

Supplementary Materials

Table S1. Abbreviations, commercial sources, and melting points of the common monomers used in this study.

Common diamines	Source	Vacuum-drying condition	Melting point (°C)
4,4'-Oxydianiline (4,4'-ODA)	Tokyo Chemical Industry (TCI)	50 °C/12h	191 ^a
2,2'-Bis(trifluoromethyl)benzidine (TFMB)	Wakayama Seika	50 °C/12 h	184 ^a
4,4'-Diaminobenzanilide (DABA)	TCI	50 °C/12 h	205 ^a
1,2,3,4-Cyclobutanetetracarboxylic dianhydride (CBDA)	TCI	200 °C / 12 h	285 ^b
Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BTA)	TCI	150°C / 24 h	----
1 <i>S</i> ,2 <i>R</i> ,4 <i>S</i> ,5 <i>R</i> -Cyclohexanetetracarboxylic dianhydride (H-PMDA)	New Japan Chemical	150 °C / 24 h	303 ^a

^a Data determined from the endothermic peak measured at a heating rate of 5 °C min⁻¹ on DSC.

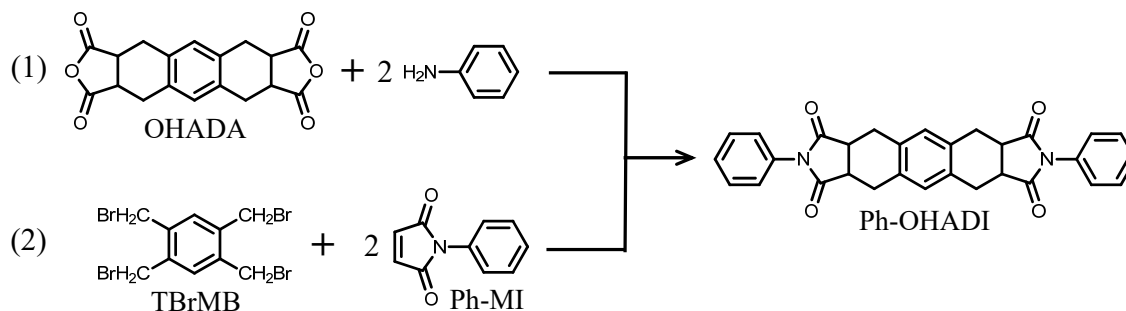
^b Data from the safety data sheet

Table S2. Abbreviations, commercial sources, and melting points of the raw materials used in this study.

Raw materials	Source	Melting point (°C) ^a
Maleic anhydride (MAn)	TCI	54
1,2,4,5-Tetramethylbenzene (Durene)	TCI	80
<i>N</i> -Bromosuccinimide (NBS)	TCI	----
2,2'-Azobisisobutyronitrile (AIBN)	TCI	103
4-Nitrobenzoyl chloride (4-NBC)	TCI	73

^a Data from the safety data sheet.

Section S1. Reaction schemes for the synthesis, detailed synthetic procedures, and the analytical results of OHADA-based diimide compound: *N*-phenyloctahydroanthracene-2,3,6,7-tetracarboxydiimide (Ph-OHADI).

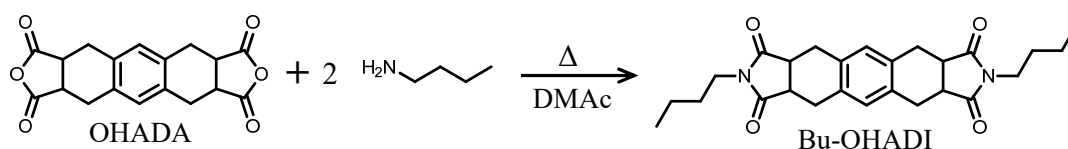


An OHADA-based diimide compound, *N*-phenyloctahydroanthracene-2,3,6,7-tetracarboxydiimide (Ph-OHADI) was synthesized via the following different routes (1 and 2), as described below.

Route (1): In a 100 mL-three-necked flask, OHADA (2 mmol, 0.656 g) and aniline (4.3 mmol, 0.397 g) were dissolved in dehydrated GBL (22 mL), and the reaction mixture was refluxed at 200 °C for 4 h in a nitrogen atmosphere. After the reaction, the reaction mixture was cooled to room temperature. The precipitate formed was collected by filtration, washed with adequate solvents, and dried at 120 °C for 12 h under vacuum. A light-brown product was obtained (yield: 47%). The analytical data of the product are as follows. ¹H-NMR (400 MHz, DMSO-*d*₆, δ, ppm): 7.41–7.32[m, 6H (6.13H), 3,3',4,4',5,5'-protons of the terminal aniline unit (AN)], 7.01 [s, 2H (2.00H), the protons of the central aromatic units], 6.82 [d, 4H (4.00H), *J* = 8.0 Hz, 2,2',6,6'-protons of AN], 3.46 [st (not well-resolved), 4H (4.08H), CH–C=O], 3.01–2.91 [m, 8H (8.23H), Ar–CH₂]. The data confirmed that the product is the desired model compound (Ph-OHADI).

