Supplementary information

Molecular imprinting into organogel nanofibers

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Materials

6-Bromohexan-1-ol, 4,4'-biphenyldiol, 4'-hydroxy-4-biphenyl-carboxylic acid, acryloyl chloride, *(E,E)*-8,10-dodecadienol, 2,6-di-*tert*-butylphenol, *N*,*N*-diethylaniline, *N*,*N*-dicyclohexylcarbodiimide (DCC), *N*,*N*-(dimethylamino)pyridine (DMAP), divinylbenzene (DVB) and azobisisobutyronitrile (AIBN) were purchased from Aldrich. Theophylline was purchased from Fluka. Pyridinium dichromate (PDC) and caffeine were purchased from Tokyo Chemical Industry. 2,2'-Azobis(2,4-dimethyl-4-methoxyvaleronitrile) (ADMV) was purchased from Wako Pure Chemical Ind., Japan. AIBN and ADMV were recrystallized before use. Reagent-grade solvents like triethylamine (Junsei), *N*,*N*-dimethylmethanamide (Junsei), methylene chloride (J. T. Baker), and methanol (Carlo Erba) were used without further purification. Tetrahydrofuran (J. T. Baker) was dried over sodium metal and distilled.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX-300 and Avance 500 spectrometer, respectively. FT-IR spectra were obtained with a Perkin–Elmer Spectrum GX I instrument using KBr pellets. Elemental analysis was performed using a CE EA 1110 analyzer. The differential scanning calorimetry (DSC) measurements were performed with a TA modulated DSC Q10 at a scanning rate of 10 ^{o}C min^{-1}. UV-vis spectra were obtained with the use of a SCINCO S-3150 instrument. SEM images were obtained by using a JEOL JSM-6330F microscope.

Synthesis

6-Bromohexyl acrylate (1). This compound was prepared according to our previous report.[1]

4-Hydroxy-4′-[6-(acryloyloxy)hexyloxy]biphenyl (2). This compound was prepared according to our previous report.[1]

***(E,E)*-8,10-Dodecadienoic acid (3).** Pyridinium dichromate (PDC, 10.30 g, 27.4 mmol) was added to a solution of *(E,E)*-8,10-dodecadienol (1.00 g, 5.5 mmol) in DMF (70 mL). The resulting mixture was stirred at room temperature until most of the starting compound was consumed. Water (50 mL) was added and the resulting mixture was extracted with ethyl acetate (70 mL x 3). The organic solution was dried

with anhydrous $MgSO_4$ and concentrated. The product was isolated by column chromatography on silica gel using ethyl acetate and *n*-hexane (1/8) as eluents to give white solids. Yield (0.74 g, 69.2 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (2H, m, =C*H*), 5.61 (2H, m, =C*H*), 2.37 (2H, t, *J* = 7.2 Hz, -OCOCH_2-), 2.06 (2H, m, =CCH_2-), 1.74 (3H, d, *J* = 6.6 Hz, =CCH_3), 1.65 (2H, m, –OCOCCH_2-), 1.40–1.26 (6H, m, –CH_2–); ^{13}C NMR (500 MHz, $CDCl_3$) δ 180.0 (*C*OOH), 132.1, 131.9, 130.6, 126.9 (-*C*=C x 4), 34.2(OCO*C*H_2), 32.6(*C*H_2CH), 29.4, 29.2, 28.9, 24.8 (*C*H_2), 18.2 (*C*H_3). Elemental analysis (Found: C, 73.42; H, 10.19. Calc. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%).

