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Synthesis of covalently bonded nanostructure from two porphyrin molecular wires leading to a molecular tube

Tamao Ishida, Yasuhiro Morisaki and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

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Abstract—Molecular wire, diacetylene-linked porphyrin dimer **6** having terminal alkenes, was synthesized. Porphyrin dimer **6** formed the 1:1 double-stranded ladder complex with 1,4-diazabicyclo[2.2.2]octane (DABCO). The co-planar stacked two porphyrin molecular wires in the ladder complex were connected by olefin metathesis in the presence of the Grubbs catalyst in order to make a covalently bonded tubular nanostructure. The obtained molecular tube **7** was characterized by ^{1}H, ^{13}C NMR spectroscopy, and MALDI-TOF MS spectrometry.

The construction of a π-stacked molecular structure is of great interest for understanding the electronic interactions between individual chromophores, since π–π interactions are important to achieve high charge carrier mobility for applications to organic electronic devices. Nakano et al. designed and synthesized poly(dibenzofulvene)s,[1] in which the side-chain chromophores were regularly π-stacked, and reported this π-stacked structure facilitated charge transfer as compared to the main-chain type π-conjugated polymers such as poly(*p*-phenylenevinylene) and photoconductive poly(*N*-vinylcarbazole).[1c] It is desirable that the molecular wire is constructed by the through-space π–π interaction rather than the through-bond π-conjugation. One simple approach to design the π-stacked structure in a π-conjugation system is the incorporation of a small cyclophane unit such as [2.2]paracyclophane,[2] which has the intramolecular π–π interaction. Bazan, Mukamel and co-workers have reported the unique photophysical properties of a series of stilbenoid dimers having a [2.2]paracyclophane core.[3] In addition, we[4] and other groups[5] have synthesized the through-space π-conjugated polymers having a cyclophane unit in the main chain. We also reported benzene ring-layered polymers comprising [2.2]paracyclophane and xanthene skeletons.[4n]

Another approach is to exploit the intermolecular interaction such as π–π interaction,[6] metal-coordination,[7] hydrogen bonds,[8] and donor–acceptor interaction[9] as a driving force for organizing aromatic compounds into well-defined supramolecular π-stacked structures. Some supramolecular π-stacked assemblies exhibited unique physical properties such as high one-dimensional charge carrier mobility parallel to the direction of π-stacking.[6a,b] In addition, a dynamic π-stacked molecular assembly in solution can tune the emission color.[6c,d,e] Although supramolecular self-assembly method can provide an easy approach to obtain the desired π-stacked structures, these structures are stable only under specific conditions. Accordingly, connecting each π-conjugated molecule in a self-assembled π-stacked structure by covalent bonds is desirable to maintain the structure under various conditions.

Anderson and co-workers reported the cooperative self-assembly of the conjugated diacetylene-linked zinc porphyrin dimer[10a] and oligomer,[10b] which formed a stable double-strand ladder complex with 1,4-diazabicyclo[2.2.2]octane (DABCO). The ladder formation is an all-or-nothing two-state assembly; no other complexes are observed apart from the ladder and the unbound oligomer by adding less than the stoichiometric amount of DABCO. We used this cooperative self-assembly for the formation of the stacked structure, and then attempted to hold the structure by the carbon–carbon bond formation. The resulting structure can be regarded as the tubular structure. The tubular structure consisting of

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Keywords: Porphyrin; Molecular tube; Molecular wire.

* Corresponding author. Tel.: +81 75 383 2604; fax: +81 75 383 2605; e-mail: chujo@chujo.synchem.kyoto-u.ac.jp

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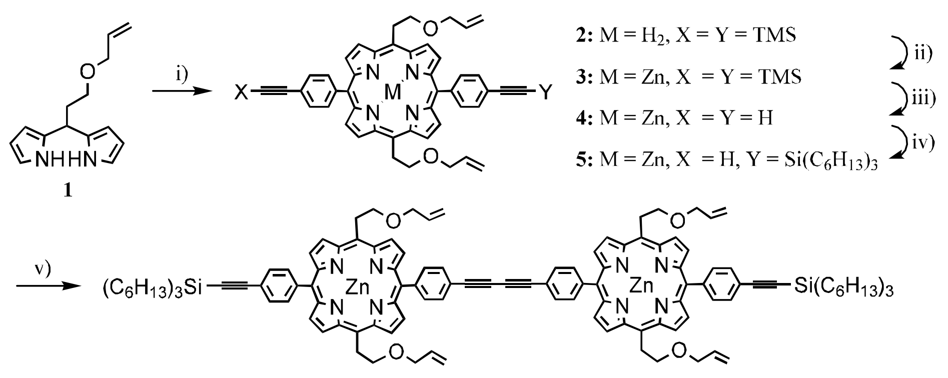


