

Supporting information for

Significant roles of lateral alkoxy and alkylthio groups on the ferroelectric nematic phase and phase transition behavior

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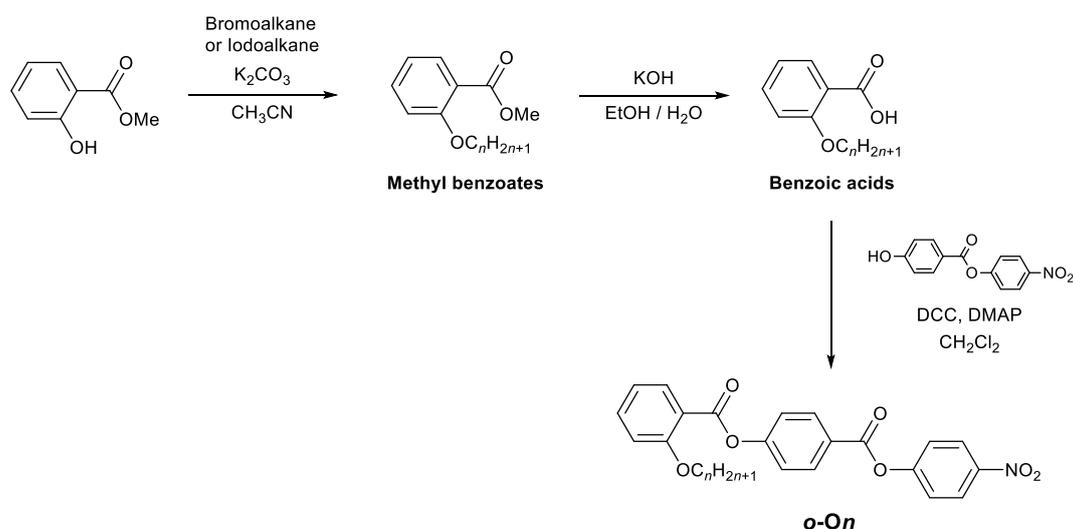
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1. Synthesis procedures and molecular characterization data

2-Ethoxybenzoic acid was purchased from TCI and 4-nitrophenyl 4-hydroxybenzoate was synthesized in the same manner with our previous report.^{S1}

1.1 Synthesis of *o-On*

2-Propoxybenzoic acid was purchased from TCI and 4-nitrophenyl 4-hydroxybenzoate was synthesized in the same manner with our previous report.^{S1}



Scheme S1. Synthesis of *o-On*.

General procedure for methyl benzoate intermediates

Methyl 2-hydroxybenzoate (800 mg, 5.26 mmol), corresponding bromoalkene or iodoalkane (1.2 eq., 6.310 mmol), K₂CO₃ (1.453 g, 10.52 mmol), and CH₃CN (5 mL) were put in a round flask and the mixture was stirred at reflux temperature. The solution was extracted with CH₂Cl₂ and washed with water and brine. The organic solution was dried over MgSO₄ and filtrated off to remove the desiccant, and the volatiles were removed by rotary evaporation. The residue was purified through silica gel column chromatography with an appropriate CH₂Cl₂/hexane-based eluent.

Methyl 2-propoxybenzoate

Yield: 91.8%. ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 6.0 Hz, Ar-*H*, 1H), 7.75 (t, *J* = 7.9 Hz, Ar-*H*, 1H), 6.96 (tt, *J* = 4.2 Hz, Ar-*H*, 2H), 4.00 (t, *J* = 6.5 Hz, O-CH₂, 2H), 3.89 (s, COO-CH₃, 3H), 1.85 (tt, O-CH₂-CH₂, 2H), 1.07 (t, *J* = 7.5 Hz, O-CH₂-CH₂-CH₃, 3H) ppm.

Methyl 2-butoxybenzoate

Yield: 68.7%. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 7.6 Hz, Ar-*H*, 1H), 7.43 (t, *J* = 7.8 Hz, Ar-*H*, 1H), 6.95 (tt, *J* = 3.8 Hz, Ar-*H*, 2H), 4.04 (t, *J* = 6.4 Hz, O-CH₂, 2H), 3.88 (s, COO-CH₃, 3H), 1.82 (tt, O-CH₂-CH₂, 2H), 1.53 (tt, *J* = 5.7 Hz, O-CH₂-CH₂-CH₂, 2H), 0.98 (t, *J* = 7.2 Hz, O-CH₂-CH₂-CH₂-CH₃, 3H) ppm.

