Synthesis of Alkyl-substituted, Strapped Porphyrin to Prepare Stable Alkyl-chain-assisted Self-assembled Monolayers of Porphyrin Conjugates

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An alkyl-substituted, strapped porphyrin was synthesized aiming at the preparation of stable alkyl-chain-assisted self-assembled monolayers (SAMs) of porphyrin conjugates. We confirmed that the synthesized strapped porphyrin could form stable SAMs by scanning tunneling microscopy (STM). This approach will lead to the functionalization of alkyl-chain-assisted SAMs by introducing a variety of functional groups in the strapped moiety.

Two-dimensional (2-D) self-assembly on a substrate has attracted much attention to arrange functional molecular devices with a regular pattern.[1] To date, SAMs of organothiol compounds on a noble metal (organothiol SAMs) are the most extensively studied SAMs to immobilize functional molecules.[2] In the organothiol SAMs, however, the control of the distance between the molecules or the symmetry of the molecular pattern is now unattainable. On the other hand, SAMs of alkyl-substituted compounds (alkyl-chain-assisted SAMs) have boomed to create periodic molecular patterns on a substrate (graphite[3] or gold[4]) and these molecular patterns were analyzed by means of STM. Recently, some groups reported 2-D array of 5,10,15,20-tetra-(4-alkyloxyphenyl) porphyrin (C_nOPP, n: number of the carbon atoms in an alkyl chain).[5] Since the porphyrins or metalloporphyrins are attractive materials for photosynthesis,[6] optoelectronic devices,[7] and catalysts,[8] the well-ordered molecular array of functionalized porphyrins on the substrate would be of great importance in the fields of nanoscience and nanotechnology. On the basis of this perspective, we have studied molecular arrangement of the porphyrin conjugates composed of C_nOPP and a functional molecule. In the previous study, we confirmed SAMs of the pyridine-coordinated C_{30}OPP rhodium chlorides, in which the pyridine molecule bound to the metalloporphyrin through axial-coordination bond (axial-coordination approach).[9] In this letter, we describe the covalently linked approach as an alternative to the axial-coordination approach. In the covalently linked approach, the functional moiety was covalently linked to C_nOPP. Therefore, we synthesized an alkyl-substituted, strapped porphyrin and confirmed the formation of stable SAMs of the synthesized strapped porphyrins.

For the simple organic synthesis, hydroquinone was covalently linked to C_{18}OPP. We considered that the strapped porphyrin **10** (Figure 1) would be superior to the non-strapped C_{18}OPP derivatives, because the strapped part hinders free rotation of the phenyl group of C_{18}OPP not only in the solution but also on the surface. Thus, the strapped porphyrin **10** has no unfavorable atropisomer for molecular adsorption, which means one porphyrin face is always free from the strapped moiety.

The strapped porphyrin **10** was synthesized via condensation of the alkyl-substituted dialdehyde (**6**) and alkyl-substituted dipyrromethane derivative (**9**) (Figure 1). The alkylation of 2,4-dihydrobenzaldehyde (**1**) with stearylbromide ($C_{18}H_{37}Br$) (molar ratio: **1**/$C_{18}H_{37}Br = 2/1$) gave the product **2**. 1 N NaOH aqueous solution containing **3** and 2-chloroethanol (molar ratio: **3**/2-chloroethanol $= 1/5$) was refluxed for 24 h under dark to obtain the diol (**4**). After the tosylation of **4**, the dialdehyde **6** was obtained from the reaction of **2** and **5** in DMF (molar ratio: **2**/**5** $= 2/1$) in the presence of $CsCO_3$ at 110 °C. The aldehyde **8** was treated with pyrrole in the presence of catalytic amount of TFA for 1 h under dark and nitrogen atmosphere to get the product **9**.