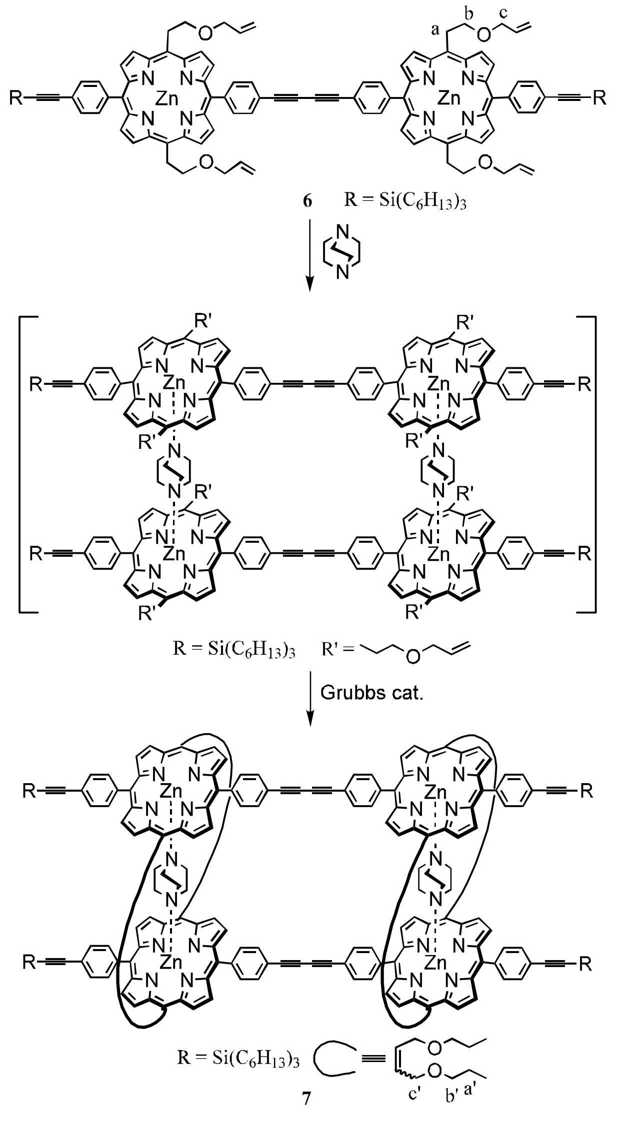
6

Scheme 1. Reagents and conditions: (i) 4-(trimethylsilylethynyl)benzaldehyde, $BF_3{\cdot}Et_2O$, at 0 °C for 30 min, (2) DDQ, at rt for 1 h, y. 20%; (ii) $Zn(OAc)_2{\cdot}2H_2O$, at rt for 45 min, y. 90%; (iii) $^{n}Bu_4NF$, at rt for 5 min, y. 74%; (iv) (1) LDA (2.0 M), at rt for 15 min, (2) $(^{n}C_6H_{13})_3SiCl$, at rt for 80 min, y. 28%; (v) CuCl, TMEDA, O_2, at rt for 1 h, y. 43%.

π-conjugated molecular wire is expected to offer not only a novel organic molecular device, but also a one-dimensional molecular host. Herein, we report the preparation and characterization of a novel nanostructured material consisting of two conjugated porphyrin dimers via the formation of the cooperative self-assembly of the porphyrin ladder complex with DABCO leading to the molecular tube.

Molecular wire, diacetylene-linked porphyrin dimer **6**, was prepared by the established procedures[10,11] as shown in Scheme 1. Free base porphyrin precursor **2** was synthesized from the corresponding dipyrromethane **1** with 4-[(trimethylsilyl)ethynyl]benzaldehyde in the presence of the boron trifluoride ethyl ether complex ($BF_3{\cdot}Et_2O$) followed by oxidation using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 20% yield. Zinc porphyrin **3** was obtained from **2** by the treatment of $Zn(OAc)_2{\cdot}2H_2O$ in 90% yield. Deprotection of **3** with $^{n}Bu_4NF$ gave **4** in 74% yield. Lithiation of **4** by lithium diisopropylamide (LDA) followed by chlorotrihexylsilane afforded mono-protected zinc porphyrin **5**[12] in 28% yield. The Hay coupling reaction[13] of **5** in the presence of an excess amount of CuCl and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) in CH_2Cl_2 with stirring for 1 h under an oxygen atmosphere gave **6**[14] in 43% yield as a reddish purple solid.