Methyl 2-pentyloxybenzoate

Yield: 75.9%. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 7.2 Hz, Ar-*H*, 1H), 7.44 (t, *J* = 5.2 Hz, Ar-*H*, 1H), 6.96 (tt, *J* = 3.9 Hz, Ar-*H*, 2H), 4.03 (t, *J* = 6.6 Hz, O-CH₂, 2H), 3.89 (s, COO-CH₃, 3H), 1.84 (tt, O-CH₂-CH₂, 2H), 1.51-1.38 (m, O-CH₂-CH₂-CH₂-CH₂, 4H), 0.94 (t, *J* = 7.0 Hz, O-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm.

Methyl 2-hexyloxybenzoate

Yield: 74.8%. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 6.0 Hz, Ar-*H*, 1H), 7.43 (t, *J* = 7.2 Hz, Ar-*H*, 1H), 6.97 (tt, *J* = 4.5 Hz, Ar-*H*, 2H), 4.03 (t, *J* = 6.6 Hz, O-CH₂, 2H), 3.89 (s, COO-CH₃, 3H), 1.83 (tt, *J* = 7.0 Hz, O-CH₂-CH₂, 2H), 1.49 (tt, *J* = 7.2 Hz, O-CH₂-CH₂-CH₂, 2H), 1.34 (tt, *J* = 3.6 Hz, O-CH₂-CH₂-CH₂-CH₂-CH₂, 4H), 0.91 (t, *J* = 7.0 Hz, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm.

Methyl 2-heptyloxybenzoate

Yield: 63.0%. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 6.0 Hz, Ar-*H*, 1H), 7.43 (t, *J* = 7.2 Hz, Ar-*H*, 1H), 6.97-6.94 (m, Ar-*H*, 2H), 4.03 (t, *J* = 6.6 Hz, O-CH₂, 2H), 3.89 (s, COO-CH₃, 3H), 1.83 (tt, *J* = 7.0 Hz, O-CH₂-CH₂, 2H), 1.48 (tt, *J* = 7.4 Hz, O-CH₂-CH₂-CH₂, 2H), 1.40-1.27 (m, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂, 6H), 0.89 (t, *J* = 8.6 Hz, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm.

Methyl 2-octyloxybenzoate

Yield: 51.3%. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 6.0 Hz, Ar-*H*, 1H), 7.43 (t, *J* = 7.0 Hz, Ar-*H*, 1H), 6.97-6.94 (m, Ar-*H*, 2H), 4.03 (t, *J* = 6.6 Hz, O-CH₂, 2H), 3.89 (s, COO-CH₃, 3H), 1.83 (tt, *J* = 7.1 Hz, O-CH₂-CH₂, 2H), 1.48 (tt, *J* = 7.3 Hz, O-CH₂-CH₂-CH₂, 2H), 1.37-1.29 (m, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂, 8H), 0.89 (t, *J* = 6.8 Hz, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm.

Methyl 2-nonyloxybenzoate

Yield: 82.3%. ¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, *J* = 6.5 Hz, Ar-*H*, 1H), 7.43 (t, *J* = 7.0 Hz, Ar-*H*, 1H), 6.97-6.94 (m, Ar-*H*, 2H), 4.03 (t, *J* = 6.5 Hz, O-CH₂, 2H), 3.89 (s, COO-CH₃, 3H), 1.83 (tt,

$J = 7.1$ Hz, O-CH₂-CH₂, 2H), 1.48 (tt, $J = 7.4$ Hz, O-CH₂-CH₂-CH₂, 2H), 1.37-1.27 (m, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂, 10H), 0.88 (t, $J = 7.0$ Hz, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm.

Methyl 2-decyloxybenzoate

Yield: 80.6%. ¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, $J = 6.5$ Hz, Ar-H, 1H), 7.43 (t, $J = 6.8$ Hz, Ar-H, 1H), 6.97-6.94 (m, Ar-H, 2H), 4.03 (t, $J = 6.5$ Hz, O-CH₂, 2H), 3.89 (s, COO-CH₃, 3H), 1.83 (tt, $J = 7.1$ Hz, O-CH₂-CH₂, 2H), 1.48 (tt, $J = 7.4$ Hz, O-CH₂-CH₂-CH₂, 2H), 1.35-1.27 (m, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂, 10H), 0.88 (t, $J = 7.0$ Hz, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm.