Route (2): In a 100 mL-three-necked flask, TBrMB (5.4 mmol, 2.409 g) and *N*-phenylmaleimide (Ph-MI, 14.9 mmol, 2.593 g) were dissolved in anhydrous GBL (20 mL) in the presence of NaI (50 mmol, 7.47 g), and the reaction mixture was refluxed at 150 °C for 6 h in a nitrogen atmosphere. After the reaction, the reaction mixture was kept in a refrigerator. The precipitate formed was collected by filtration, washed with cold GBL and water, and dried at 160 °C for 12 h under vacuum. A light-brown product was obtained (yield: 19%). The crude product was recrystallized from GBL, and fine needle crystal was obtained (recrystallization yield: 73%). The analytical data of the product are as follows. Melting point (DSC): 418 °C. FT-IR (KBr plate method, cm⁻¹): 3107/3065/3011 (C_{arom}–H stretching), 2942/2902/2836 (C_{aliph}–H), 1773/1700 (imide group, C=O), 1497 (phenyl group), 1388 (imide group, N–C_{arom}), ¹H-NMR (400 MHz, DMSO-*d*₆, δ, ppm): 7.41–7.32[m, 6H (6.06H), 3,3',4,4',5,5'-protons of AN], 7.01 [s, 2H (2.00H), the protons of the central aromatic units], 6.82 [d, 4H (4.01H), *J* = 7.8 Hz, 2,2',6,6'-protons of AN], 3.46 [st (not well-resolved), 4H (4.12H), CH–C=O], 3.02–2.91 [m, 8H (8.05H), Ar–CH₂]. The results confirmed that the product is the desired model compound (Ph-OHADI).

Section S2. Reaction scheme for the synthesis, detailed synthetic procedures, and the analytical results of OHADA-based diimide compound: *N-n*-butyloctahydroanthracene-2,3,6,7-tetracarboxydiimide (Bu-OHADI).



Another OHADA-based diimide compound, *N-n*-butyloctahydroanthracene-2,3,6,7-tetracarboxydiimide (Bu-OHADI) was synthesized, as described below. In a 100 mL-three-necked flask, OHADA (2 mmol, 0.657 g) and *n*-butylamine (5 mmol, 0.384 g) were dissolved in dehydrated DMAc (5 mL), and the reaction mixture was stirred at 1 h, then refluxed at 170 °C for 4 h in a nitrogen atmosphere. After the reaction, the reaction mixture was kept in a refrigerator for one day. However, no precipitation was formed. Then, the reaction mixture was gradually poured into a large quantity of water. The precipitation formed was collected by filtration, washed with a small quantity of methanol, and dried at 120 °C for 12 h under vacuum. A white product was obtained (yield: 77%). The analytical data of the product are as follows. FT-IR (KBr plate method, cm^{-1}): 3020 ($\text{C}_{\text{arom}}\text{-H}$ stretching), 2952/2887 ($\text{C}_{\text{aliph}}\text{-H}$), 1775/1698 (imide group, C=O). $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, δ , ppm): 6.86 [s, 2H (2.00H), Ar-H], 3.29 [st (not well-resolved (close to the proton signal of water contained in the solvent), 4H, CH-C=O], 3.13 [t, 4H (3.90H), $J = 6.4$ Hz, N-CH_2], 2.93 [d, 4H (3.86H), $J = 14.4$ Hz, $\text{Ar-CH}_a\text{H}_b$], 2.69 [d (br), 4H (3.30H), $\text{Ar-CH}_a\text{H}_b$], 1.03 [sext (not well-resolved), 4H (4.33H), $\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$], 0.50 [t, 6H (5.99H), $J = 7.2$ Hz, $\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$], 0.37 [quin (not well-resolved), 4H (3.42H), $\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$]. The results confirmed that the product is the desired model compound (Bu-OHADI). This model compound showed no optically anisotropic liquid-crystalline textures during both the heating and cooling processes on a polarizing optical microscope. Thus, the OHADA-based diimide unit did not behave as a mesogen, probably reflecting its distorted structure.

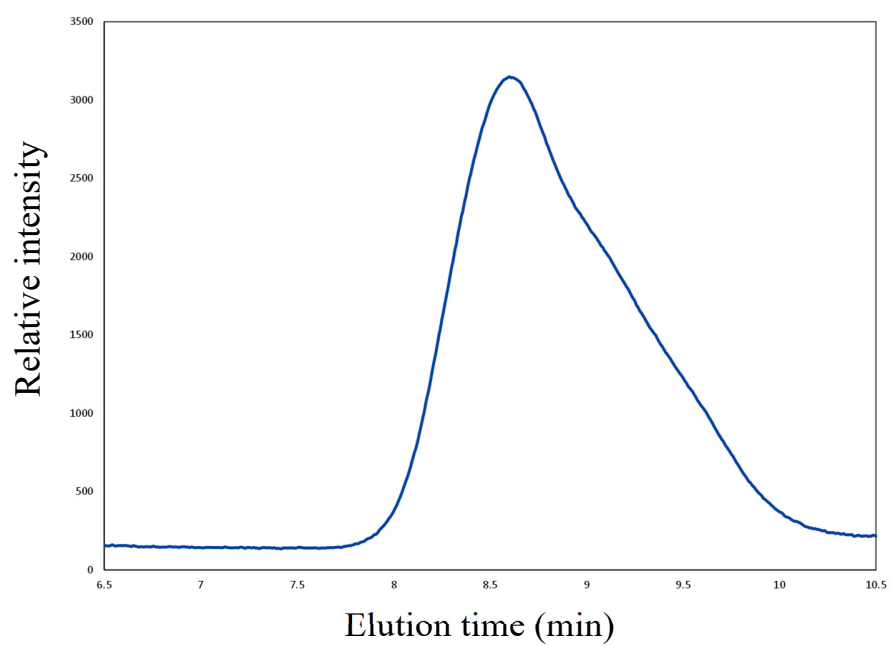


Figure S1. GPC curve of OHADA/TFMB polyimide obtained by the modified one-pot process.



Figure S2. Appearance of the reaction mixture after the one-pot polycondensation process for the CBDA/TFMB system.