The condensation reaction between the dialdehyde **6** and dipyrrolylmethane derivative **9** was conducted in CH_2Cl_2 with

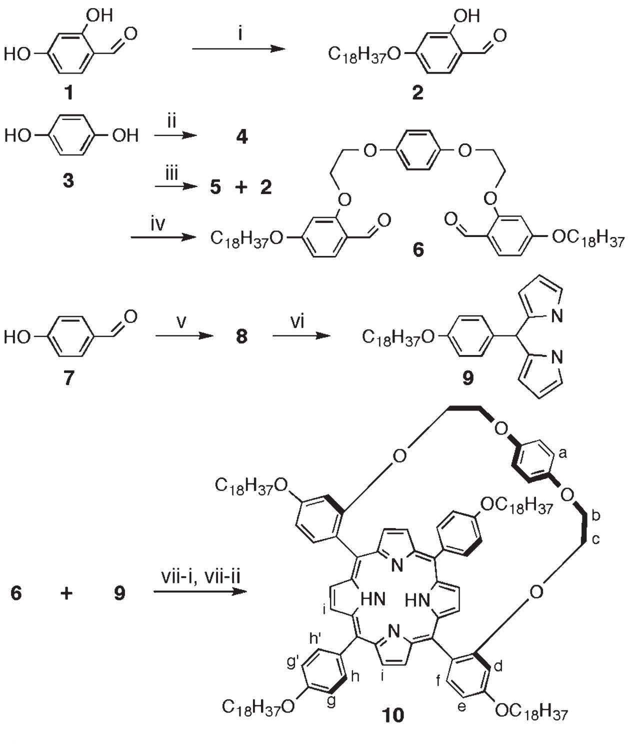

Figure 1. Reaction scheme for the synthesis of strapped porphyrin **10**. Reagents and conditions: (i) $C_{18}H_{37}Br$, KI, K_2CO_3, butanone, reflux, 57%; (ii) 2-chloroethanol, NaOH, water, under dark, reflux, 60%; (iii) Ts-Cl, pyridine, DMAP, THF, N_2, rt, 72%; (iv) $CsCO_3$, DMF, 110 °C, 70%; (v) $C_{18}H_{37}Br$, K_2CO_3, DMF, reflux, 85%; (vi) pyrrole, TFA, under dark, rt, 55%; (vii–i) BF_3•OEt, TFA, CH_2Cl_2, N_2, under dark, rt; (vii–ii) DDQ, reflux, 8%.

$BF_3 \cdot OEt_2$ and TFA catalysis for 3 h under dark and nitrogen atmosphere. After the addition of DDQ, the solution was refluxed for 1 h under dark. After cooling to room temperature, the solution was directly adsorbed to dry silica gel and eluted the crude product by $CHCl_3$. The recovered product was purified by silica gel chromatography twice [First: $CHCl_3$/hexane = 7/3 (v/v), Second: hexane/AcOEt = 10/1 (v/v)]. The product **10** was confirmed by ^1H, ^{13}C NMR, MS, and elemental analysis.[10]

SAMs of the strapped porphyrin **10** were confirmed by STM. STM observations were conducted in a droplet of the sample solution (solvent: dichlorobenzene) on a fleshly cleaved graphite surface. Figure 2a is a representative STM image of SAMs of the strapped porphyrin **10**. We were able to confirm the characteristic two-fold symmetry structure.[5] The bright spots aligned in lines and the dark stripes correspond to the strapped porphyrin moiety and the closely packed alkyl chains on the graphite surface, respectively. The lattice parameters of the unit cell $a \times b$ and β (Figure 2c) were $3.94 \pm 0.1 \times 2.01 \pm 0.1$ nm and $101 \pm 5^\circ$. As for the proposed structure of SAMs shown in Figure 2c, the lattice parameters were 3.96×2.02 nm and 104.8° ($a \times b$ and β). These values are well consistent with the observed ones.

