Supplementary material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information

Synthetic procedures for **T-1** and **B-1**.

Spectroscopic analysis

Purification of final products was carried out using column chromatography over silica gel (63-210μm) (KANTO CHEMICAL Co., INC.) using dichloromethane or a dichloromethane-ethyl acetate mixture as the eluent, followed by the recrystallization from ethanol. The purities of final compounds were checked by thin layer chromatography (TLC, aluminum sheets, silica gel 60 F254 from Merck). Dichloromethane was used as the solvent. Detection of products was achieved by UV irradiation (λ = 254 and 365 nm). The purities of the final compounds were also checked by normal phase HPLC (Intersil SIL 150A-5 column). A dichloromethane-isopropylalcohol (1000 : 2) mixture was used as eluent. Detection of products was achieved by UV irradiation (λ= 254 nm).

The structures of the final products were elucidated by infrared (IR) spectroscopy (BIO RAD FTS-30) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (JEOL JNM-GX270).

Preparation of materials

(*R*)-2-octanol was obtained from Tokyo Kasei Kogyo Co., Ltd. 5-Octyl-2-(4-hydroxyphenyl)pyrimidine was obtained from Midori Kagaku Co., Ltd.

(*R*)-1-Methylhepthyl-4'-{4-octyloxy-2-{11-[4-(5-octylpyrimidin-2-yl)phenoxy]undecanoyloxy}benzoyloxy}biphenyl-4-carboxylate, T-1

(*R*)-1-Methylhepthyl 4-methoxycarbonyloxybiphenyl-4'-carboxylate

To a solution of 4-methoxycarbonyloxybiphenyl-4'-carboxylic acid (2.2 g, 8.0 mmol), (*R*)-2-octanol (1.04 g, 8.0 mmol) and diethylazodicarboxylate (3.5 g, 8.0 mmol) in tetrahydrofuran (THF, 120 ml) was added triphenylphosphine (2.4 g, 9.0 mmol) in THF (40 ml). The reaction mixture was stirred at room temperature for 24 h. After the filtration of participate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with dichloromethane. The desired product was obtained. Yield: 1.94 g (68%).

^{1}H NMR (270MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.10(d, 2H, Ar-**H,** J=8.4Hz), 7.62(d, 4H, Ar-**H**, J=8.4Hz), 7.28(m, 2H, Ar-**H**), 5.17(m, 1H, -C***H**(CH_3)), 3.93(s, 3H, -OC**H**$_3$), 1.79-1.28(m, 13H, aliphatic-**H**), 0.88(t, 3H, -C**H**$_3$, J=6.8Hz)

(*R*)-1-Methylhepthyl 4-hydroxybiphenyl-4'-carboxylate

To a solution of (*R*)-1-methylhepthyl 4-methoxycarbonyloxybiphenyl-4'-carboxylate (1.94 g, 5.0 mmol) in ethanol (75 ml) was added an aqueous ammonia solution (28~30%, 12.5 ml). The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by evaporation. To the residue was added water and the solution was extracted with diethylether (100 ml). The combined organic layers were dried over anhydrous sodium sulfate. After the drying agent and the solvent were removed, the desired product was obtained without further purification. Yield: 1.50 g (91%)

^{1}H NMR (270MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.06(d, 2H, Ar-**H,** J=8.4Hz), 7.60(d, 2H, Ar-**H**, J=8.4Hz), 7.51(d, 2H, Ar-**H**, J=8.6HHz), 6.95(d, 2H, Ar-**H**, J=8.6Hz), 5.17(m, 1H, -C***H**(CH_3)), 3.93(s, 3H, -OC**H**$_3$), 1.78-1.29(m, 11H, aliphatic-**H**), 0.88(t, 3H, -C**H**$_3$, J=6.8Hz)

11-[4-(5-Octylpyrimidin-2-yl)phenoxy]undecanoic acid

To a solution of 5-octyl-2-(4-hydroxyphenyl)pyrimidine (1.7 g, 6.0 mmol) and 1, 11-bromoundecanoic acid ethyl ester (1.9 g, 6.5 mmol) in acetone (12 ml) was added potassium carbonate (0.9 g, 6.5 mmol). The reaction mixture was stirred under reflux for 20 h. After the filtration of participate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with a toluene-ethylacetate (10:1) mixture as the eluent. The intermediate product, 11-[4-(5-octylpyrimidin-2-yl)phenoxy]undecanoic acid ethyl ester, was obtained. Yield: 0.89 g (30%).

