

Supporting Information

Synthesis and Characterization of Oligo(9,9-dihexyl-2,7-fluorene ethynylene)s: For Application to Blue Light-Emitting Diode

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General. Tetrahydrofuran was distilled over sodium/benzophenone. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with silica gel 60 F₂₅₄ (Merck, 0.2 mm). Column chromatography was carried out on Wakogel C-200 (75-150 μ m). ¹H NMR spectra were recorded on a JEOL JNM-LA 400 spectrometer (400 MHz) with chloroform-*d* as solvents and tetramethylsilane (TMS) as internal standard. Mass spectra were obtained with a JEOL JMS-70 spectrometer in FAB mode and a MALDI-TOF-MS mass spectrometer Voyager PR (PerSeptive Biosystems). Elemental analyses were performed on Analytical Center, Kyushu University.

2-Iodofluorene (1). Fluorene (100 g, 0.6 mol) was dissolved in 1 L of the boiling solvent (CH₃COOH : H₂O : H₂SO₄ = 100 : 20 : 3) with mechanical stirrer, followed by cooling to 60-65°C, adding periodic acid dihydrate (23 g, 0.1 mol) and iodine (51 g, 0.2 mol). After 4h, the elementary iodine almost disappeared and the precipitate was formed. Upon cooling, the pale yellow solid was collected by filtration and washed with 2N aqueous Na₂CO₃ and water. The crude product was recrystallized from hexane to give a white solid (140 g, 77%). mp 120-121 °C; ¹H-NMR (400 MHz, CDCl₃): δ 3.87 (s, 2H), 7.30-7.56 (m, 4H), 7.66-7.90 (m, 3H). Anal. Calcd for C₁₃H₉I: C, 53.45; H, 3.11. Found: C, 52.86; H, 3.01.

2-Iodo-9,9-dihexylfluorene (2). To a mixture of **1** (13.2 g, 43.5 mmol) and catalytic amounts of triethylbenzylammonium chloride in 900 mL of DMSO and 9.3 mL of 50% aqueous NaOH, 1-bromohexane (26.6 g, 0.16 mmol) was added. The reaction mixture was stirred at room temperature for 6h. The organic layer was washed with dilute HCl (2 times) and H₂O (3 times), and dried over MgSO₄. The resulting oil was purified by column chromatography (silica gel, hexane) to afford a pale yellow solid (14.9 g,

74.4 %). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 0.51-0.66 (m, 4H), 0.76 (t, $J = 7.0$ Hz, 6H), 0.96-1.16 (m, 12H), 1.93 (t, $J = 8.2$ Hz, 4H), 7.29-7.47 (m, 4H), 7.61-7.70 (m, 3H). Anal. Calcd for $\text{C}_{25}\text{H}_{33}\text{I}$: C, 65.21; H, 7.22. Found: C, 63.98; H, 7.08.

2-(3-hydroxy-3-methylbutynyl)-9,9-dihexylfluorene (3). To a solution of **2** (31.2 g, 67.7 mmol) in 220 mL of triethylamine was added 3-methyl-1-butyn-3-ol (7.4 g, 87.9 mmol). After the solution was degassed with nitrogen for 30 min, dichlorobis(triphenylphosphine)palladium(II) (0.06 g, 0.09 mmol), triphenylphosphine (0.07 g, 0.3 mmol), and cuprous iodide (0.16 g, 0.8 mmol) were added. The reaction mixture was then refluxed under nitrogen for 6 h. Excess of triethylamine was removed under the reduced pressure. To the resulting dark brown solid was then added ethyl acetate and water. The organic phase was separated and extracted with brine (2 times), then dried over MgSO_4 . The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate = 6/1) to afford a white solid (24.9 g, 88.2 %). mp 85.5-86 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 0.53-0.61 (m, 4H), 0.76 (t, $J = 7.1$ Hz, 6H), 0.98-1.14 (m, 12H), 1.66 (s, 6H), 1.94 (t, $J = 8.3$ Hz, 4H), 2.05 (s, 1H), 7.28-7.41 (m, 5H), 7.59-7.69 (m, 2H). Anal. Calcd for $\text{C}_{30}\text{H}_{40}\text{O}$: C, 86.48; H, 9.68. Found: C, 86.16; H, 9.65.

