Journal of
Nanoscience and Nanotechnology
Vol. 12, 7885–7895, 2012

Coordinative Nanoporous Polymers Synthesized with Hydrogen-Bonded Columnar Liquid Crystals

Shinsuke Ishihara[1, 2, 3,*], Yusuke Furuki[1], Jonathan P. Hill[2, 3], Katsuhiko Ariga[2, 3], and Shinji Takeoka[4,*]

[1] *Department of Applied Chemistry, Graduate School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjyuku-ku, Tokyo 169-8555, Japan*
[2] *World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*
[3] *Japan Science and Technology Agency (JST), Core Research for Evolutional Science and Technology (CREST), Go-bancho, Chiyoda-ku, Tokyo 102-0076, Japan*
[4] *Department of Life Science and Medical Bioscience, Graduate School of Advanced Science and Engineering, Waseda University (TWIns), 2-2 Wakamatsucho, Tokyo 162-8480, Japan*

In this paper, we report the development of nanoporous polymer which demonstrates the coordination property toward zinc porphyrin. A hydrogen-bonded columnar liquid crystalline precursor composed of a triphenylene template and three equivalent of the surrounding dendric amphiphile bearing a pyridyl head group and a polymerizable aliphatic chain, was covalently fixed by photopolymerization, and then the subsequent selective removal of the template successively resulted in a nanoporous polymer in which the pore wall is modified with pyridyl groups. The nanoporous polymer reflected the conformation of template, and displayed considerable coordination ability of the pyridyl groups towards zinc porphyrin. The coordinative nanoporous polymer is promising as a nano-scaled scaffold for the organization of dyes into functional supramolecular architectures.

Keywords: Nanoporous Polymer, Coordination, Supramolecular Chemistry, Coordination, Liquid Crystal.

RESEARCH ARTICLE

1. INTRODUCTION

Development of nanoscience and nanotechnology[1–3] depends strongly on creation of nano-sized structures and nanospaces as can be found in the various excellent investigations of nanotubes,[4, 5] nanoparticles,[6–10] nano-layered structures,[11–14] and nanoporous materials.[15, 16] Selective inclusion of guest molecules into such nanospaces[17, 18] and regulation of the properties of trapped molecules under dynamic stimuli[19–24] often results in innovative functions including advanced sensing,[25–27] materials sequestration,[28] and controlled materials release especially of therapeutic substances.[29–31] In particular, design and synthesis of nanoporous materials of specific dimensions and surface modification has been a subject of considerable research interest over the past two decades, and various synthetic strategies using surfactant templates,[32–34] coordination polymers,[35, 36] block copolymers,[37–39] and nano-segregated supramolecular assemblies[40–43] have been developed. Of these, template polymerization[44, 45] of supramolecular columnar liquid crystals, including lyotropic liquid crystals[46,47] and thermotropic liquid crystals,[48] is an effective method for fabrication of size-controlled nanoporous polymers, and the resulting nanoporous polymer in which the pore wall is modified with concentrated functional groups are potentially nanomaterials for use as molecular sieves,[49] in anisotropic transportation,[50–52] enantioselection,[53] or heterogeneous catalytic[54] applications.

Surface modification of nanoporous materials is a critical issue in the optimization of the affinity of the pore toward guest molecules. In particular the pyridyl group, as a typical ligand, is a valuable functional group for the modification of pore walls due to its coordinative

*Authors to whom correspondence should be addressed.

properties towards metal ions or organometallics. Guest molecules introduced into a nanopore are sterically and electronically coupled to each other and are expected to present cooperative catalytic or electromagnetic functions, which are not present in the isolated unconstrained molecules.[55–58]

In this paper, we report the template polymerization of a hydrogen-bonded columnar liquid crystalline precursor for construction of a nanoporous polymer in which the pore wall is modified with pyridyl groups (Fig. 1). Subsequently, the coordinative ability of the nanoporous polymer due to the pyridyl groups in the pore was confirmed in an absorption experiment using zinc porphyrin.

2. EXPERIMENTAL SECTION

2.1. Materials

2-Methoxyphenol (Kanto Chemical Co., Inc), 1-bromopentane (Kanto Chemical Co., Inc), trimethylsilyl iodide (Tokyo Chemical Industry Co., Ltd), bromoacetic acid ethyl ester (Tokyo Chemical Industry Co., Ltd), methanesulfonic acid (Kanto Chemical Co., Inc), 3,4-dihydroxybenzaldehyde (Tokyo Chemical Industry Co., Ltd), 12-bromo-1-dodecanol (Tokyo Chemical Industry Co., Ltd), benzoyl chloride (Kanto Chemical Co., Inc), triethylamine (Kanto Chemical Co., Inc), 3,5-dihydroxybenzoic acid methyl ester (Tokyo Chemical Industry Co., Ltd), methacryloyl chloride (Tokyo Chemical Industry Co., Ltd), 2,6-di-*tert*-butyl-*p*-cresol (Tokyo Chemical Industry Co., Ltd), 4-aminopyridine (Kanto Chemical Co., Inc), 1H-benzotriazole-1-yloxytris(dimethylamino) phosphonium hexafluorophosphate (Tokyo Chemical Industry Co., Ltd), anhydrous potassium carbonate (Kanto Chemical Co., Inc), potassium hydrate (Kanto Chemical Co., Inc), anhydrous iron(III) chloride (Kanto Chemical Co., Inc), sodium borohydride (Kanto Chemical Co., Inc), and thionyl chloride (Kanto Chemical Co., Inc) were used as received. $CHCl_3$ was distilled over P_2O_5, and all other solvents were used without purification. 21*H*, 23*H*-porphine **P2H** and 21*H*, 23*H*-porphine zinc(II) **PZn** were prepared according to Neya's method.[59]

2.2. General Methods

^{1}H-NMR spectra were recorded from solutions of analytes dissolved in a deuterated solvent such as $CDCl_3$ using a JEOL JNM-LA 500 (500 MH_Z) NMR spectrometer. Electrospray ionization mass spectra (ESI-MS) were recorded on a Thermo Quest FINNIGAN LCQ DECA mass spectrometer. Differential scanning calorimetry (DSC) was measured on a Rigaku Thermo plus DSC 8230 with a heating and cooling rate of 5 °C min^{-1} from −40 °C to 60 °C. X-ray diffraction (XRD) patterns were recorded using a RIGAKU R-AXIS RAPID-R with Cu Kα radiation at room temperature. An infrared (IR) spectrum was recorded at room temperature with a JASCO FI/IR-410 Fourier transform infrared spectrometer. Temperature dependence of polarized optical microscopy textures was observed using an OLYMPUS BX51 microscope equipped with a cross-polarizing filter, an OLYMPUS CCD CS230B color camera, and a KITAZATO MP-200 DMSH micro-heat plate. UV-Vis spectra were recorded at room temperature with a JASCO V-660 spectrophotometer.

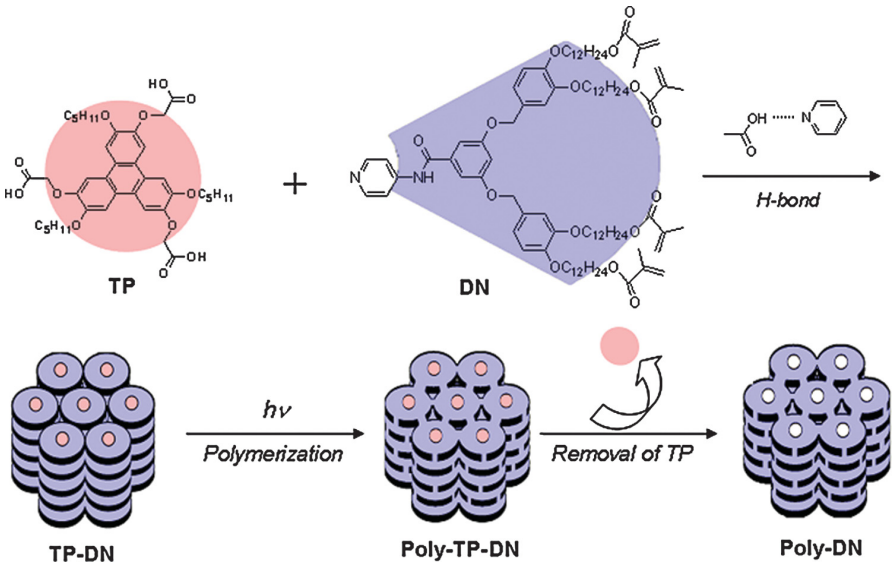

Fig. 1. Template polymerization of the hydrogen-bonded columnar liquid crystalline precursor **TP-DN** for construction of the nanoporous polymer **Poly-DN**.

