A *Mandala*-Patterned *Bandanna*-Shaped Porphyrin Oligomer, $C_{1244}H_{1350}N_{84}Ni_{20}O_{88}$, Having a Unique Size and Geometry

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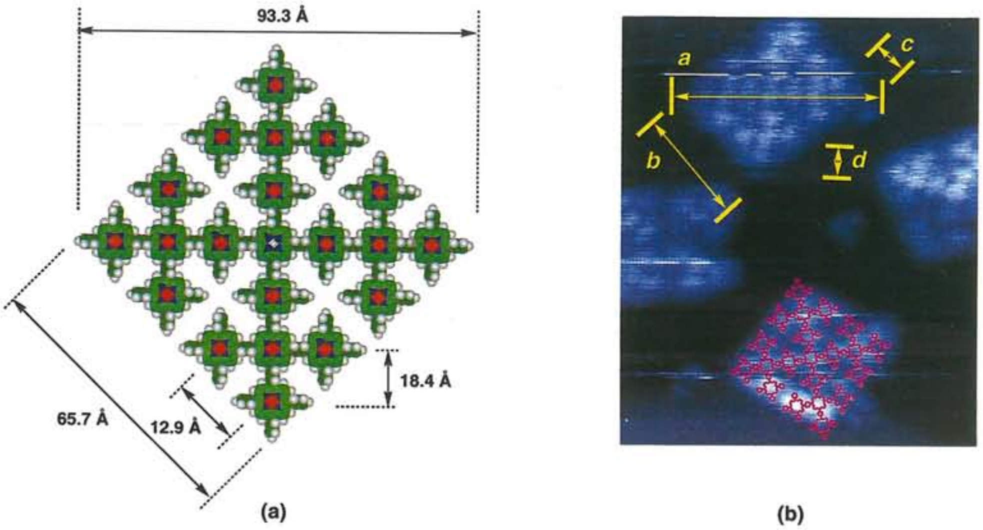
A porphyrin henicosamer was designed, synthesized, and structurally characterized using scanning tunnelling microscopy.

Achieving direct access to single molecules has become a growing area of contemporary interdisciplinary research since the discovery of scanning tunnelling microscopy (STM) in 1982.[1] Research in this area has been aimed at the engineering of single molecules and/or atoms and at the exploration of molecular properties on an individual nonstatistical basis.[1] To achieve these results, three specific characteristics are considered to visualize a molecule easily, i.e., unique shape, large size, and rigidity. Oligomeric porphyrins (OP)[2] are good candidates for this purpose because a porphyrin macrocycle is large in size, having a four-fold axis.[3] Additionally, its peculiar physical properties, which sensitively reflects the electronic state of the molecules, e.g., photo-emission and the magnetism of incorporated paramagnetic metals,[4] could be useful in future nano-scaled advanced materials. It is in this context that we report here the molecular design, synthesis, and direct observation of rigid-sheet OP, henicosamer **1**, having a molecular weight of 20061 Da (for $C_{1244}H_{1350}N_{84}Ni_{20}O_{88}$), with a well-defined structure.[5]

To achieve the synthesis, we designed the sheet molecule **1**, in which four porphyrin pentamers are attached to a porphyrin, considering the followings. A *para*-phenylene spacer was selected to connect each porphyrin at the *meso*-position, since the spacer group produces the dihedral angle of nearly 90° between the spacer ring and each porphyrin.[6] Therefore, the 21 porphyrin rings in **1** are expected to be placed in the same plane, and this linking behaviour produces a large square-shaped sheet molecule. The shape is similar to a *Bandanna* having a *Mandala* pattern.[7] As shown in Scheme 1, repeated condensation reactions of porphyrin-substituted benzaldehyde derivatives such as **7**, **8**, and **10** with pyrrole are needed to produce the final compound **1**. This strategy avoids the structural defects usually seen in dendritic compounds.[8,9]

