Preparation of Porphyrin-stoppered Rotaxane Aiming at Immobilization on Substrate

Masumi Asakawa*, Taichi Ikeda†, Nobuhiko Yui†, and Toshimi Shimizu*
Nanoarchitectonics Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565
†*School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292*

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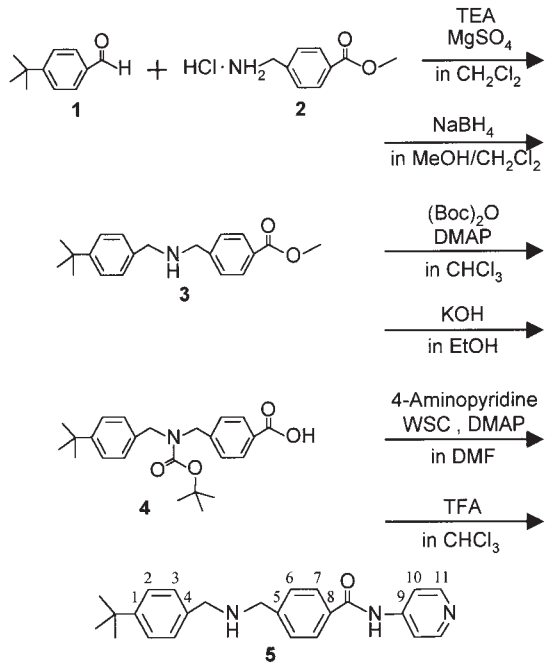
The porphyrin-stoppered rotaxane was prepared from dibenzo-24-crown-8 (DB24C8) and the secondary ammonium ion derivative end-capped by the axial coordination of rhodium(III) tetra-(3,5-di-*tert*-butylphenyl) porphyrin [TBPP Rh(III) Cl]. This rotaxane molecule was designed aiming at the immobilization on a substrate and the analysis of the physicochemical properties as a single molecule.

The interlocked molecules, e.g. rotaxane in which a cyclic molecule is threaded on a linear compound capped with bulky end groups, has attracted much attention as a candidate for the molecular devices in nanotechnology.[1] The molecular devices should be immobilized on a substrate in practical use. The immobilization of the functional interlocked molecules by Langmuir-Blodgett technique or self-assembled monolayer on the gold surface has been demonstrated.[2] The property of the immobilized molecules may be different from the real properties of the single molecule. This is because the functional molecules should be affected by the surrounding molecules. The characteristic of the rotaxane molecule is the rotational and translational motions of a cyclic molecule against a linear component. Therefore, the immobilization of the rotaxane molecule in the isolated state is an important subject to minimize the steric hindrance of the surrounding molecule.

Recently, some research groups reported the STM observation of the immobilized porphyrin derivatives on a substrate.[3] It was found that porphyrin ring of TBPP stands on the noble metal surface by using four 3,5-di-*tert*-butylphenyl groups as the legs. Since the porphyrin ring occupies much room on the substrate, the coordinated rotaxane molecule on TBPP should be in the isolated state. From CPK model, it was confirmed that the cross-sectional areas of TBPP and DB24C8 are almost same. The STM observation of the isolated rotaxane molecule should accelerate the analysis of the physicochemical properties of the rotaxane as a single molecule and clarify the feasibility of the rotaxane molecule as a molecular device.

In this letter, we report the preparation of the porphyrin-stoppered rotaxane aiming at the immobilization of the interlocked molecules on a substrate.

The molecule **5** was synthesized in conventional chemistry (Scheme 1). **3** was synthesized by reductive amination of 4-*tert*-benzaldehyde with 4-methoxycarbonylbenzylamine hydrochloride. The secondary amino group was protected by Boc group, then the ester was hydrolyzed to yield **4**. The condensation reaction between **4** and 4-aminopyridine by 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (WSC) and the deprotecton of secondary amino group yield **5**. Total yield was 50%. The synthesis of **5** was confirmed by ^{1}H, ^{13}C NMR, FAB-MS and the elemental analysis.[4] **5** is the guest molecule for DB24C8 (**6**) and the axial ligand for TBPP Rh(III) Cl (**8**) simultaneously.