Molecular tube **7** was synthesized from **6** by the ruthenium-catalyzed olefin metathesis as shown in Scheme 2. At first, 0.5 equiv of DABCO per porphyrin unit was added to a solution of **6** in CH_2Cl_2, and then the 1:1 ladder complex of **6** was formed. The color of the solution was changed from reddish purple to bluish purple. Olefin metathesis of the ladder complex was performed in the presence of the Grubbs catalyst (first generation), benzylidenebis(tricyclohexylphosphine)-dichlororuthenium,[15] with a rapid stirring at room temperature for 24 h under a nitrogen atmosphere. After the reaction was complete, the crude product was purified by silica gel column chromatography and by the recycling preparative HPLC using $CHCl_3$ as an eluent to obtain **7**[16] in 7% yield. The molecular tube complex **7**, including DABCO, was stable during purification. The low yield (7%) was due to the loss of the target materials during the purification processes and low solubility derived from the rigid rod structure.



Scheme 2.

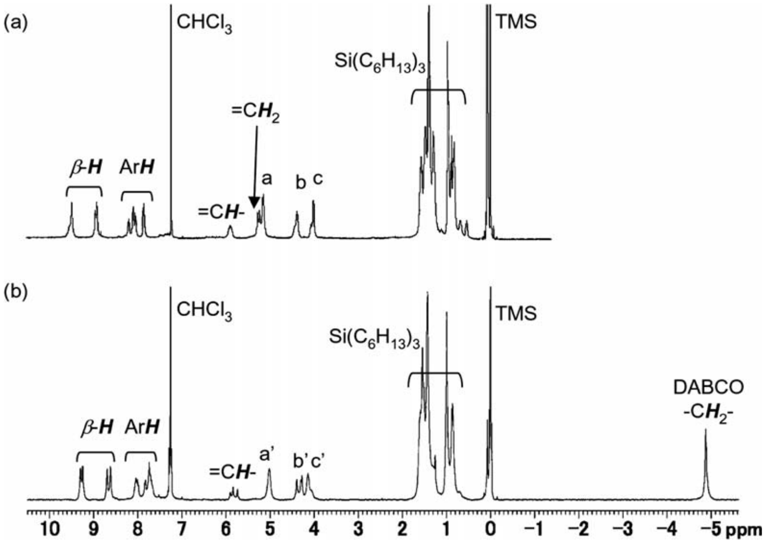


Figure 1. ^{1}H NMR spectra of (a) diacetylene-linked porphyrin dimer **6** and (b) molecular tube **7** in CDCl$_3$.

The structure of the molecular tube **7** was confirmed by ^{1}H, ^{13}C NMR, and MALDI-TOF MS spectra. Figure 1a shows the ^{1}H NMR spectrum of **6** in CDCl$_3$. The signals of the olefinic methylene and methyne protons appeared at 5.16, 5.26, and 5.90 ppm, respectively. In the ^{1}H NMR spectrum of **7** (Fig. 1b), the signal of the methylene protons of DABCO appeared at −4.9 ppm, indicating that two DABCO were incorporated into a porphyrin sandwich dimer.[17] The integral ratio of DABCO supported the formation of the 1:2 (**7**:DABCO) ladder complex. No alternate ladder complex was obtained, because the signal at around −3 ppm corresponding to the 1:1 (porphyrin:DABCO) open complex was not observed. The terminal olefinic methylene protons of **6** at 5.16 and 5.26 ppm completely disappeared, and the new signals appeared at 5.74–5.90 ppm, which was consistent with the internal olefinic methyne protons (Fig. 1b). This suggests that the olefin metathesis proceeded completely to form the tubular structure. Figure 2 shows the MALDI-TOF MS spectrum of the molecular tube **7**. DABCO was removed by ionization, and the peak was detected at 3980.99, which was in agreement with the calculated value of the desired molecular tube (3979.79) and one proton without DABCO. Other by-products derived from the alternate ladder complex or incompletely connected tubular structures were not obtained.

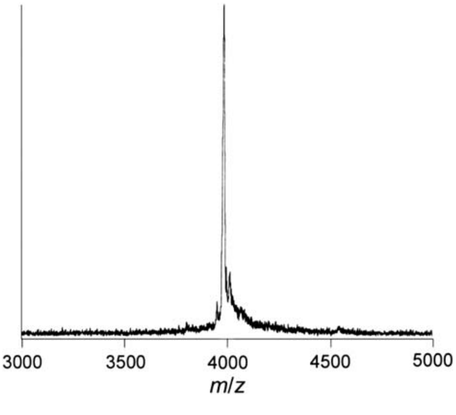


Figure 2. MALDI-TOF MS spectrum of **7**.

In conclusion, molecular tube **7** was successfully synthesized from porphyrin molecular wire **6** via the formation of the 1:1 ladder complex with DABCO followed by olefin metathesis. The obtained molecular tube **7** was characterized by ^{1}H, ^{13}C NMR spectroscopy, and MALDI-TOF MS spectrometry. Further studies on physical properties and the synthesis of molecular tube without DABCO are currently underway.