General procedure for benzoic acid intermediates

Methyl 2-propyloxy benzoate (700 mg, 3.60 mmol), ethanol (15 mL), and KOH (607 mg, 10.8 mmol) dissolved in distilled water (20 mL) were put in a round flask and the mixture was stirred at reflux temperature overnight. After the solution was cooled to ambient temperature, 2M hydrochloric acid was added into the flask for neutralization. The neutralized solution was extracted with CH₂Cl₂ and washed with water and brine. The organic layer was dried over MgSO₄ and the volatiles were evaporated to afford the benzoic acid intermediates.

2-Propoxybenzoic acid

Yield: 88.0%. ¹H NMR (500 MHz, CDCl₃) δ 11.0 (s, Ar-COOH, 1H), 8.20 (d, $J = 9.5$ Hz, Ar-H, 1H), 7.55 (t, $J = 8.0$ Hz, Ar-H, 1H), 7.14 (d, $J = 7.5$ Hz, Ar-H, 1H), 7.05 (d, $J = 8.5$ Hz, Ar-H, 1H), 4.23 (t, $J = 6.5$ Hz, O-CH₂, 2H), 1.96 (tt, O-CH₂-CH₂, 2H), 1.11 (t, $J = 7.3$ Hz, O-CH₂-CH₂-CH₃, 3H) ppm.

2-Butoxybenzoic acid

Yield: 78.5%. ¹H NMR (400 MHz, CDCl₃) δ 11.0 (s, Ar-COOH, 1H), 8.19 (d, $J = 7.6$ Hz, Ar-H, 1H), 7.56 (t, $J = 8.8$ Hz, Ar-H, 1H), 7.13 (d, $J = 8.0$ Hz, Ar-H, 1H), 7.05 (d, $J = 8.0$ Hz, Ar-H, 1H), 4.27 (t, $J = 6.4$ Hz, O-CH₂, 2H), 1.91 (tt, $J = 7.1$ Hz, O-CH₂-CH₂, 2H), 1.54 (tt, $J = 5.6$ Hz, O-CH₂-CH₂-CH₂, 2H), 1.02 (t, $J = 7.4$ Hz, O-CH₂-CH₂-CH₂-CH₃, 3H) ppm.

2-Pentyloxybenzoic acid

Yield: 88.0%. ¹H NMR (400 MHz, CDCl₃) δ 11.0 (s, Ar-COOH, 1H), 8.17 (d, $J = 7.6$ Hz, Ar-H, 1H), 7.53 (t, $J = 7.0$ Hz, Ar-H, 1H), 7.11 (d, $J = 7.6$ Hz, Ar-H, 1H), 7.03 (d, $J = 8.0$ Hz, Ar-H, 1H), 4.24 (t, $J = 6.6$ Hz, O-CH₂, 2H), 1.91 (tt, $J = 7.1$ Hz, O-CH₂-CH₂, 2H), 1.48-1.36 (m, O-CH₂-CH₂-CH₂-CH₂, 4H), 0.93 (t, $J = 7.2$ Hz, O-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm.

General procedure for the Steglich esterification

4'-Nitrophenyl 4-hydroxybenzoate (200 mg, 0.772 mmol), 2-propoxy benzoic acid (1.5 eq., 1.157 mmol), 4-dimethylaminopyridine (DMAP) (4.72 mg), and dehydrated CH₂Cl₂ (1 mL) were put in a double-necked round flask and the flask was quickly charged with an argon gas and placed in an ice bath. *N,N'*-dicyclohexylcarbodiimide (DCC) (478 mg, 2.315 mmol) was dissolved in dehydrated CH₂Cl₂ (2 mL) in another flask under argon atmosphere and the solution was added into the prior flask at 0 °C. The mixture was stirred at room temperature for 2h. The solution was filtrated off to remove insoluble solids and the residue was purified by silica gel column chromatography with a CH₂Cl₂/hexane eluent and recrystallized in CH₂Cl₂/hexane-based solvents to afford ***o-On***.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-ethoxybenzoate (***o-O2***)