RESEARCH ARTICLE

2.3. Synthesis of TP

2.3.1. 1-Methoxy-2-Pentyloxybenzene

2-Methoxyphenol (12.4 g, 0.100 mol), 1-bromopentane (18.1 g, 0.121 mol), and anhydrous K_2CO_3 (16.6 g, 0.120 mol) were stirred in refluxing CH_3CN (150 ml) for 12 h then the solvent was evaporated under reduced pressure. The crude residue was dissolved in chloroform, washed with 10% aqueous HCl, and dried over Na_2SO_4. The light yellow solution was concentrated under reduced pressure followed by purification by column chromatography on silica gel ($CHCl_3$/hexane: 1/1) which afforded 1-methoxy-2-pentyloxybenzene as a colorless liquid (23.1 g, 79.0%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.89 (m, 4H, Ar*H*), 3.85 (s, 3H, OCH_3), 3.36 (t, 2H, OCH_2), 1.98 (m, 2H, CH_2), 1.58 (m, 2H, CH_2), 1.47 (m, 2H, CH_2), 0.99 (t, 3H, CH_3). ESI-MS: m/z = 293.6 $[M+H]^+$.

2.3.2. 2,6,10-Trimethoxy-3,7,11-Tripentyloxytriphenylene

Anhydrous $FeCl_3$ (16.7 g, 0.103 mol) was added to a stirred solution of 1-methoxy-2-pentyloxybenzene (10.0 g, 0.342 mmol) and H_2SO_4 (1 drop) in CH_2Cl_2 (24 ml). After 45 min, the reaction was quenched with CH_3OH and left at 0 °C for 1 h. The resulting precipitate was filtered, and the residue was purified by flash column chromatography on silica gel (chloroform/hexane: 4/1) to obtain 2,6,10-trimethoxy-3,7,11-tripentyloxytriphenylene (600 mg, 9.1%) as a light brown solid. The structural isomer (2,6,11-trimethoxy-3,7,10-tripentyloxytriphenylene) was removed during this step. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.85, 7.82 (2S, 6H, Ar*H*), 4.26 (t, 6H, OCH_2), 4.10 (s, 9H, OCH_3), 1.97 (m, 6H, CH_2), 1.58 (m, 6H, CH_2), 1.51 (m, 6H, CH_2), 0.87 (t, 9H, CH_3). ESI-MS: m/z = 599.8 $[M+Na]^+$.

2.3.3. 2,6,10-Trihydroxy-3,7,11-Tripentyloxytriphenylene

Trimethylsilyl iodide (1.04 g, 5.20 mmol) was added to a stirred solution of 2,6,10-trimethoxy-3,7,11-tripentyloxytriphenylene (600 mg, 1.04 mmol) in chloroform (10 ml) at room temperature, and the solution was stirred at 45 °C for 2 h. Then, the solution was poured into 10% aqueous HCl, and extracted with $CHCl_3$ three times. The solution was dried with $MgSO_4$, and concentrated under reduced pressure. The purification of the brown solid by column chromatography on silica gel (ethyl acetate/hexane: 1/5) afforded 2,6,10-trihydroxy-3,7,11-tripentyloxytriphenylene as a white solid (200 mg, 36.0%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.85, 7.77 (2S, 6H, Ar*H*), 5.93 (s, 3H, OH), 4.17 (t, 6H, OCH_2), 1.92 (m, 6H, CH_2), 1.48 (m, 12H, CH_2), 0.99 (t, 9H, CH_3). ESI-MS: m/z = 535.8 $[M+H]^+$.

2.3.4. 2,6,10-Tris(ethoxycarbonylmethoxy)-3,7,11-Tripentyloxytriphenylene

2,6,10-Trihydroxy-3,7,11-tripentyloxytriphenylene (200 mg, 0.374 mmol), ethyl bromoacetate (200 mg, 1.20 mmol), and anhydrous K_2CO_3 (500 mg, 3.62 mmol) were stirred in DMF (10 ml) at 65 °C for 12 h. The resulting light yellow suspension was poured into 10% aqueous HCl and extracted twice with $CHCl_3$. The solution was concentrated under reduced pressure and purified by column chromatography on silica gel (ethyl acetate/hexane: 1/3) to obtain 2,6,10-tris(ethoxycarbonylmethoxy)- 3,7,11-tripentyloxytriphenylene as a white solid (199 mg, 67.1%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.95, 7.80 (2s, 6H, Ar*H*), 4.86 (s, 6H, OCH_2COO), 4.30(q, 6H, COOCH_2CH$_3$), 4.26(t, 6H, OCH_2), 1.99(m, 6H, CH_2) 1.57(m, 6H, CH_2), 1.48(m, 6H, CH_2), 1.32(t, 9H, COOCH$_2$CH_3), 0.99(t, 9H, CH_3). ESI-MS: m/z = 794.1 $[M+H]^+$.

2.3.5. 2,6,10-Tris(carboxymethoxy)-3,7,11-Tris(pentyloxy)Triphenylene (TP)

2,6,10-Tris(ethoxycarbonylmethoxy)-3,7,11-tris(pentyl oxy)triphenylene (100 mg, 0.0252 mmol) and methane sulfonic acid (1 drop) were dissolved in formic acid (10 ml). The solution was refluxed for 24 h then cooled to room temperature. Distilled water was then poured into the solution, and the resulting white precipitate was collected using a sintered glass filter, and washed with distilled water three times. The white solid was dried *in vacuo.* to obtain 2,6,10-tris(carboxymethoxy)-3,7,11-tris(pentyloxy)triphenylene **TP** (80.0 mg, 89.6%). ^{1}H-NMR (500 MHz, $CDCl_3$/CD_3OD: 4/1): δ 7.91, 7.75 (2s, 6H, Ar*H*), 4.86 (s, 6H, OCH_2COO), 4.26 (t, 6H, OCH_2) 1.98 (m, 6H, CH_2),1.57 (m, 6H, CH_2), 1.48 (m, 6H, CH_2), 0.99 (t, 9H, CH_3). ^{13}C-NMR (500 MHz, $CDCl_3$/CD_3OD): δ 171.8, 149.7, 147.5, 125.6, 123.2, 110.8, 100.9, 69.5, 68.0, 29.2, 28.5, 22.7, 14.1. ESI-MS: m/z = 707.6 $[M-H]^-$. Anal. calcd. for $C_{39}H_{48}O_{12}$: C, 66.09; H, 6.83; O, 27.09. Found: C, 67.2; H, 6.93.

2.4. Synthesis of DN

2.4.1. 3,4-Bis(12-Hydroxydodecyloxy)Benzaldehyde

3,4-Dihydroxybenzaldehyde (3.45 g, 0.0250 mol), 12-bromo-1-dodecanol (13.3 g, 0.0500 mol), and anhydrous K_2CO_3 (13.9 g, 0.100 mol) were stirred in DMF (150 ml) at 70 °C for 4 h, and then H_2O was added to the solution. The precipitation was collected on a sintered glass filter, and washed with H_2O twice. The crude product was dissolved in $CHCl_3$, and then recrystalized from CH_3OH to afford 3,4-bis(12-hydroxydodecyloxy)-benzaldehyde as a white solid (11.2 g, 88.5%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.82 (s, 1H, C*H*O), 7.41 (dd, 1H, Ar*H*), 7.39 (d, 1H, Ar*H*), 6.95 (d, 1H, Ar*H*), 4.07 (t, 2H, ArOCH_2), 4.05

(t, 2H, ArOCH_2), 3.63 (t, 4H, CH_2OH), 1.84 (m, 4H, CH_2), 1.56 (m, 4H, CH_2), 1.47 (m, 4H, CH_2), 1.35–1.28 (br, 28H, CH_2). ESI-MS: m/z = 507.9 $[M+H]^+$.