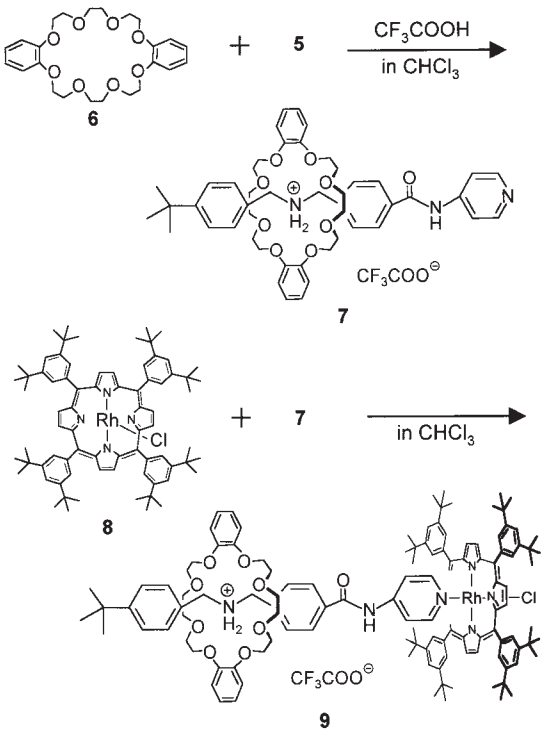


Scheme 1. Synthesis of axis molecule for porphyrin-stoppered rotaxane. Aromatic carbons of **5** was numbered from C^1 to C^{11}.

TBPP was synthesized from 3,5-di-*tert*-butylbenzaldehyde and pyrrole (see elsewhere).[5] **8** was prepared by the reaction of TBPP with $[Rh(CO)_2Cl_2]_2$.[6]

Prior to the preparation of the porphyrin-stoppered rotaxane, the inclusion complexation between **5** and **6** was examined (**7** in Scheme 2). The secondary amino group was converted to the ammonium salt ($\mathbf{5}^+$) by the addition of trifluoroacetic acid. It was confirmed that the peaks assigned to the protons around the secondary ammonium ion group shifted towards down-field by the mixing of $\mathbf{5}^+$ and **6**.[7] This result suggests that the $\mathbf{5}^+$ forms an inclusion complex with **6**.[8] The chemical shift change towards down-field is attributed to the anisotropic shielding of DB24C8 aromatic rings. The stability constant of the complex was estimated to be ca. 3000 $L \cdot mol^{-1}$ from the peak integrals of ^{1}H NMR spectrum (concentration: 1.2×10^{-3} $mol \cdot L^{-1}$).

The porphyrin-stoppered rotaxane (**9**) could be obtained easily from **7** and **8**.[9] After purification, the yield of the rotaxane was 70%. The preparation of the rotaxane was confirmed by ^{1}H NMR and FAB-MS spectrum.[10] The ^{1}H NMR peaks of **9** appears in higher field than those of **7**. This is due to the diamagnetic ring current of the porphyrin ring. The intensity of the anisotropic shielding effect by the porphyrin ring depends on the distance



Scheme 2. Preparation of porphyrin-stoppered rotaxane.

from the porphyrin ring.[6a] For instance, the peak assigned to $C^{11}H$ shifts towards up-field drastically ($\Delta\delta = 8.53 - 0.75 = 7.78$ ppm). On the other hand, the peak assigned to *tert*-butyl group of $\mathbf{5}^+$, which are the most far from the porphyrin ring, shifts slightly ($\Delta\delta = 0.11$ ppm). The peaks of DB24C8 also shift towards up-field ($\Delta\delta =$ ca. 0.22 ppm). The intensity of the anisotropic shielding effect on DB24C8 is almost same for that on the methylene protons of the axis (C^4-CH_2) ($\Delta\delta = 0.23$ ppm). This result suggests that DB24C8 locate around the methylene group of $\mathbf{5}^+$.

The absorption maxima of the Soret and Q bands of **8** shifted towards longer wavelength by the formation of **9**. This result is consistent with that for the axial coordination of pyridine derivatives to **8**.

Recently, some groups reported the porphyrin-stoppered rotaxanes.[11] In these studies, the end capping reaction by the axial coordination of porphyrin derivatives is thermodynamically unstable. In our study, the coordination of **7** to **8** is quite stable. No dissociated species could be observed by ^{1}H NMR spectrum even if it heated to 323 K.

The preparation of the porphyrin-stoppered rotaxane monolayer on a substrate and the observation of the physicochemical properties of the rotaxane as a single molecule are now in progress.

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This paper is dedicated to Professor Teruaki Mukaiyama on the occasion of his 75th birthday.