Yield: 16.9%. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 9.5 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 9.0 Hz, Ar-*H*, 2H), 8.02 (d, *J* = 7.5 Hz, Ar-*H*, 1H), 7.56 (t, *J* = 7.3 Hz, Ar-*H*, 1H), 7.43 (t, *J* = 8.3 Hz, Ar-*H*, 4H), 7.06 (t, *J* = 8.0 Hz, Ar-*H*, 2H), 4.18 (q, *J* = 7.0 Hz, O-CH₂, 2H), 1.49 (t, *J* = 6.8 Hz, O-CH₂-CH₃, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 163.8, 163.6, 159.5, 155.9, 155.7, 145.4, 134.7, 132.3, 132.0×2, 125.8, 125.3×2, 122.6×2, 122.4×2, 120.2, 118.6, 113.3, 64.6, 14.7 ppm. HRMS (ESI, *m/z*): [M+Na]⁺ calcd. for C₂₂H₁₇NNaO₇, 430.0897; found, 430.0911.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-propoxybenzoate (***o-O3***)

Yield: 22.6%. ¹H NMR (500 MHz, CDCl₃) δ 8.34 (d, *J* = 9.0 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 8.5 Hz, Ar-*H*, 2H), 8.02 (d, *J* = 8.0 Hz, Ar-*H*, 1H), 7.56 (t, *J* = 6.8 Hz, Ar-*H*, 1H), 7.42 (q, *J* = 6.5 Hz, Ar-*H*, 4H), 7.05 (t, *J* = 7.8 Hz, Ar-*H*, 2H), 4.07 (t, *J* = 6.3 Hz, O-CH₂, 2H), 1.92-1.85 (m, O-CH₂-CH₂, 2H), 1.08 (t, *J* = 7.5 Hz, O-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 163.9, 160.0, 155.9, 155.7, 145.4, 134.7, 132.3, 132.0×2, 125.3×2, 122.6×2, 122.4×2, 120.1, 118.5, 113.2, 70.4, 22.6, 10.6 ppm. HRMS (ESI, *m/z*): [M+Na]⁺ calcd. for C₂₃H₁₉NNaO₇, 444.1054; found, 444.1065.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-butoxybenzoate (***o-O4***)

Yield: 47.8%. ¹H NMR (500 MHz, CDCl₃) δ 8.34 (d, *J* = 7.0 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 7.0 Hz, Ar-*H*, 2H), 8.02 (d, *J* = 6.5 Hz, Ar-*H*, 1H), 7.56 (t, *J* = 7.0 Hz, Ar-*H*, 1H), 7.42 (q, *J* = 7.5 Hz, Ar-*H*, 4H), 7.05 (t, *J* = 7.0 Hz, Ar-*H*, 2H), 4.11 (t, *J* = 6.5 Hz, O-CH₂, 2H), 1.84 (tt, *J* = 7.0 Hz, O-CH₂-CH₂, 2H), 1.58-1.50 (m, O-CH₂-CH₂-CH₂, 2H), 0.96 (t, *J* = 7.5 Hz, O-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 163.9, 163.6, 160.0, 155.9, 155.6, 145.4, 134.7, 132.3, 132.0, 125.3×2, 122.6×2, 122.4×2, 120.7, 118.4, 113.4, 68.6, 31.2, 19.2, 13.4 ppm. HRMS (ESI, *m/z*): [M+Na]⁺ calcd. for C₂₄H₂₁NNaO₇, 458.1210; found, 458.1221.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-pentyloxybenzoate (***o*-O5**)

Yield: 26.5%. ¹H NMR (500 MHz, CDCl₃) δ 8.33 (d, *J* = 9.5 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 8.5 Hz, Ar-*H*, 2H), 8.01 (d, *J* = 6.0 Hz, Ar-*H*, 1H), 7.55 (t, *J* = 7.0 Hz, Ar-*H*, 1H), 7.42 (q, *J* = 6.8 Hz, Ar-*H*, 4H), 7.05 (t, *J* = 7.3 Hz, Ar-*H*, 2H), 4.10 (t, *J* = 6.5 Hz, O-CH₂, 2H), 1.86 (tt, *J* = 7.0 Hz, O-CH₂-CH₂, 2H), 1.49 (tt, *J* = 7.5 Hz, O-CH₂-CH₂, 2H), 1.40-1.33 (m, O-CH₂-CH₂-CH₂-CH₂, 2H), 0.89 (t, *J* = 7.3 Hz, O-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 164.0, 163.5, 159.6, 155.9, 155.6, 145.4, 134.7, 132.3, 132.0×2, 125.3×2, 122.6×2, 122.3×2, 120.1, 118.5, 113.2, 68.9, 28.9, 28.1, 22.4, 14.0 ppm. HRMS (ESI, *m/z*): [M+Na]⁺ calcd. for C₂₅H₂₃NNaO₇, 472.1367; found, 472.1367.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-hexyloxybenzoate (***o*-O6**)