2.4.2. 3,4-Bis(12-Benzoyloxydodecyloxy)-Benzaldehyde

Benzoyl chloride (6.70 g, 0.0477 mol) was added to a stirred solution of 3,4-bis(12-hydroxydodecyloxyl)-benzaldehyde (11.0 g, 0.0217 mol) and triethylamine (5.10 g, 0.0504 mol) in CH_2Cl_2 (100 ml) at 0 °C. The solution was allowed to warm to room temperature, and then stirred for an additional 3 h. Then the solution was washed with 10% aqueous HCl, dried with Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (ethylacetate/hexane: 1/5) to afford 3,4-bis(12-benzoyloxydodecyloxy)benzaldehyde as a white solid (13.1 g, 84.4%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.83 (s, 1H, C*H*O), 8.03 (d, 4H, Bz*H*), 7.54 (t, 2H, Bz*H*), 7.43 (t, 4H, Bz*H*), 7.41-7.26 (m, 2H, Ar*H*), 6.94 (d, 1H, Ar*H*), 4.31 (t, 4H, CH_2OBz), 4.07 (t, 2H, ArOCH_2), 4.04 (t, 2H, ArOCH_2), 1.84 (m, 4H, CH_2), 1.76 (m, 4H, CH_2), 1.44 (m, 8H, CH_2), 1.35–1.29 (br, 24H, CH_2). ESI-MS: m/z = 715.8 $[M+H]^+$.

2.4.3. 3,4-Bis(12-Benzoyloxydodecyloxy)Benzyl Alcohol

Sodium borohydride (3.00 g, 0.0793 mol) was slowly added to a solution of 3,4-bis(12-benzoyloxydodecyloxy)benzaldehyde (13.0 g, 0.0182 mol) in THF/ ethanol (200 ml/ 40 ml) at 0 °C, and the solution was stirred for 2 h at room temperature. Then the solution was cooled to 0 °C, and 10% HCl aq. was slowly added. After the generation of H_2 gas had ceased the organic solvent was removed under reduced pressure. The resulting precipitate was collected on a glass filter, and washed twice with water. The product was dried *in vacuo* to afford 3,4-bis(12-benzoyloxydodecyloxy)benzyl alcohol as a white solid (12.8 g, 98.1%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.04 (d, 4H, Bz*H*), 7.54 (t, 2H, Bz*H*), 7.43 (t, 4H, Bz*H*), 6.92 (s, 1H, Ar*H*), 6.85 (s, 2H, Ar*H*), 4.60 (d, 2H, CH_2OH), 4.31 (t, 4H, CH_2OBz), 3.99, 3.98 (2t, 4H, ArOCH_2), 1.83–1,73 (m, 8H, CH_2), 1.49–1.42 (m, 8H, CH_2), 1.38–1.28 (br, 24H, CH_2). ESI-MS: m/z = 718.2 $[M+H]^+$.

2.4.4. 3,4-Bis(12-Benzoyloxydodecyloxy)Benzyl Chloride

Thionyl chloride (10.0 g, 0.0840 mol) was slowly added to a solution of 3,4-bis(12-benzoyloxydodecyloxy)benzyl alcohol (10.0 g, 0.0139 mol) and one drop of DMF in $CHCl_3$ (100 ml), and the solution was refluxed for 3 h. Then the solution including the excess thionyl chloride was removed under a dried N_2 stream. Quantitative conversion to the benzyl chloride derivative was confirmed by thin layer chromatography, and all of the pale yellow residue was used in the next synthesis without further purification.

2.4.5. 3,5-Bis-[3,4-bis-(12-Benzoyloxydodecyloxy) Benzyloxy]Benzoic Acid Methyl Ester

3,4-Bis(12-benzoyloxydodecyloxy)benzyl chloride was added to a suspension of 3,5-dihydroxybenzoic acid methyl ester (1.17 g, 0.00696 mol) and K_2CO_3 (2.00 g, 0.0144 mol) in DMF (100 ml). The solution was stirred for 24 h at 75 °C. H_2O was added to the solution and the precipitate was collected on a glass filter, and washed twice with H_2O. The crude product was purified by column chromatography on silica gel (ethylacetate/hexane: 1/2) affording 3,5-bis[3,4-bis(12-benzoyloxydodecyloxy) benzyloxy]benzoic acid methyl ester as pale yellow wax (6.12 g, 56.1%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.03 (d, 8H, Bz*H*), 7.54 (t, 4H, Bz*H*), 7.43 (t, 8H, Bz*H*), 7.28 (d, 2H, Ar*H*), 6.95-6.86 (m, 6H, Ar*H*), 6.79 (t, 1H, Ar*H*), 4.96 (s, 4H, Bzl-*H*), 4.30 (2t, 8H, ArOCH_2), 3.99 (m, 8H, ArOCH_2), 3.90 (s, 3H, COOCH_3), 1.81 (m, 8H, CH_2), 1.76 (m, 8H, CH_2), 1.44 (m, 16H, CH_2), 1.34–1.29 (br, 48H, CH_2). ESI-MS: m/z = 1566.9 $[M+H]^+$.

2.4.6. 3,5-Bis[3,4-bis(12-Hydroxydodecyloxy) Benzyloxy]Benzoic Acid

KOH (3.0 g 0.0535 mol) in H_2O (15 ml) was added to a solution of 3,5-bis[3,4-bis(12-benzoyloxydodecyloxy)benzyloxy]benzoic acid methyl ester (5.00 g, 0.00319 mol) in THF/CH_3OH (100 ml/ 30 ml) and the solution was refluxed for 12 h. The organic solvent was evaporated under reduced pressure and the solid was washed with 3% NaOH aq. on a sintered glass filter. The solid was dissolved in $CHCl_3$ and washed with 10% HCl. The solution was dried with Na_2SO_4, and concentrated under reduced pressure. The white solid was dried *in vacuo* to afford 3,5-bis[3,4-bis(12-hydroxydodecyloxy)benzyloxy]benzoic acid as a white solid (3.35 g, 92.4%). ^{1}H-NMR (500 MHz, CD_3OD): δ 7.29 (d, 2H, Ar*H*), 6.98-6.87 (m, 6H, Ar*H*), 6.78 (t, 1H, Ar*H*), 4.96 (s, 4H, Bzl-*H*), 3.99 (m, 8H, ArOCH_2), 3.56 (t, 8H, CH_2OH), 1.80 (m, 8H, CH_2), 1.54 (m, 8H, CH_2), 1.47 (m, 8H, CH_2), 1.29 (br, 56H, CH_2). ESI-MS: m/z = 1134.5 $[M-H]^-$.

2.4.7. 3,5-Bis[3,4-bis(12-Methacryloxydodecyloxy) Benzyloxy]Benzoic Acid

Methacryloyl chloride (220 mg, 2.10 mmol) was added to a stirred CH_2Cl_2 solution (50 ml) of 3,5-bis[3,4-bis (12-hydroxydodecyloxy) benzyloxy]benzoic acid (400 mg, 0.352 mmol), triethylamine (214 mg, 2.10 mmol), and 2,6-di-*tert*-butyl-*p*-cresol (10 mg, 0.0454 mmol) at 0 °C, and then the solution was stirred at room temperature for 8 hr. The solution was washed with 10% HCl aq., and dried over Na_2SO_4. Solvents were evaporated under reduced pressure, and the residue dissolved in pyridine (30 ml). To the stirred pyridine solution, 3 ml of H_2O

RESEARCH ARTICLE

and 2,6-di-*tert*-butyl-*p*-cresol (10 mg, 0.0454 mmol) were added, and the mixture was refluxed for 10 min. The solution was extracted with $CHCl_3$/10%HCl aq., and the crude product was purified by column chromatography on silica gel ($CHCl_3$/CH_3OH: 20/1), and the product freeze dried from benzene to afford 3,5-bis[3,4-bis(12-methacryloxy dodecyloxy)benzyloxy]benzoic acid as a white powder (280 mg, 56.5%). The product was stored with care at 0 °C in the dark. ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 7.35 (d, 2H, Ar-*H*), 6.98-6.86 (m, 6H, Ar-*H*), 6.83 (t, 1H, Ar-*H*), 6.09 (s, 4H, OCO(CH_3)=CH_2), 5.53 (m, 4H, OCO(CH_3)=CH_2), 4.97 (s, 4H, Bzl-*H*), 4.13 (2t, 8H, ArOCH_2CH_2), 4.00, 3.98 (2t, 8H, CH_2OCO(CH_3)=CH_2), 1.93 (s, 12H, OCO(CH_3)=CH_2), 1.67 (m, 8H, CH_2), 1.63 (m, 8H, CH_2), 1.36–1.25 (br, 56H, CH_2).