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4 Data for **5**: white solid. ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) δ 1.31 (s, 9H, $C(CH_3)_3$), 1.77 (br, CH_2NHCH_2), 3.77 (s, 2H, C^4-CH_2), 3.88 (s, 2H, C^5-CH_2), 7.25 (d, $J = 8.1$ Hz, 2H, C^3H), 7.35 (d, $J = 8.1$ Hz, 2H, C^2H), 7.47 (d, $J = 8.1$ Hz, 2H, C^6H), 7.60 (d, $J = 6.2$ Hz, 2H, C^{10}H), 7.82 (d, $J = 8.1$ Hz, 2H, C^7H), 8.16 (br, CONH), 8.51 (d, $J = 6.2$ Hz, 2H, C^{11}H). ^{13}C NMR ($CDCl_3$, 600 MHz, 298 K): $\delta = 31.36$ ($C(CH_3)_3$), 34.48 ($C(CH_3)_3$), 52.66, 52.87 (CH_2NHCH_2), 113.81 (C^{10}), 125.39 (C^2), 127.29 (C^7), 127.83 (C^3), 128.32 (C^6), 133.62 (C^8), 136.87 (C^4), 145.12 (C^5), 145.50 (C^1), 150.10 (C^9), 150.77 (C^{11}), 166.03 ($C=O$). MS (FAB) found: m/z 374. Calcd for $C_{24}H_{27}N_3O$: M^+, 374. Anal. Calcd for $C_{24}H_{27}N_3O\_0.5H_2O$: C, 75.36; H, 7.38; N, 10.99%. Found: C, 75.26; H, 7.37; N, 10.66%.

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6 a) H. Ogishi, J. Setsume, T. Omura, and Z. Yoshida, *J. Am. Chem. Soc.*, **97**, 6461 (1975). b) Data for **8**: purple solid. ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) δ 1.51 (s, 36H, $C(CH_3)_3$), 7.77 (s, 4H, Py), 8.06 (s, 4H, Py), 8.15 (s, 4H, Ar), 9.00 (s, 8H, Ar). MS (FAB) found: m/z 1200. Calcd for $C_{76}H_{92}ClN_4Rh$: M^+, 1200. UV-vis ($CHCl_3$): λ_{max}: 425, 535, 569 nm.

7 Data for **7**: ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) δ 1.25 (s, 9H, $C(CH_3)_3$), 3.39 (m, 8H, CH_2 of **6**), 3.73 (m, 8H, CH_2 of **6**), 4.09 (m, 8H, CH_2 of **6**), 4.43 (m, 2H, C^4-CH_2), 4.74 (m, 2H, C^5-CH_2), 6.75 (m, 4H, Ar of **6**), 6.87 (m, 4H, Ar of **6**), 7.15 (d, $J = 7.3$ Hz, 2H, C^3H), 7.24 (d, $J = 7.3$ Hz, 2H, C^2H), 7.47 (d, $J = 8.1$ Hz, 2H, C^6H), 7.67 (br, 2H, $CH_2NH_2CH_2$), 7.89 (d, $J = 8.4$ Hz, 2H, C^{10}H), 8.39 (d, $J = 8.1$ Hz, 2H, C^7H), 8.53 (d, $J = 8.4$ Hz, 2H, C^{11}H), 10.88 (s, 1H, CONH).

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9 **6** (6.4×10^{-5} mol) was dissolved in 1.6 mL of $CHCl_3$ solution containing **5** (3.2×10^{-5} mol). TFA (1.9×10^{-4} mol) was added, and then **8** (3.2×10^{-5} mol) was dissolved in the solution. After complete dissolution of **8**, the product was immediately purified by GPC (Sephadex LH20, solvent: MeOH). Moreover, the product was purified by SiO_2 column (solvent: CH_2Cl_2 then MeOH).

10 Data for **9**: purple solid. ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K) δ 0.75 (d, $J = 7.7$ Hz, 2H, C^{11}H), 1.14 (s, 9H, $C(CH_3)_3$ of **5**), 1.44 (m, 72H, $4 \times C(CH_3)_3$ of **8**), 3.16 (m, 8H, CH_2 of **6**), 3.52 (m, 8H, CH_2 of **6**), 3.87 (m, 8H, CH_2 of **6**) 4.20 (m, 2H, C^4-CH_2), 4.42 (m, 2H, C^5-CH_2), 5.71 (d, $J = 7.7$ Hz, 2H, C^{10}H), 6.54 (m, 4H, Ar of **6**), 6.64 (m, 4H, Ar of **6**), 6.95 (d, $J = 8.4$ Hz, 2H, C^3H), 7.05 (d, $J = 8.4$ Hz, 2H, C^6H), 7.07 (d, $J = 8.4$ Hz, 2H, C^2H), 7.38 (d, $J = 8.4$ Hz, 2H, C^7H), 7.39 (br, 2H, $CH_2NH_2CH_2$), 7.67 (s, 4H, Ar of **8**), 7.96 (s, 4H, Py of **8**), 8.09 (s, 4H, Py of **8**), 8.85 (s, 8H, Ar of **8**), 10.29 (br, 1H, CONH). MS (FAB) found: m/z 2021. Calcd for $C_{124}H_{151}ClN_7O_9Rh$: M^+, 2021.

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