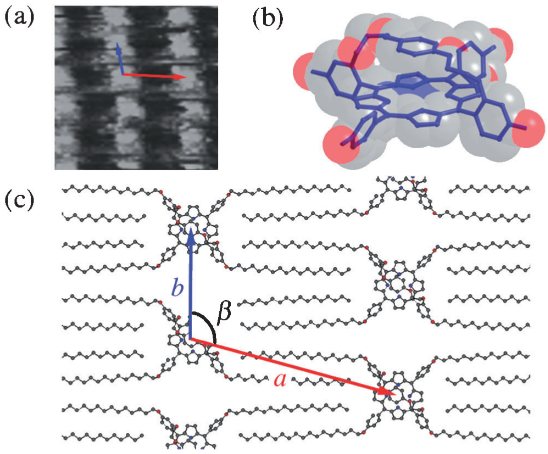

Figure 2. (a) STM image of self-assembled monolayers consisting of strapped porphyrin **10** on a graphite surface ($10 \times 10\,nm^2$). Solvent: dichlorobenzene. Tunneling conditions: $I = 200$ pA, $V = -1000$ mV. (b) Partial molecular structure of the strapped porphyrin **10** (MM2 calculation). (c) Proposed structure of SAMs consisting of the strapped porphyrin **10**. Each molecular structure was optimized using MM2 calculation.

From the section analysis of STM image, the average apparent height of the strapped porphyrin **10** was 0.57 ± 0.05 nm, which is clearly more than that of C_{18}OPP (0.20 ± 0.03 nm). In the molecular structure calculated by MM2 (Figure 2b), the average distance between the porphyrin (pyrrole and *meso* carbons) and strapped benzene planes was 0.38 nm.[11] However, we must consider the fluttering of the strapped moiety and the interaction between the strapped benzene and porphyrin. In principle, the apparent STM height is not comparable to the real height of the molecule.[12]

In compared to C_{18}OPP, the molecular adsorption of the strapped porphyrin **10** is entropically unfavorable owing to less molecular symmetry. Namely, C_{18}OPP has two equivalent faces to adsorb to the surface while the strapped porphyrin **10** has only one. We believe that the porphyrin free face, not hydroquinone face, should attach to the graphite surface. The entropic contribution to the adsorption free energy is calculated to be ca. $1.7\,kJ\,mol^{-1}$ ($= RT \ln 2$, $T = 293$ K) from the difference in symmetry number.[13] In the case of pyridine-coordinated rhodium chloride with the same alkyl chain length (C_{18}), we had no molecular image.[9] Therefore, the covalently linked approach using the strapped porphyrin **10** is more attractive than the axial-coordination approach from the viewpoint of the formation of stable alkyl-chain-assisted SAMs.

This protocol will lead to the functionalization of alkyl-chain-assisted SAMs by introducing the functional molecule in the strapped moiety. The molecular design of the strapped moiety is considered to be free since the structure of the opposite side (porphyrin free face) is always the same. 2-D array of the functional porphyrin conjugates is expected to exhibit the novel attractive characteristics. The detailed STM characterization of the strapped porphyrin **10**, characterization of SAMs as a functional device, and further functionalization of the strapped porphyrin are now in progress.

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[10] ^1H NMR (400 MHz, $CDCl_3$): δ −2.63 (s, NH), 0.88 (t, CH_3), 1.20–1.55 (m, CH_2), 1.62 (m, CH_2), 1.97 (m, CH_2), 2.77 (br, C^bH_2), 3.62 (s, C^aH), 3.81 (br, C^cH_2), 4.24 (m, OCH_2), 6.79 (s, C^dH), 7.03 (d, $J = 8.4$ Hz, C^eH), 7.20, 7.25 (br, C^gH), 7.87, 8.22 (br, C^hH), 8.37 (d, $J = 8.4$ Hz, C^fH), 8.83 (m, C^iH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.6, 23.2, 26.7, 29.9, 30.0, 30.1, 30.2, 32.4, 68.8, 69.0, 69.1, 69.6, 101.6, 105.6, 113.1, 115.4, 115.8, 119.6, 125.3, 131 (br), 134.9, 135.8, 136.2, 151.0 (br), 152.8, 159.3, 160.8, 161.2; MS (MALDI): *m/z*: 1881.8 $[M]^+$; $C_{126}H_{184}N_4O_8$ (1882.8): calcd C 80.38, H 9.85, N 2.98; found C 80.74, H 9.80, N 2.71%.

[11] This value is consistent with that for the crystal structure of the capped porphyrin. See: M. R. Johnson, W. K. Seok, and J. A. Ibers, *J. Am. Chem. Soc.*, **113**, 3398 (1991).

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