2.4.8. 3,5-Bis-[3,4-bis-(12-Methacryloxydodecyloxy)-Benzyloxy]-N-pyridin-4-yl-Benzamide (DN)

3,5-Bis[3,4-bis(12-methacryloxydodecyloxy)benzyloxy] benzoic acid (250 mg, 0.178 mmol), 1H-benzotriazole-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate (102 mg, 0.231 mmol), and triethylamine (23.4 mg, 0.231 mmol) in CH_2Cl_2 (10 ml) and DMF (5 ml) were stirred for 10 min at room temperature. Then 4-aminopyridine (165 mg, 1.75 mmol) was added, and the mixture was stirred for 12 h at room temperature. The light yellow suspension was poured into distilled water, and the precipitate was washed with distilled water an a sintered glass filter three times. The solid was dissolved in $CHCl_3$ and dried over $MgSO_4$. The concentrated residue was purified by flash column chromatography on silica gel (chloroform/methanol: 15/1), and then freeze dried from benzene to afford 3,5-bis[3,4-bis(12-methacryloxydodecyloxy) benzyloxy]-N-pyridin-4-yl-benzamide (160 mg, 60.6%) as a white powder. The product was stored with care at 0 °C in the dark. ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 8.60 (d, 2H, Pyridine-*H*), 8.20 (s, 1H, CON*H*), 7.69 (d, 2H, Pyridine-*H*), 7.17 (d, 2H, Ar-*H*), 7.06-6.97 (m, 6H, Ar-*H*), 6.89 (t, 1H, Ar-*H*), 6.15 (s, 4H, OCO(CH_3)=CH_2), 5.63 (m, 4H, OCO(CH_3)=CH_2), 5.01 (s, 4H, Bzl-*H*), 4.19 (m, 8H, ArOCH_2CH_2), 4.07 (t, 8H, CH_2OCO(CH_3)=CH_2), 2.01 (s, 12H, OCO(CH_3)=CH_2), 1.88 (m, 8H, CH_2), 1.75 (m, 8H, CH_2), 1.56 (m, 8H, CH_2), 1.47–1.39 (br, 56H, CH_2). ^{13}C-NMR (500MHz, CD_2Cl_2): δ 167.7, 166.1, 160.7, 151.0, 149.71, 149.68, 145.59, 137.2, 136.7, 129.3, 125.0, 121.0, 114.15, 114.10, 114.01, 106.7, 106.0, 70.9, 69.7, 69.6, 65.1, 30.00, 29.97, 29.92, 29.79, 29.76, 29.74, 29.65, 18.4. ESI-MS: m/z = 1485.5 $[M+H]^+$. Anal. calcd. for $C_{90}H_{134}N_2O_{15}$: C, 72.84; H, 9.10; N, 1.89; O, 16.17. Found: C, 74.1; H, 9.31.

Table I. Phase transition and lattice parameters of TP-DN, Poly-TP-DN, and Poly-DN estimated by DSC and XRD experiments.

Compound	Phase transition	Lattice constant (Å)	Diffraction obsd (Å)	Miller index
TP-DN	G-12 (-8.7) → Col_{hd}39 (-0.4) →Iso	43.6	37.8	(100)
Poly-TP-DN	—	42.5	36.8	(100)
Poly-DN	—	41.4	35.9, 20.7, 13.9	(100), (110) (210)

(a) Transition temperatures (°C) and enthalpies in parentheses (cal/g) were measured by DSC (second heating scan at 5 °C/min). The designation G, Col , and Iso represent glassy, hexagonal disordered columnar, and isotropic phases, respectively.

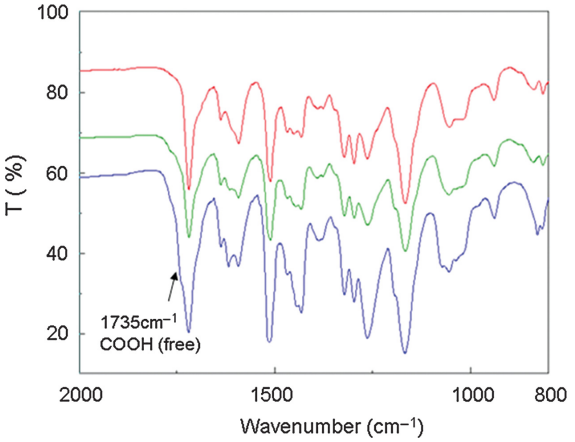

Fig. 2. IR spectra of the 1:3 (red line), 1:1 (green line), and 2:1 (blue line) molar complex of **TP** and **DN**.

2.5. Preparation of TP-DN

Just before mixing, **DN** was purified by column chromatography on silica gel ($CHCl_3$/CH_3 OH: 20/1) to remove the stabilizer, 2,6-di-*tert*-butyl-*p*-cresol, and then **DN** was freeze dried from benzene in vacuum. Powdered **TP** (7.1 mg, 0.01 mmol) and **DN** (44.6 mg, 0.03 mmol) were mixed in a 1:3 molar ratio, and dissolved in benzene/CH_3OH. The organic solvents were evaporated at 30 °C in dark. The residue was again

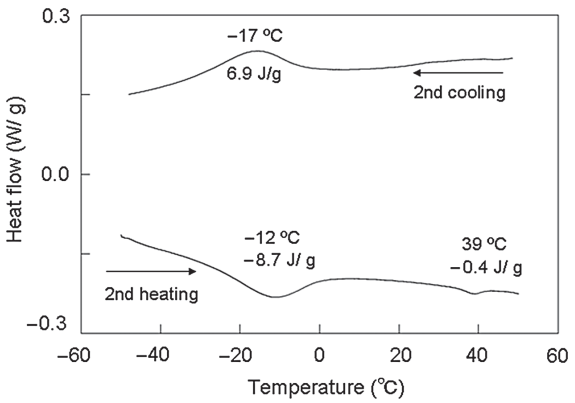

Fig. 3. DSC trace of **TP-DN** at a scan rate of 5 °C/min.

RESEARCH ARTICLE

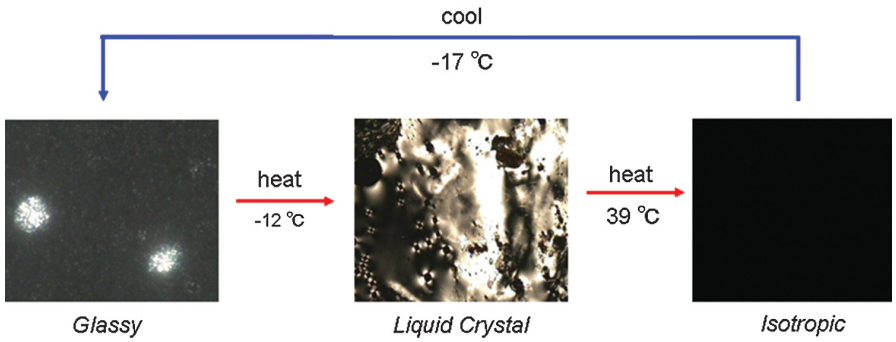

Fig. 4. Thermal phase transition behaviors of **TP-DN** observed by variable temperature polarized optical microscopy.

dissolved in benzene, and freeze dried in vacuum. The viscous solid **TP-DN** was stored at –20 °C in the dark.