2-ethynyl-9,9-dihexylfluorene (4). A mixture of **3** (5.5 g, 13.2 mmol) and potassium hydroxide (3.0 g, 0.05 mol) in 60 mL of 2-propanol was heated at reflux under nitrogen with vigorous stirring for 3 h. The solvent was then removed and the crude product was purified by column chromatography (silica gel, hexane) to afford a pale yellow solid (4.1 g, 86.9 %). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 0.53-0.63 (m, 4H), 0.76 (t, $J = 7.2$ Hz, 6H), 0.98-1.15 (m, 12H), 1.94 (t, $J = 8.4$ Hz, 4H), 3.14 (s, 1H), 7.30-7.50 (m, 5H), 7.62-7.70 (m, 2H). Anal. Calcd for $\text{C}_{27}\text{H}_{34}$: C, 90.44; H, 9.56. Found: C, 90.35; H, 9.55.

2,7-diiodofluorene (5). The procedure is analogous to that described for **1**. mp 216-217 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 3.83 (s, 2H), 7.49 (d, $J = 8.2$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.87 (s, 2H). Anal. Calcd for $\text{C}_{13}\text{H}_8\text{I}_2$: C, 37.35; H, 1.93. Found: C, 37.36; H, 1.82.

2,7-diiodo-9,9-dihexylfluorene (6). The procedure is analogous to that described for **2**. mp 58.5-60 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 0.53-0.61 (m, 4H), 0.78 (t, $J = 7.1$ Hz, 6H), 1.00-1.18 (m, 12H), 1.88 (t, $J = 8.2$ Hz, 4H), 7.40 (d, $J = 8.5$ Hz, 2H), 7.62-7.67 (m, 4H). Anal. Calcd for $\text{C}_{25}\text{H}_{32}\text{I}_2$: C, 51.21; H, 5.50. Found: C, 51.35; H, 5.52.

2,7-di(3-hydroxy-3-methylbutynyl)-9,9-dihexylfluorene (7). The procedure is analogous to that described for **3**. mp 60.5-61.5 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 0.48-0.60 (m, 4H), 0.76 (t, $J = 7.2$ Hz, 6H), 0.96-1.15 (m, 12H), 1.66 (s, 12H), 1.93 (t, $J = 8.3$ Hz, 4H), 2.05 (s, 2H), 7.36-7.41 (m, 4H), 7.59 (d, $J = 7.8$ Hz, 2H). Anal. Calcd for

$C_{35}H_{46}O_2$: C, 84.29; H, 9.30. Found: C, 83.06; H, 8.96.

2,7-diethynyl-9,9-dihexylfluorene (8). The procedure is analogous to that described for **4**. mp 36-38 °C; 1H -NMR (400 MHz, $CDCl_3$): δ 0.53-0.61 (m, 4H), 0.76 (t, J = 7.2 Hz, 6H), 0.96-1.15 (m, 12H), 1.94 (t, J = 8.3 Hz, 4H), 3.14 (s, 2H), 7.45-7.50 (m, 4H), 7.62 (d, J = 7.8 Hz, 2H). Anal. Calcd for $C_{29}H_{34}$: C, 91.04; H, 8.96. Found: C, 90.38; H, 8.87.

Dimer (9). The procedure is analogous to that described for **3**. mp 116-116.5 °C; 1H -NMR (400 MHz, $CDCl_3$): δ 0.53-0.61 (m, 8H), 0.76 (t, J = 7.1 Hz, 12H), 0.98-1.15 (m, 24H), 1.98 (t, J = 8.3 Hz, 8H), 7.29-7.37 (m, 6H), 7.51-7.57 (m, 4H), 7.64-7.72 (m, 4H); FABMS m/z 690 ($M + H$)⁺.