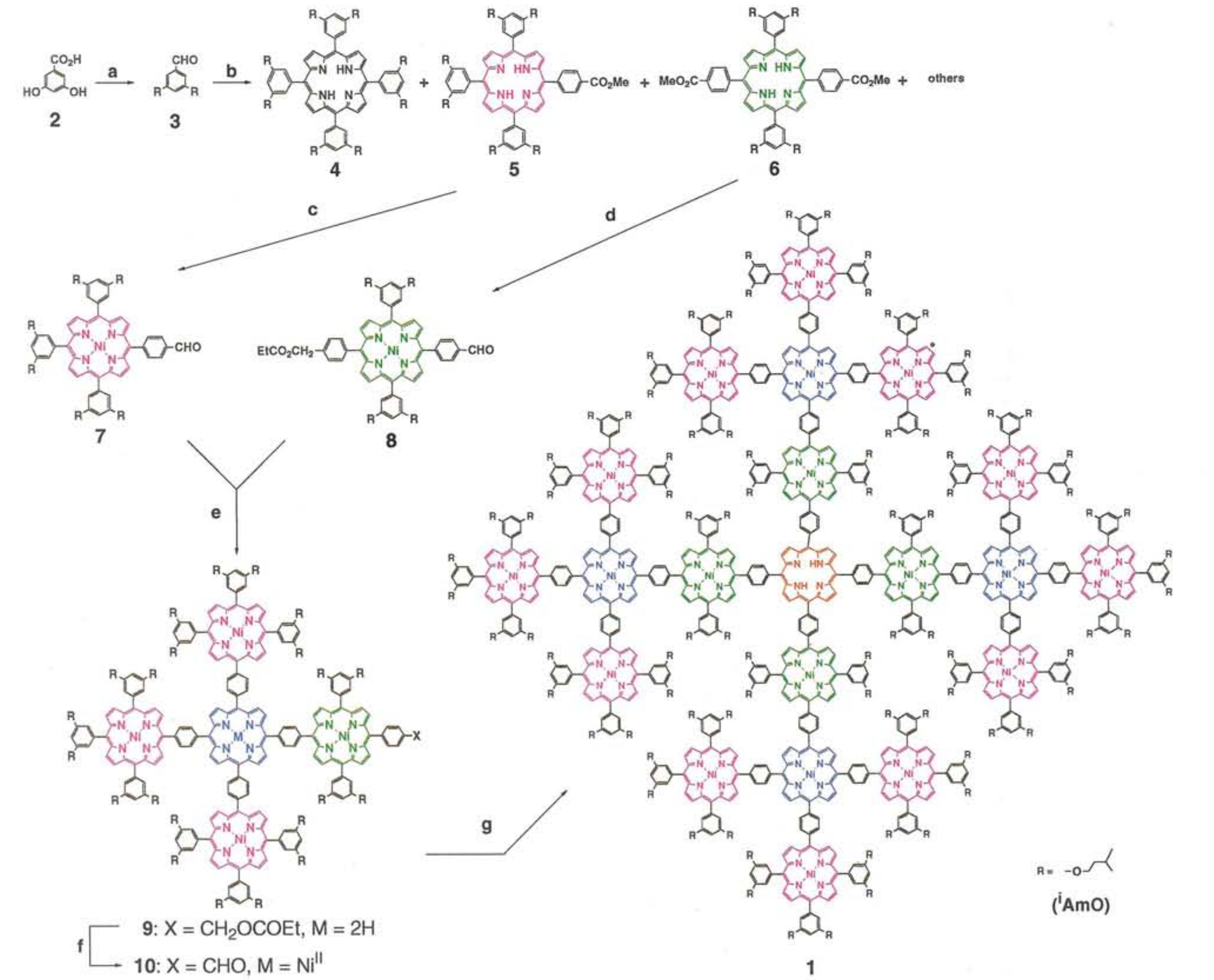
The synthesis is shown in Scheme 1. The benzaldehyde **3** with two ^{i}AmO groups was prepared from the commercially available **2** in four steps with nearly quantitative yield for each step. The mono- and bis-functionalized porphyrin derivatives were prepared by the mixed condensation reaction to give **5** and **6** in 12% and 3% yields, respectively. After the functional group transformations on **5** and **6**, a second coupling reaction using a mixture of **7** and **8** in a 3:1 ratio was performed. The desired pentamer **9** having one ester group was isolated in 25% yield. The final coupling reaction of **10** with an equivalent amount of pyrrole was achieved using Lindsey's hindered porphyrin synthesis conditions[10] to give the desired porphyrin heneicosamer **1** in 44% yield; the total yield was 0.15% in 17 steps.