2.6. Photo-Polymerization of TP-DN

TP-DN was sandwiched between two glass slides and heated at 50 °C. The hot melt sample was cooled to room temperature, and then cooled to −20 °C for 24 hr in the dark. Then the sample was allowed to warm up at room temperature. The sample was irradiated using an ultraviolet light at 0 °C (365 nm, 5 W) for 180 min. The two adhered glass slides were mechanically separated, and the glass slide attached with the polymeric film was soaked in methanol. The free-standing film **Poly-TP-DN** with a thickness of c.a. 15 μm was obtained. The time course IR spectra of **TP-DN** during UV irradiation were measured to investigate the progress of photopolymerization. The liquid crystalline thin film of **TP-DN** was cast on a NaCl crystal and IR spectra were recorded over time.

2.7. Removal of TP from Poly-TP-DN

Poly-TP-DN was soaked in 4 ml CH_2Cl_2/CH_3OH (1:1 in volume), and **TP** was extracted to the solution. The time course UV-vis spectra were measured to estimate the percentage of **TP** extracted into solution. Thus, the nanoporous polymer **Poly-DN** was obtained.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Assembly

Our synthetic strategy for constructing a nanoporous polymer is summarized in Figure 1. The hydrogen-bonded columnar liquid crystalline precursor **TP-DN** composed of the proton donating triphenylene derivative **TP** [2,6,10-tris(carboxymethoxy)-3,7,11-tris(pentyloxy)triphenylene] and three equivalents of the proton accepting dendritic amphiphile bearing a pyridyl head group and four polymerizable aliphatic chains **DN** [3,5-bis-[3,4-bis-(12-methacryloxydodecyloxy)-benzyloxy]-N-pyridine-4-yl-benzamide] were designed based on our previous work by taking a cooperative hydrogen-bonding system and molecular symmetry into account.[60, 61] The estimated diameter of the pore prepared by the cross-linking photopolymerization followed by the removal of the template **TP** is approximately 1.5 nm. Based on the size of the template **TP**, the resulting nanopore should be large enough to accept heterogeneous guest molecules such as zinc porphyrin **PZn**.

The liquid crystalline properties of **TP-DN** were characterized by infrared spectroscopy (IR), differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffractometry (XRD). The phase transition behavior and lattice parameter of **TP-DN** are summarized in Table I. An IR study on **TP-DN** (Fig. 2) proved the formation of complementary hydrogen bonding between the carboxylic acid of **TP** and the pyridyl group of **DN**. The IR absorption peak of **TP** at 1729 cm^{-1}, assigned to the free C═O stretching, disappeared after being mixed with more than three equivalents of **DN**. The IR absorption peak assigned to the hydrogen-bonded C═O stretching should have shifted to a lower frequency compared to that of the free C═O stretching and, in this case, became completely overlapped with the other strong IR absorption peaks derived from ester and amide bonds. A DSC study

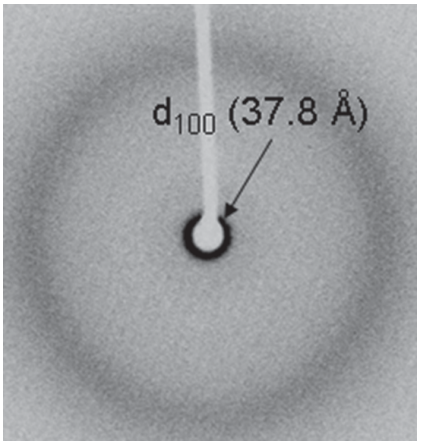

Fig. 5. 2D-XRD pattern of **TP-DN**.

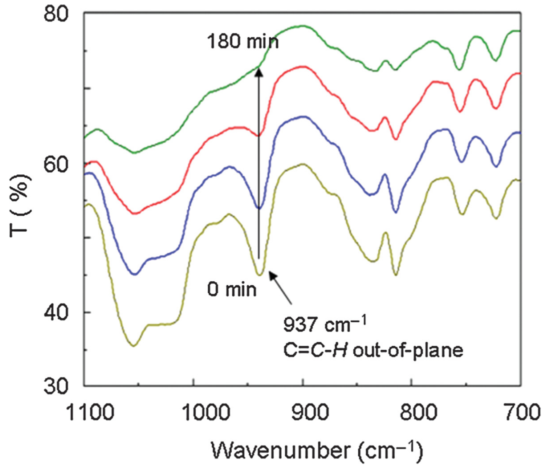

Fig. 6. The time course IR spectra of **TP-DN** during photopolymerization.

on **TP-DN** (Fig. 3) demonstrated its thermotropic liquid crystalline properties between −12 °C and 37 °C on heating. A single phase transition from an isotropic state to a crystalline state was observed at −17 °C on cooling, probably because the methacryloyl group at the tail of alkyl chains obstructs sterically the self-organization process.

POM observation of **TP-DN** (Fig. 4) also supports the DSC result since **TP-DN** exhibited birefringence up to 35 °C on heating, and the polarized texture was isotropic at 0 °C on cooling from a hot melt state. X-ray diffraction measurements on a thin film of **TP-DN** at 20 °C (Fig. 5) are consistent with formation of a hexagonal disordered columnar liquid crystal. The X-ray diffraction pattern of **TP-DN** gave a sharp peak at 37.8 Å and a diffuse halo peak around 4.4 Å. The sharp peak at 37.8 Å is assigned to the diffraction from the d_{100} face of a hexagonal lattice. The other diffraction peaks (e.g., d_{110}) were too weak to be detected in the low angle region due to a minimum in the form factor.[62] The diffuse halo was assigned to aliphatic chain packing in a molten state, and the absence of sharp diffraction peaks in the wide angle region indicates an unequally-spaced intracolumnar packing.

Covalent fixation of the hydrogen-bonded columnar liquid crystalline precursor **TP-DN** was accomplished by photopolymerization. The liquid crystalline thin film **TP-DN** prepared between two slide glasses was mechanically sheared to clarify the birefringence, and the film was irradiated using ultraviolet light (365 nm, 5 W) at 0 °C for 180 min. The time course IR spectra (Fig. 6) of **TP-DN** around the IR band at 937 cm^{-1} (assigned to the C=C stretching vibration of the methacryloyl groups) revealed that about 80% of the methacryloyl groups finally contributed to the cross-linking photopolymerization. After the two slide glasses were mechanically separated, the slide glass holding the polymerized liquid crystalline film was soaked in CH_3OH to peal off the polymerized film from the glass slide. Thus, a free standing film of **Poly-TP-DN** (ca. 15 μm thick) was successfully obtained (Fig. 7(a)). The resulting film was insoluble in most organic solvents

RESEARCH ARTICLE

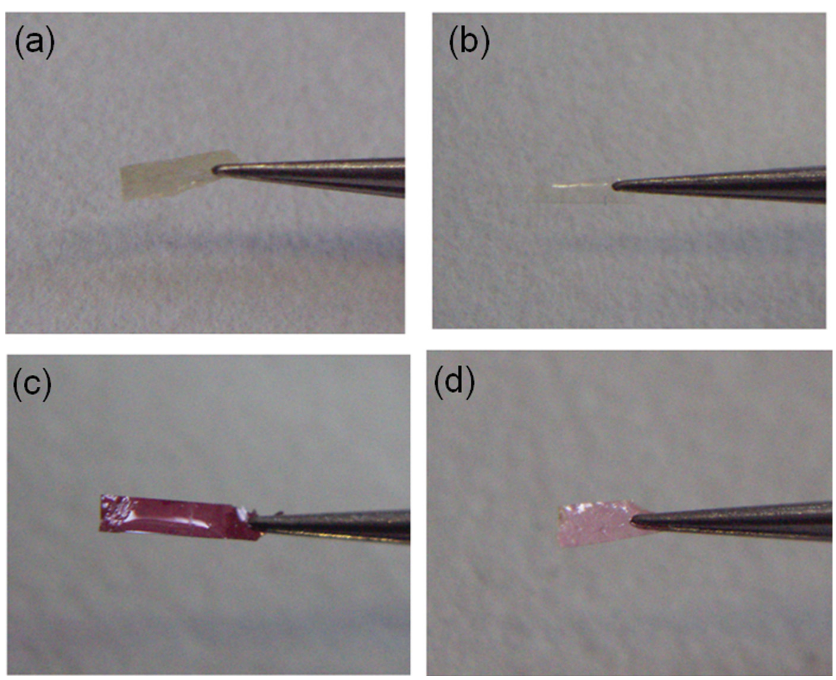

Fig. 7. Images of (a) **Poly-TP-DN**, (b) **Poly-DN**, (c) **Poly-DN** after soaking in **PZn** solution, and (d) **Poly-DN** after soaking in **P2H** solution.