Trimer (10). To a degassed solution of **4** (1.16 g, 3.2 mmol) and **6** (1.8 g, 3.1 mmol) in THF (200 mL) and piperidine (4 mL), dichlorobis(triphenylphosphine)palladium(II) (0.06 g, 0.09 mmol), triphenylphosphine (0.07 g, 0.3 mmol), and cuprous iodide (0.16 g, 0.8 mmol) were added. The reaction mixture was then stirred at room temperature for 24 h. After the reaction was complete, the mixture was diluted with ethyl acetate and washed with water and brine, then dried over $MgSO_4$. The crude product was purified by column chromatography (silica gel, hexane) to afford a white solid as trimer **10** (0.9 g, 27.7 %) and 2-iodo-7-[2-(9',9'-dihexylfluorenyl)ethynyl]-9,9-dihexylfluorene (iodo dimer) **11** (0.6 g, 23.8 %), which is coupled with **13** to give tetramer **14**. mp 134-135 °C; 1H -NMR (400 MHz, $CDCl_3$): δ 0.46-0.65 (m, 12H), 0.67-0.75 (m, 18H), 0.91-1.10 (m, 36H), 1.93 (t, J = 8.3 Hz, 12H), 7.25-7.32 (m, 6H), 7.45-7.53 (m, 8H), 7.61-7.70 (m, 6H); FABMS m/z 1047 ($M + H$)⁺.

2-Ethynyl-7-[2-(9',9'-dihexylfluorenyl)ethynyl]-9,9-dihexylfluorene (acetyl dimer, 13). To a solution of **11** (0.5 g, 0.6 mmol) in 100 mL of triethylamine was added 3-methyl-1-butyne-3-ol (0.77 g, 12.4 mmol). After the solution was degassed with nitrogen for 30 min, dichlorobis(triphenylphosphine)palladium(II) (3 mg, 0.004 mmol), triphenylphosphine (0.01 g, 0.04 mmol), and cuprous iodide (0.01 g, 0.05 mmol) were added. The reaction mixture was then refluxed under nitrogen for 6 h. Excess of triethylamine was removed under the reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/ethyl acetate = 30/1) to afford **12**. Subsequently, to **12** in 100 mL of 2-propanol was added potassium hydroxide (0.14 g, 2.5 mmol). The mixture was heated at reflux under nitrogen with vigorous stirring for 6 h. The solvent was then removed and the crude product was purified by column chromatography (silica gel, hexane) to afford a pale yellow solid (0.2 g, 46.6 %). mp 115-116 °C; 1H -NMR (400 MHz, $CDCl_3$): δ 0.54-0.68 (m, 8H), 0.74-0.80 (m, 12H), 0.98-1.18 (m, 24H), 1.92-2.01 (m, 8H), 3.16 (s, 1H), 7.30-7.72 (m, 13H). Anal. Calcd for $C_{54}H_{66}$: C, 90.70; H, 9.30. Found: C, 89.67; H, 9.29.

Tetramer (14). The procedure is analogous to that described for **3**. mp 206-207 °C; ¹H-NMR (400 MHz, CDCl₃): δ 0.53-0.70 (m, 16H), 0.74-0.81 (m, 24H), 1.00-1.18 (m, 48H), 1.95-2.05 (m, 16H), 7.29-7.37 (m, 6H), 7.54-7.59 (m, 12H), 7.68-7.72 (m, 8H); FABMS *m/z* 1403 (M + H)⁺.

Pentamer (15). The procedure is analogous to that described for **3**. mp 246.5-247 °C; ¹H-NMR (400 MHz, CDCl₃): δ 0.48-0.61 (m, 20H), 0.67-0.74 (m, 30H), 0.92-1.11 (m, 60H), 1.83-1.98 (m, 20H), 7.23-7.30 (m, 6H), 7.47-7.53 (m, 16H), 7.60-7.65 (m, 10H); MALDI TOF MS *m/z* 1760.2 (M + H)⁺.