The laser desorption time-of-flight mass spectroscopy results supported the structure of **1**, $M^+ = 20095$, calcd $M^+ = 20061$ for $C_{1244}H_{1350}N_{84}Ni_{20}O_{88}$. Additional reliable evidence for the structure of **1** was provided by direct observation of the molecular shape using STM (Figure 1). The STM image of **1** in its adsorbed state on a Cu (111) surface, prepared using our pulse injection technique,[11] consists of 21 major lobes aligned in a perfectly square shape with a *Mandala* pattern where each lobe is attributable to a porphyrinatonickel(II) unit. The size of the square, the *Bandanna*, is 95 Å along the diagonal and 65 Å along the sides, which is consistent with the molecular size of **1** estimated by a molecular geometry calculation (93.3 and 65.7 Å in calculation). In the molecule, each major lobe is separated by 13 Å in the diagonal direction and by 18 Å along the sides (12.9 and 18.4 Å in calculation). Some of the major lobes are observed as an ensemble of a further four small lobes attributable to the phenyl



(a) (b)

Figure 1. (a) Structure of a porphyrin henicosamer **1**. The CPK model consideration indicates that the size of **1** is 93.3 Å along the diagonal and 65.7 Å along the sides. Metal-to-metal distances between the adjacent porphyrins are estimated to be 12.9 and 18.4 Å, respectively. (b) The direct molecular observation using the STM technique. An ultra high-vacuum apparatus made in-house equipped with a pulse injection valve was used.[11] An atomically clean single crystal Cu (111) surface was used. Details of the STM experiments will be published elsewhere. The observed molecular geometries of **1** are the following (Å) (the values in the parentheses are the calculated values; *a*: 95 (93.3), *b*: 65 (65.7), *c*: 18 (18.4), and *d*: 13 (12.9).



Scheme 1. Reagents and conditions. **a**: 1) MeOH, *p*-TsOH, 2) 3-methyl-1-bromobutane, K_2CO_3, methylethylketone, 3) $LiAlH_4$, THF, 4) chemical manganese dioxide (CMD), PhMe. **b**: pyrrole, methyl 4-formybenzoate, propionic acid. **c**: 1) $LiAlH_4$, THF, 2) $Ni(OAc)_2{\bullet}4H_2O$, DMF, 3) CMD, PhMe. **d**: 1) $LiAlH_4$, THF, 2) $Ni(OAc)_2{\bullet}4H_2O$, DMF, 3) pyridinium chlorochromate, CH_2Cl_2, 4) $(EtCO)_2O$, $N(C_2H_5)_3$, DMAP, CH_2Cl_2, **e**: pyrrole, $BF_3{\bullet}OEt_2$, EtOH, CH_2Cl_2. **f**: 1) KOH, 18-crown-6, PhMe-H_2O, 2) $Ni(OAc)_2{\bullet}4H_2O$, DMF, 3) CMD, PhMe. **g**: pyrrole, $BF_3{\bullet}OEt_2$, EtOH, CH_2Cl_2. CMD was purchased from Wako Pure Chemical Ind., Ltd.

groups.[3] The UV-vis. spectrum of **1** showed only a small bathochromic shift and an increment of the full width at half maximum for the Soret-band (422 nm for **1**, 418 nm for **4**). The molar absorption coefficient is 3560000, which is 13 times larger than that of monomer **4**.

We have shown here the molecular design and synthesis of a well-arranged porphyrin oligomer and have described our direct molecular observations. Additionally, we have introduced the novel concept of a "sheet (*Bandanna*) molecule" stretching in a two-dimensional direction, to the known geometries of molecules, e.g., wire- and/or rod-shaped, sphere-shaped, cage-shaped, dendron-shaped, and polyhedron molecules.[12] The chemistry described here opens up a new area for nano-scaled advanced materials research.

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