11-[4-(5-Octylpyrimidin-2-yl)phenoxy]undecanoic acid ethyl ester (0.89 g, 1.8 mmol) was added to a solution of NaOH (0.16 g, 4.0 mmol) in an ethanol-water (17:7) mixture. The resulting solution was stirred under reflux for 4 h. The solution was acidified with aq. HCl. The solution was extracted with dichloromethane (3 x 50 ml). The organic layers were combined, dried over magnesium sulfate, filtered and evaporated. Yield: 0.81 g (97%).

^{1}H NMR (270MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.59(s, 2H, Ar-**H**), 8.34(d, 2H, Ar-**H**, J=8.9Hz), 6.98(d, 2H, Ar-**H**, J=8.9Hz), 4.03(t, 2H, -OC**H**$_2$-, J=6.6Hz), 2.60(t, 2H, Ar-C**H**$_2$-, J=7.6Hz), 2.34(t, 2H, -OCOC**H**$_2$-, J=7.4Hz), 1.86-1.22(m, 33H, aliphatic-**H**), 0.88(t, 3H, -C**H**$_3$, J=6.8Hz)

(*R*)-1-Methylhepthyl-4'-(2-hydroxy-4-octyloxybenzoyloxy)biphenyl-4-carboxylate

To a solution of 2, 4-dihydroxybenzoic acid (7.7 g, 50 mmol) and 1-bromooctane (10.4 g, 53 mmol) in ethanol (70 ml) was added a solution of KOH (10.3 g, 1.85 mol) in water (40 ml). The mixture was stirred under reflux for 10 h. After the solvent was removed, the residue was acidified with aq. HCl. The solution was extracted with diethylether (3 x 50 ml). The organic layers were combined, dried over magnesium sulfate, filtered and evaporated. The intermediate product, 2-hydroxy-4-octyloxybenzoic acid, was obtained. Yield: 1.23 g (9%).

To a solution of 2-hydroxy-4-octyloxybenzoic acid (0.65 g, 2.0 mmol) in dicchloromethane (20 ml), (*R*)-1-Methylhepthyl 4-hydroxybiphenyl-4'-carboxylate (0.56 g, 2.1 mmol), dicyclohexylcarbodiimide (0.43 g, 2.1 mmol), and 4-(*N*, *N*-dimethylamino)pyridine (0.024 g, 0.2 mmol) were added. The resulting solution was stirred at room temperature for 18 h. Precipitated materials were removed by filtration. After removal of the solvent by evaporation, the residue was purified by column chromatography on silica gel with toluene as the eluent. The desired product was obtained. Yield: 0.68 g (59 %).

^{1}H NMR (270MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 10.63(s, 1H, Ar-O**H**), 8.11(d, 2H, Ar-**H,** J=8.4Hz), 7.98(d, 1H, Ar-**H**, J=8.6Hz), 7.70-7.60 (m, 4H, Ar-**H**), 7.30(d, 2H, Ar-**H**, J=8.6HHz), 6.55-6.49(m, 2H, Ar-**H**), 5.24-5.12(m, 1H, -C***H**(CH_3)), 4.02(t, 2H, -OC**H**$_2$, J=6.5 Hz), 1.87-1.26(m, 27H, aliphatic-**H**), 0.90(t, 3H, -C**H**$_3$, J=6.5Hz), 0.88(t, 3H, -C**H**$_3$, J=6.8Hz).