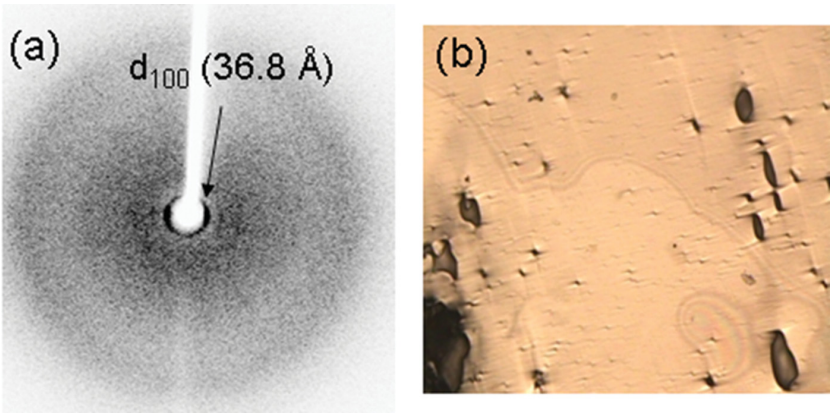

Fig. 8. (a) 2D-XRD pattern and (b) polarized optical microscopic observation both of **Poly-TP-DN**.

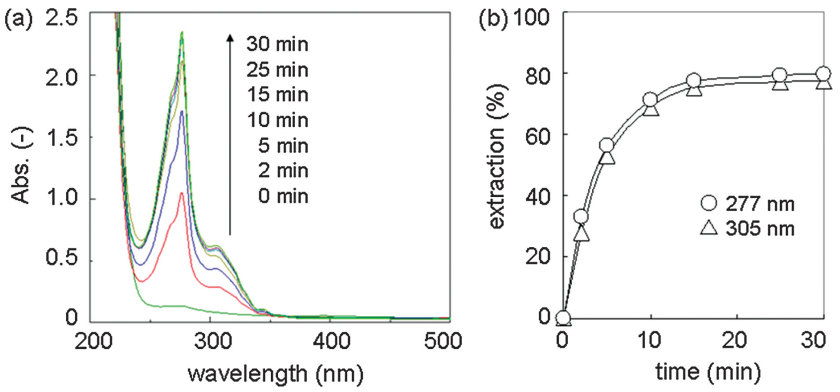

Fig. 9. (a) Time dependency of UV-Vis spectra and (b) percentage of extracted template **TP** from **Poly-TP-DN** into extractant solvent CH_2Cl_2/CH_3OH.

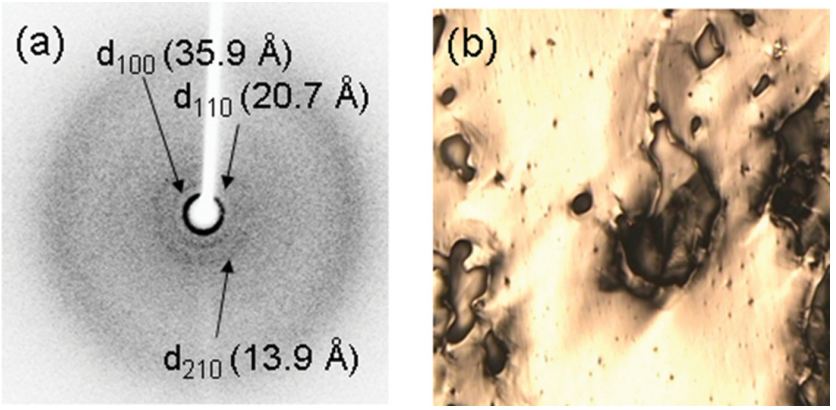

Fig. 10. (a) 2D-XRD pattern and (b) polarized optical microscopic observation of **Poly-DN**.

as usually are cross-linked polymers. The POM texture and XRD pattern of **Poly-TP-DN** were almost identical to those of **TP-DN** prior to photopolymerization (Fig. 8). Moreover, the invariable POM texture and XRD patterns of **Poly-TP-DN** at 100 °C, which is above the melting point of **TP-DN**, proved the robust fixation of the columnar structure by cross-linked photo-polymerization.

Subsequent removal of **TP** from **Poly-TP-DN** was conducted by selective cleavage of hydrogen-bonding with a polar-protic solvent such as CH_3OH. The time course plots (Fig. 9) of the percentage of **TP** extracted into CH_3OH/CH_2Cl_2 solution, which was measured by UV-Vis titration at 277 nm and 303 nm, indicate that about 82% of **TP** was finally removed from **Poly-TP-DN**. In addition, the colorless transparent appearance of the resulting film **Poly-DN** compared with the light brown film **Poly-TP-DN** also strongly suggest that most of the **TP** was removed. (Fig. 7(b)). X-ray diffraction patterns of **Poly-DN** (Fig. 10(a)) revealed three distinct peaks at 35.9 Å, 20.7 Å, and 13.9 Å, with the ratios of d-spacing values at 1: $3^{-1/2}$: $7^{-1/2}$. Thus, the peaks could be assigned to the d_{100}, d_{110}, and d_{210} faces of a hexagonal columnar lattice, respectively. In addition, the column diameter of **Poly-DN** is identical to that of **Poly-TP-DN**. Therefore, we can state that the removal of the template **TP** was successful and did not cause decomposition of the hexagonal structured framework. Only minor changes were detected in POM images (Fig. 10(b)).

3.2. Guest Binding

The construction of nanopores that reflect the conformation of the template **TP** was confirmed by competitive absorption experiments between the original template **TP** and pyrene butyric acid **Py**. **Py** is an ideal competitive guest molecule against **TP** since it possesses a carboxylic acid moiety, is of smaller size than **TP**, and has a characteristic UV-Vis spectrum. When a piece of **Poly-DN** (0.91 μmol based on pyridine units) was soaked in a concentrated CH_2Cl_2 solution of **TP** (3.7 μmol), **Py** (17.0 μmol), and **DN** (28.1 μmol), UV-vis measurement revealed that **TP** was selectively adsorbed by **Poly-DN** (Fig. 11(a)). Subsequent extraction of the contents absorbed in the pores with CH_3OH/CH_2Cl_2 and analysis of the extract by using UV-Vis spectrometry (Fig. 11(b)) revealed that the extract was identical with simple **TP**, and the binding affinity of **TP** to **Poly-DN** was at least ten times higher than that of **Py**. In addition, **Poly-DN** quantitatively absorbed the original template **TP**. These results indicate that **Poly-DN** memorizes the conformation of the **TP** template molecule leading us to the assumption that the diameter of the pores are approximately 1.5 nm and that the pyridyl groups within the pore are arranged in a quite symmetric manner reflecting the conformation of **TP**.