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12. Mono-protected porphyrin **5**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.82 (t, $J = 8.4$ Hz, 6H), 0.96 (br, 9H), 1.39 (br, 14 H), 1.48 (br, 10H), 3,34 (s, 1H), 4.12 (d, $J = 5.2$ Hz, 4H), 4.50 (t, $J = 7.6$ Hz, 4H), 5.18 (d, $J = 10.0$ Hz, 2H), 5.29–5.31 (br, 6H), 5.97 (ddt, $J = 11.2$, 16.8, and 5.2 Hz, 2H), 7.87 (d, $J = 7.6$ Hz, 2H), 7.90 (d, $J = 8.0$ Hz, 2H), 8.13 (d, $J = 9.2$ Hz, 2H), 8.15 (d, $J = 8.4$ Hz, 2H), 8.95 (d, $J = 3.6$ Hz, 2H), 8.96 (d, $J = 4.0$ Hz, 2H), 9.59 (d, $J = 4.8$ Hz, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.5, 14.2, 22.7, 24.1, 31.7, 33.3, 35.8, 72.1, 75.4, 78.2, 83.8, 96.1, 106.3, 115.7, 117.1, 119.2, 119.6, 121.4, 122.7, 129.1, 130.2, 130.3, 130.4, 132.2, 132.3, 134.2, 134.3, 134.7, 143.0, 143.4, 143.5, 149.1, 149.2, 150.5. HRMS (FAB): found $m/z = [M^{+}]$ 1022.4862. Calcd for $C_{64}H_{74}N_4O_2SiZn$ 1022.4872.
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14. Diacetylene-linked porphyrin dimer **6**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.81–0.97 (br, 24H), 1.30–1.57 (br, 54H), 4.02 (br, 8H), 4.38 (br, 8H), 5.16 (br, 8H), 5.16 (d, $J = 10.0$ Hz, 4H), 5.26 (d, $J = 17.6$ Hz, 4H), 5.90 (br, 4H), 7.87 (d, $J = 7.6$ Hz, 4H), 8.05 (d, $J = 7.6$ Hz, 4H), 8.10 (br, 4H), 8.20 (br, 4H), 8.93 (br, 4H), 8.96 (br, 4H), 9.50 (br, 8H).
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16. Molecular tube **7**: To a solution of porphyrin dimer **6** (46 mg, 0.023 mmol) in CH_2Cl_2 (65 mL) was added a solution (258 μL) of DABCO, which dissolved in CH_2Cl_2 (88 mM) to make the double-strand ladder complex. Then the Grubbs catalyst (first generation), benzylidenebis(tricyclohexylphosphine)dichlororuthenium (39 mg, 0.045 mmol), was added to the solution. The reaction mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. After the reaction was complete, the reaction mixture was washed with water. The organic layer was dried over Na_2SO_4, and the solvent was evaporated. The residue was subjected to a silica gel column chromatography using $CHCl_3$ as an eluent. The obtained product was further purified by recycling preparative HPLC using $CHCl_3$ as an eluent, and dried in vacuo to give **7** as a dark green solid (3.4 mg, 0.81 μmol, 7%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ −4.89 (s, 12H), −4.87 (s, 12H), 0.86 (br, 24H), 0.99 (br, 36H), 1.43 (br, 56H), 1.55 (br, 40H), 4.14 (br, 16H), 4.28 (br, 8H), 4.39 (br, 8H), 5.02 (br, 16H), 5.74–5.90 (br, 8H), 7.60–7.80 (br, 16H), 7.82 (br, 4H), 8.00–8.10 (br, 12H), 8.62 (br, 8H), 8.69 (br, 8H), 9.24 (br, 8H), 9.30 (br, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.5, 14.3, 22.8, 24.1, 31.7, 33.3, 36.1, 38.5, 66.8, 75.4, 94.0, 103.0, 114.6, 118.9, 121.1, 128.6, 129.4, 129.9, 130.4, 131.9, 132.0, 134.4, 142.7, 144.0, 148.3, 148.6, 150.0, 150.1. Internal acetylenic carbons were not detected due to low solubility. MS (MALDI-TOF, dithranol as a matrix): found $m/z = [M+H]^{+}$ 3980.99. Calcd for $C_{248}H_{276}N_{16}O_8Si_4Zn_4$ 3979.79. Three kinds of olefinic methyne protons and two kinds of methylene protons ('b' in Fig. 1b) have two possibilities; (a) mixtures of (*E*,*Z*), (*E*,*E*), and (*Z*,*Z*) isomers (Refs. 18 and 19) and (b) intramoelcular olefin metathesis. Further investigation is currently underway.
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