °C under vacuum. The latter process is effective for complete propagation starting even from **1a**.

Unfortunately, quantitative analysis of the degree of polymerization was difficult: MALDI-TOF and ESI mass spectra gave mostly monomeric species and GPC analysis gave predominantly a dimeric peak accompanied even by peaks of shorter retention times, indicating dissociation of the polymer and operation of adsorption to the resin as well as size discrimination. Even so, the polymer peak appeared near the exclusion limit and suggested the formation of a long assembly with a molecular weight over 30,000 dalton. The eluting polymer fraction showed the Soret band of a splitting width of 76 nm in harmony with the extended propagation structure.

In order to confirm the structure, we examined the molecular image by use of atomic force microscopy. Many rod-like assemblies were observed when chloroform solution (*ca.* 10^{-6} M) of **1a** was applied onto mica substrate (Fig. 2). The uniform height (0.9–1.3 nm) of the rods corresponds to the molecular height of the coordination-organized porphyrin polymer (1.1 nm) and each rod is regarded as a single molecular chain. The lengths of most of the polymeric species are in a range *ca.* 50–300 nm (corresponding to 90–500 porphyrin units) and the maximum length in the scale was 1.1 μm, corresponding to 1900-mer. The straight shape of each rod suggested the rigid nature of the polymer, which might be of advantage in future applications. When a chloroform solution (2–4 mM) of polymer from **1b** was left standing for several days, assemblies of rectangular shape grew to a visible size (100–300 μm). Polarized microscopy of the assemblies showed a strong birefringence, indicating crystalline character with a regular arrangement of polymer (Fig. 3). The absorption spectra using polarized light showed clear anisotropy for Q bands and red-shifted Soret peak (*ca.* 470 nm) that should originate from exciton coupling along the polymer chain. The absorbance became larger with the incident light parallel and smaller with the light perpendicular to the long axis of the assemblies. The polymer chain should be arranged along the long axis of the assembly.

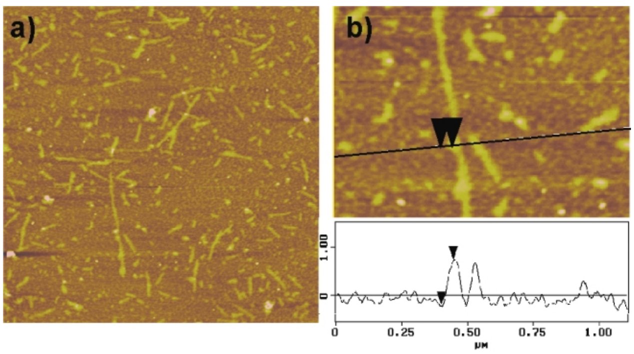

Fig. 2 a) AFM image of the rod-like assembly of **1a** deposited onto mica substrate. b) Enlarged image with a cross-section along the line. Vertical distance between two triangles is 0.94 nm. Image size: a) 3 μm × 3 μm, b) 1.1 μm × 0.8 μm.

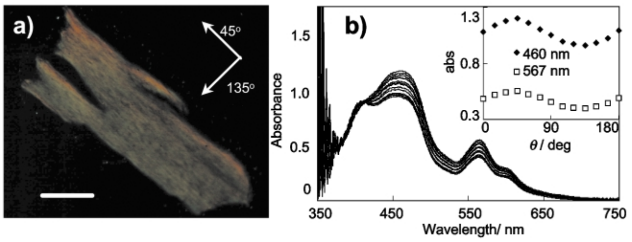

Fig. 3 a) Microscopic image of the higher-ordered assembly of **1b** under polarized light (bar = 50 μm). b) The absorption anisotropy of the assembly in a). Rotational angle θ of the linear polarized light corresponds to the direction of the arrows in a).

In summary, we demonstrated that cobalt(III) bis(imidazolyl)porphyrin could be grown into long, rigid rod assemblies by continuous extension of complementary coordination. The propagation kinetics depended on the nature of counter ions and choice of solvent. The self-assembled porphyrin rods studied here are of particular interest in that redox-active metal ions and exciton coupled large π-orbitals are arranged linearly throughout the polymer chain. This supramolecular rod has the possibility of providing a novel functional nano-assembly from easily accessible and simple molecules. Further studies on the conductivity of the materials are currently under investigation.

Notes and references

‡ As another factor influencing the time dependent organization, atropisomerization of the imidazole group may be involved. The *cis* atropisomer must be converted to the *trans* isomer to form oligomers higher than dimer.

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