4-*(E,E)*-8,10-(Dodeca-8,10-dienoyloxy)-4′-[6-(acryloyloxy)hexyloxy]biphenyl (4). DCC (0.76 g, 3.68 mmol) and DMAP (0.08 g, 0.74 mmol) were added to a solution of compounds **2** (1.04 g, 3.06 mmol) and **3** (0.60 g, 3.06 mmol) in methylene chloride (50 mL), and the mixture was stirred for 6 h at room temperature. Insoluble solids were removed by filtration through a silica gel column. After evaporation of the solvent, the product was isolated by column chromatography on silica gel using tetrahydrofuran and *n*-hexane (1/4) as eluents to give white solids. Yield (1.07 g, 67.3 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (4H, dd, overlap, Ar), 7.13 (2H, d, *J* = 8.7 Hz, COOAr), 6.97 (2H, d, *J* = 8.7 Hz, -OAr), 6.44 (1H, d, *J* = 17.1 Hz, =C*H*), 6.17 (1H, m, =C*H*), 6.04 (2H, m, =C*H*), 5.84 (1H, d, *J* = 1.5 Hz, =C*H*), 5.57 (2H, m, =C*H*), 4.20 (2H, t, *J* = 6.3 Hz, –OCH_2), 4.02 (2H, t, *J* = 6.3 Hz, -ArOCH_2-), 2.59 (2H, t, *J* = 7.2 Hz, -OCOCH_2-), 2.08 (2H, m, =CCH_2-), 1.85–1.72 (3H, overlap, =CCH_3, 2H, -ArOCCH_2-, 2H, -COOCCH_2-, 2H, –OCOCCH_2-), 1.57–1.39 (10H, m, -CH_2-); ^{13}C NMR (500 MHz, $CDCl_3$) δ 172.6 (*C*OOAr), 166.5 (CH*C*OO), 158.9, 149.9 (OAr x 2), 138.8, 133.1 (Ar-Ar x 2), 132.1, 131.9, 130.7, 128.8, 128.3, 127.9, 127.0 (-*C*=C x 6, Ar x 2), 122.0, 115.0 (OAr x 2), 68.1 (*C*H_2OAr), 64.7 (COO*C*H_2), 34.6 (OCO*C*H_2), 32.7(*C*H_2CH), 29.4, 29.2, 29.0, 28.8, 26.0, 25.1 (*C*H_2), 18.2 (*C*H_3). Elemental analysis (Found: C, 76.47; H, 8.16. Calc. for $C_{33}H_{42}O_5$: C, 76.42; H, 8.16%).

Ethyl 4-(4-hydroxyphenyl)benzoate (5). This compound was prepared according to our previous report.[2]

Ethyl 4-[4-(6-hydroxyhexyloxy)phenyl]benzoate (6). This compound was prepared according to our previous report.[2]

4-[4-(6-acryloyloxyhexyloxy)phenyl]benzoic acid (7). This compound was prepared according to our previous report.[2]

Preparation of theophylline imprinted polymerized organogel nanofibers

The template, theophylline (4.5 mg, 0.025 mmol) and functional monomer **7** (36.8 mg, 0.10 mmol) were dissolved in methanol (2.2 g) in a 20 mL vial. To a solution, organogelator **4** (259.3 mg) and divinylbenzene (129.7 mg) were added and the mixture was sonicated at 65 ^{o}C for 10 min. Immediately after dissolving the two thermal initiators, ADMV (13.0 mg) and AIBN (13.0 mg), the solution was cooled down to room temperature to form a stable organogel. The organogel was polymerized at at 35 ^{o}C for 16 h and then at 50 ^{o}C for 32 h. Theophylline trapped in polymerized organogel nanofibers was

removed by washing with a mixture of methanol/acetic acid (9:1, v/v) for 24 h and Soxhlet extraction with methanol for 48 h. The non-imprinted polymerized organogel nanofibers were prepared in the same manner except that theophylline was not added.

1 S. H. Kang, B. M. Jung and J. Y. Chang, *Adv. Mater.*, 2007, **19**, 2780-2784.

2 S. H. Kang, K. S. Jang, P. Theato, R. Zentel and J. Y. Chang, *Macromolecules*, 2007, **40**, 8349-8354.