(*R*)-1-Methylhepthyl-4'-{4-octyloxy-2-{11-[4-(5-octylpyrimidin-2-yl)phenoxy]undecanoyloxy}benzoyloxy}biphenyl-4-carboxylate, T-1

To a solution of 11-[4-(5-octylpyrimidin-2-yl)phenoxy]undecanoic acid (0.52 g, 1.1 mmol) in dichloromethane (20 ml), (*R*)-1-Methylhepthyl-4'-(2-hydroxy-4-octyloxybenzoyloxy)biphenyl-4-carboxylate (0.57 g, 1.0 mmol), dicyclohexylcarbodiimide (0.23 g, 1.1 mmol), and 4-(*N*,

N-dimethylamino)pyridine (0.013 g, 0.11 mmol) were added. The resulting solution was stirred at room temperature for 18 h. Precipitated materials were removed by filtration. After removal of the solvent by evaporation, the residue was purified by column chromatography on silica gel with a toluene-ethylacetate (30:1) mixture as the eluent. Recrystallization from an ethanol-ethylacetate mixture gave the desired product. Yield: 0.40 g (40 %).

^{1}H NMR (270MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.60(s, 2H, Ar-**H**), 8.38(d, 2H, Ar-**H,** J=8.9Hz), 8.17(d, 1H, Ar-**H,** J=8.9Hz), 8.10(d, 2H, Ar-**H,** J=8.6Hz), 7.64(d, 2H, Ar-**H**, J=8.6Hz), 7.63(d, 2H, Ar-**H**, J=8.6Hz),7.25(d, 2H, Ar-**H**, J=8.6Hz), 6.98(d, 2H, Ar-**H**, J=8.9Hz), 6.88(d, 1H, Ar-**H**, J=2.4Hz), 6.85(d, 1H, Ar-**H**, J=2.4Hz), 6.65(d, 1H, Ar-**H**, J=2.2Hz), 5.23-5.12(m, 1H, -C*H(CH_3)), 4.06-3.98(m, 4H, -OC**H**$_2$), 2.63-2.56(m, 2H, Ar-C**H**$_2$-, 2H, -OCOC**H**$_2$-), 1.86-1.29(m, 55H, aliphatic-**H**), 0.88(m, 9H, -C**H**$_3$); IR (KBr) ν_{max}/cm^{-1}: 2927, 2854, 1614, 1436, 1251, 1110; Purity: 99.9 %.

(*R*)-1-Methylhepthyl-4'-{11-[4-(5-octylpyrimidin-2-yl)phenoxy]undecanoyloxy}biphenyl-4-carboxylate, **B-1**

To a solution of 11-[4-(5-octylpyrimidin-2-yl)phenoxy]undecanoic acid (0.23g, 0.5 mmol) in dichloromethane (6ml), (*R*)-1-Methylhepthyl 4-hydroxybiphenyl-4'-carboxylate (0.20 g, 0.6 mmol), dicyclohexylcarbodiimide (0.12 g, 0.6 mmol), and 4-(*N*, *N*-dimethylamino)pyridine (0.007 g, 0.06 mmol) were added. The resulting solution was stirred at room temperature for 4 h. Precipitated materials were removed by filtration. After removal of the solvent by evaporation, the residue was purified by column chromatography on silica gel with a toluene-ethylacetate (11:1) mixture as the eluent. Recrystallization from ethanol gave the desired product. Yield: 0.28 g (72 %).

^{1}H NMR (270MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.60(s, 2H, Ar-**H**), 8.39(d, 2H, Ar-**H**, J=8.9Hz), 8.09(d, 2H, Ar-**H,** J=8.4Hz), 7.62(d, 2H, Ar-**H**, J=8.6Hz), 7.61(d, 2H, Ar-**H**, J=8.4Hz), 7.18(d, 2H, Ar-**H**, J=8.6Hz), 6.99(d, 2H, Ar-**H**, J=8.9Hz), 5.23-5.21(m, 1H, -C*H(CH_3)), 4.03(t, 2H, -OC**H**$_2$, J=6.6Hz), 2.64-2.55(m, 2H, Ar-C**H**$_2$-, 2H, -OCOC**H**$_2$-), 1.87-1.28(m, 41H, aliphatic-**H**), 0.88(t, 9H, -C**H**$_3$, J=6.8Hz); IR (KBr) ν_{max}/cm^{-1}: 2921, 2851, 1607, 1432, 1254, 1109; Purity: 100 %.