Finally, we investigated the coordinative ability of **Poly-DN** to zinc porphyrin. The molecular diameter of the porphyrin ring is approximately 1 nm, and so it is small enough to be accommodated in the nanoporous polymer formed after the removal of the 1.5 nm template **TP**. **Poly-DN** films were soaked in a 20 μM solution of zinc porphyrin **PZn** or free-base porphyrin **P2H** for 3 hr, and the color variations of the films derived from absorption of the porphyrin were observed. **Poly-DN** film soaked in **PZn** solution became deep purple whereas **Poly-DN** soaked in **P2H** solution stained light pink, indicating that coordination of zinc with pyridine is a crucial factor for the strong absorption of the porphyrin molecules (Figs. 7(c and d)). The solid state UV-Vis spectra of **PZn** in **Poly-DN** contained a Q-band at 537 nm and Soret band at 408 nm, (Fig. 12(a)). The Q-band at 537 nm is identical with that of **PZn** in pyridine/CH_2Cl_2 (1:10), proving that all **PZn** molecules absorbed in **Poly-DN** were coordinated by the pyridyl groups. The Soret-band at 408 nm was still red-shifted by 3 nm compared with that of **PZn** at 405 nm in pyridine/CH_2Cl_2 (1:10), suggesting that **PZn** in **Poly-DN**

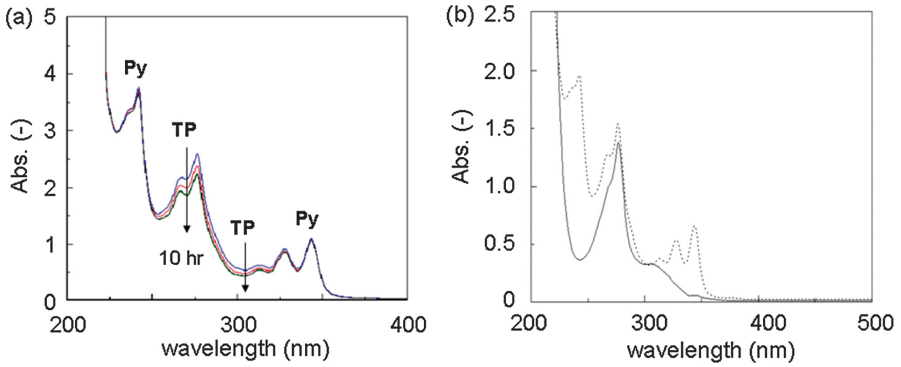

Fig. 11. (a) Time dependency of UV-Vis spectra of a CH_2Cl_2solution containing **TP** (0.06 μmol), **Py** (0.27 μmol), and **DN** (0.45 μmol) after the addition of **Poly-DN** (0.7 μmol based on pyridine unit); (b) UV-Vis spectra of the contents extracted from **Poly-DN** which was soaked in a concentrated CH_2Cl_2 solution of **TP** (3.7 μmol), **Py** (17.0 μmol), and **DN** (28.1 mmol) for 1 h (solid line). The dotted line is UV-Vis spectrum of a diluted portion of the original immersion solution.

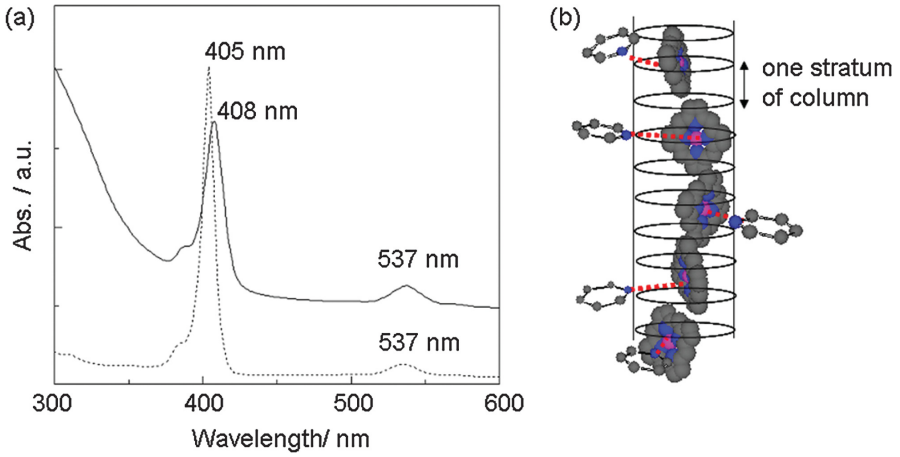

Fig. 12. (a) UV-Vis spectrum of **PZn** in **Poly-DN** (solid line) and **PZn** in CH_2Cl_2-pyridine (dashed line); (b) Estimated structure of **PZn** coordinated in the nanoporous polymer **Poly-DN**. One **PZn** molecule in the pore occupies two stratum of column.

is arranged to form a *J*-aggregated superstructure according to Kasha's principle.[63–66] **PZn** coordinated in **Poly-DN** was extracted to a pyridine/CH_2Cl_2 solution, and quantified from the UV-Vis absorption peak at 405 nm. The estimated content of **PZn** was 16% relative to the pyridyl groups in **Poly-DN**, indicating that one **PZn** molecule in the pore occupies two strata of the column. These results suggest that the pore should be actually almost filled with **PZn** in the formation of what we might call a porphyrin array constructed in the pore as illustrated in Figure 12(b).

4. CONCLUSION

In conclusion, nanoporous polymers in which the pore wall is functionalized by pyridyl groups were successively constructed by template polymerization of a hydrogen-bonded columnar liquid crystalline precursor. The nanoporous polymer reflects the conformation of template molecule, and demonstrated strong coordination properties useful for fillingl the pore with zinc porphyrins. The coordinative nanoporous polymer described here is promising as a nanoscale scaffold for the organization of metal complexes or simple structured dyes into functional supramolecular architectures.

Acknowledgment: This work was partially supported by GCOE program "Practical Chemical Wisdom" from MEXT, Japan, World Premier International Research Center Initiative (WPI Initiative), MEXT, Japan, the Core Research for Evolutional Science and Technology (CREST) program of Japan Science and Technology Agency (JST), Japan. S. Ishihara thanks the JSPS for a research fellowship as a young scientist. Y. Furuki is grateful for a scholarship from FUJIFILM, Inc.

References and Notes

1. S. Mandal, M. V. Lee, J. P. Hill, A. Vinu, and K. Ariga, *J. Nanosci. Nanotechnol.* 10, 21 **(2010)**.
2. K. Ariga, M. Li, G. J. Richards, and J. P. Hill, *J. Nanosci. Nanotechnol.* 11, 1 **(2011)**.
3. Y. Lang, R. R. Arnepalli, and A. Tiwari, *J. Nanosci. Nanotechnol.* 11, 3719 **(2011)**.
4. Y. Ando, *J. Nanosci. Nanotechnol.* 10, 3726 **(2010)**.
5. E. Abdullayev and Y. Lvov, *J. Nanosci. Nanotechnol.* 11, 10007 **(2011)**.
6. D. P. Mohapatra, F. Gassara, and S. K. Brar, *J. Nanosci. Nanotechnol.* 11, 899 **(2011)**.
7. R. A. Rippel and A. M. Seifalian, *J. Nanosci. Nanotechnol.* 11, 3740 **(2011)**.
8. T. Panda and K. Deepa, *J. Nanosci. Nanotechnol.* 11, 10279 **(2011)**.
9. V. Chegel, O. Rachkov, A. Lopatynskyi, S. Ishihara, I. Yanchuk, Y. Nemoto, J. P. Hill, and K. Ariga, *J. Phys. Chem. C* 116, 2683 **(2012)**.
10. V. Chegel, A. Lopatynskyi, S. Ishihara, J. P. Hill, and K. Ariga, *Aust. J. Chem.* in press. DOI: 10.1071/CH12119.
11. K. Ariga, Q. Ji, and J. P. Hill, *Adv. Polym. Sci.* 229, 51 **(2010)**.
12. Q. Ji, I. Honma, S.-M. Paek, M. Akada, J. P. Hill, A. Vinu, and K. Ariga, *Angew. Chem. Int. Ed.* 49, 9737 **(2010)**.
13. M. Li, S. Ishihara, M. Akada, M. Liao, L. Sang, J. P. Hill, V. Krishnan, Y. Ma, and K. Ariga, *J. Am. Chem. Soc.* 133, 7348 **(2011)**.
14. K. Ariga, Q. Ji, J. P. Hill, Y. Bando, and M. Aono, *NPG Asia Mater.* 4, e17 **(2012)**.
15. K. Ariga, A. Vinu, Y. Yamauchi, Q. Ji, and J. P. Hill, *Bull. Chem. Soc. Jpn.* 85, 1 **(2012)**.
16. M. Hu, J. Reboul, S. Furukawa, N. L. Torad, Q. Ji, P. Srinivasu, K. Ariga, S. Kitagawa, and Y. Yamauchi, *J. Am. Chem. Soc.* 134, 2864 **(2012)**.
17. M. Ramanathan, M. Kilbey II, Q. Ji, J. P. Hill, and K. Ariga, *J. Mater. Chem.* 22, 10389 **(2012)**.
18. K. Ariga, H. Ito, J. P. Hill, and H. Tsukube, *Chem. Soc. Rev.* in press. DOI:10.1039/C2CS35162E.
19. T. Mori, K. Okamoto, H. Endo, J. P. Hill, S. Shinoda, M. Matsukura, H. Tsukube, Y. Suzuki, Y. Kanekiyo, and K. Ariga, *J. Am. Chem. Soc.* 132, 12868 **(2010)**.
20. K. Ariga, T. Mori, and J. P. Hill, *Chem. Sci.* 2, 195 **(2011)**.
21. K. Ariga, S. Ishihara, H. Izawa, H. Xia, and J. P. Hill, *Phys. Chem. Chem. Phys.* 13, 4802 **(2011)**.

RESEARCH ARTICLE

22. S. Ishihara, J. P. Hill, A. Shundo, G. J. Richards, J. Labuta, K. Ohkubo, S. Fukuzumi, A. Sato, M. R. J. Elsegood, S. J. Teat, and K. Ariga, *J. Am. Chem. Soc.* 133, 16119 **(2011)**.
23. K. Ariga, T. Mori, and J. P. Hill, *Soft Matter* 8, 15 **(2012)**.
24. K. Ariga, T. Mori, and J. P. Hill, *Adv. Mater.* 24, 158 **(2012)**.
25. K. Ariga, A. Vinu, Q. Ji, O. Ohmori, J. P. Hill, S. Acharya, J. Koike, and S. Shiratori, *Angew. Chem. Int. Ed.* 47, 7254 **(2008)**.
26. Q. Ji, S. B. Yoon, J. P. Hill, A. Vinu, J.-S. Yu, and K. Ariga, *J. Am. Chem. Soc.* 131, 4220 **(2009)**.
27. S. Ishihara, J. Labuta, T. Šikorský, J. V. Burda, N. Okamoto, H. Abe, K. Ariga, and J. P. Hill, *Chem. Commun.* 3933 **(2012)**.
28. K. Ariga, S. Ishihara, H. Abe, M. Li, and J. P. Hill, *J. Mater. Chem.* 22, 2369 **(2012)**.
29. K. Ariga, M. McShane, Y. M. Lvov, Q. Ji, and J. P. Hill, *Expert Opin. Drug Deliv.* 8, 633 **(2011)**.
30. K. Ariga, Y. M. Lvov, K. Kawakami, Q. Ji, and J. P. Hill, *Adv. Drug Deliv. Rev.* 63, 762 **(2011)**.
31. K. Ariga, Q. Ji, M. J. McShane, Y. M. Lvov, A. Vinu, and J. P. Hill, *Chem. Mater*. 24, 728 **(2012)**.
32. T. Yanagisawa, T. Shimizu, K. Kuroda, and C. Kato, *Bull. Chem. Soc. Jpn.* 63, 988 **(1990)**.
33. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature* 359, 710 **(1992)**.
34. Y. Wan and D. Y. Zhao, *Chem. Rev.* 107, 2821 **(2007)**.
35. O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, and J. Kim, *Nature* 423, 705 **(2003)**.
36. S. Kitagawa, R. Kitaura, and S. Noro, *Angew. Chem. Int. Ed.*, 43, 2334 **(2004)**.
37. L. Zhang, K. Yu, and A. Eisenberg, *Science* 272, 1777 **(1996)**.
38. M. Muthukumar, C. K. Ober, and E. L. Thomas, *Science* 277, 1225 **(1997)**.
39. Y. Tian, K. Watanabe, X. Kong, J. Abe, and T. Iyoda, *Macromolecules* 35, 3739 **(2002)**.
40. J. A. A. W. Elemans, A. E. Rowan, and R. J. M. Nolte, *J. Mater. Chem.* 13, 2661 **(2003)**.
41. D. T. Bong, T. D. Clark, J. R. Granja, and M. R. Ghadiri, *Angew. Chem. Int. Ed.* 40, 988 **(2001)**.
42. V. Percec, A. E. Dulcey, V. S. K. Balagurusamy, Y. Miura, J. Smidrkal, M. Peterca, S. Nummelln, U. Edlund, S. D. Hudson, P. A. Heiney, H. Duan, S. N. Magonov, and S. A. Vinogradov, *Nature* 430, 764 **(2004)**.
43. V. Percec, A. E. Dulcey, M. Peterca, M. Ilies, S. Nummelin, and M. J. Sienkowska, *Proc. Nat. Acad. Sci.* 103, 2518 **(2006)**.
44. S. C. Zimmerman, M. S. Wendland, N. A. Rakow, L. Zharov, and K. S. Suslick, *Nature* 481, 399 **(2002)**.
45. O. Ikkala and G. ten Brinke, *Science* 295, 2407 **(2002)**.
46. R. C. Smith, W. M. Fischer, and D. L. Gin, *J. Am. Chem. Soc.* 119, 4092 **(1997)**.
47. D. L. Gin, W. Gu, B. A. Pindzola, and W.-J. Zhou, *Acc. Chem. Res.* 34, 973 **(2001)**.
48. H.-K. Lee, H. Lee, Y. H. Ko, Y. J. Chang, N.-K. Oh, W.-C. Zin, and K. Kim, *Angew. Chem. Int. Ed.* 40, 2669 **(2001)**.
49. M. Zhou, T. J. Kidd, R. D. Noble, and D. L. Gin, *Adv. Mater.* 17, 1850 **(2005)**.
50. V. Percec, G. Johansson, J. Heck, G. Ungar, and S. V. Batty, *J. Chem. Soc. Perkin Trans.* 1, 1411 **(1993)**.
51. U. Beginn, G. Zipp, A. Mourran, P. Walther, and M. Möller, *Adv. Mater.* 12, 510 **(2000)**.
52. M. Yoshio, T. Kagata, K. Hoshino, T. Mukai, H. Ohno, and T. Kato, *J. Am. Chem. Soc.* 128, 5570 **(2006)**.
53. Y. Ishida, S. Amano, and K. Saigo, *Chem. Commun.* 2338 **(2003)**.
54. Y. Xu, W. Gu, and D. L. Gin, *J. Am. Chem. Soc.* 126, 1616 **(2004)**.
55. M. Ogawa and K. Kuroda, *Chem. Rev.* 95, 399 **(1995)**.
56. P. J. Langley and J. Hulliger, *Chem. Soc. Rev.* 28, 279 **(1999)**.
57. G. Schulz-Ekloff, D. Wöhrle, B. van Duffel, and R. A. Schoonheydt, *Micropor. Mesopor. Mater.* 51, 91 **(2002)**.
58. S. Takamizawa, E. Nakata, and T. Akatsuka, *Angew. Chem. Int. Ed.* 45, 2216 **(2006)**.
59. M. Nakamura, T. Ikeue, H. Fujii, and T. Yoshimura, *J. Am. Chem. Soc.* 119, 6284 **(1997)**.
60. S. Ishihara, Y. Furuki, and S. Takeoka, *Chem. Lett.* 36, 282 **(2007)**.
61. S. Ishihara, Y. Furiki, and S. Takeoka, *Polym. Adv. Technol.* 19, 1097 **(2008)**.
62. C. Cafargna, A. Roviello, and A. Sirigu, *Mol. Cryst. Liq. Cryst.* 122, 151 **(1985)**.
63. E. G. McRae and M. Kasha, *J. Chem. Phys.* 28, 721 **(1958)**.
64. M. Kasha, *Radiation Res.* 20, 51 **(1963)**.
65. T. Komatsu, M. Moritake, A. Nakagawa, and E. Tsuchida, *Chem. Eur. J.* 8, 5469 **(2002)**.
66. T. Komatsu, M. Moritake, and E. Tsuchida, *Chem. Eur. J.* 9, 4626 **(2003)**.

Received: 29 May 2012. Accepted: 19 June 2012.

RESEARCH ARTICLE