Yield: 17.9%. ¹H NMR (500 MHz, CDCl₃) δ 8.34 (d, *J* = 9.5 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 9.0 Hz, Ar-*H*, 2H), 8.01 (d, *J* = 6.5 Hz, Ar-*H*, 1H), 7.55 (t, *J* = 7.8 Hz, Ar-*H*, 1H), 7.42 (q, *J* = 7.7 Hz, Ar-*H*, 4H), 7.05 (t, *J* = 7.5 Hz, Ar-*H*, 2H), 4.10 (t, *J* = 6.5 Hz, O-CH₂, 2H), 1.85 (tt, *J* = 7.0 Hz, O-CH₂-CH₂, 2H), 1.53-1.46 (m, O-CH₂-CH₂, 2H), 1.35-1.27 (m, O-CH₂-CH₂-CH₂-CH₂-CH₂, 4H), 0.87 (t, *J* = 7.0 Hz, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 163.6, 159.6, 155.9, 155.7, 145.4, 134.7, 132.3, 132.0×2, 125.3×2, 122.6×2, 122.4×2, 120.1, 118.5, 113.2, 68.9, 31.5, 29.1, 25.7, 22.6, 14.0 ppm. HRMS (ESI, *m/z*): [M+Na]⁺ calcd. for C₂₆H₂₅NNaO₇, 486.1523; found, 486.1527.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-heptyloxybenzoate (***o*-O7**)

Yield: 17.3%. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 9.2 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 8.8 Hz, Ar-*H*, 2H), 8.01 (d, *J* = 6.4 Hz, Ar-*H*, 1H), 7.56 (t, *J* = 7.0 Hz, Ar-*H*, 1H), 7.42 (t, *J* = 9.2 Hz, Ar-*H*, 4H), 7.05 (t, *J* = 7.2 Hz, Ar-*H*, 2H), 4.10 (t, *J* = 6.4 Hz, O-CH₂, 2H), 1.85 (tt, *J* = 7.0 Hz, O-CH₂-CH₂, 2H), 1.49 (tt, *J* = 7.4 Hz, O-CH₂-CH₂, 2H), 1.37-1.23 (m, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂, 6H), 0.86 (t, *J* = 6.6 Hz, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 163.6, 159.6, 155.9, 155.6, 145.4, 134.7, 132.3, 132.0×2, 125.7, 125.3×2, 122.6×2, 122.3×2, 120.1, 118.5, 113.1, 68.9, 31.7, 29.2, 29.0, 25.9, 22.6, 14.0 ppm. HRMS (ESI, *m/z*): [M+Na]⁺ calcd. for C₂₇H₂₇NNaO₇, 500.1680; found, 500.1675.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-octyloxybenzoate (***o*-O8**)

Yield: 18.3%. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 9.2 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 9.2 Hz, Ar-*H*, 2H), 8.01 (d, *J* = 6.4 Hz, Ar-*H*, 1H), 7.56 (t, *J* = 6.8 Hz, Ar-*H*, 1H), 7.42 (t, *J* = 9.2 Hz, Ar-*H*, 4H), 7.05 (t, *J* = 7.4 Hz, Ar-*H*, 2H), 4.10 (t, *J* = 6.4 Hz, O-CH₂, 2H), 1.85 (tt, *J* = 7.0 Hz,

O-CH₂-CH₂, 2H), 1.49 (tt, *J* = 7.4 Hz, O-CH₂-CH₂, 2H), 1.34-1.24 (m, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂, 8H), 0.86 (t, *J* = 7.0 Hz, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 163.5, 159.6, 155.9, 155.6, 145.4, 134.7, 132.3, 132.0×2, 125.7, 125.3×2, 122.6×2, 122.3×2, 120.1, 118.4, 113.1, 68.9, 31.8, 29.3, 29.2×2, 26.0, 22.6, 14.1 ppm. HRMS (ESI, *m/z*): [M+Na]⁺ calcd. for C₂₈H₂₉NNaO₇, 514.1836; found, 514.1836.

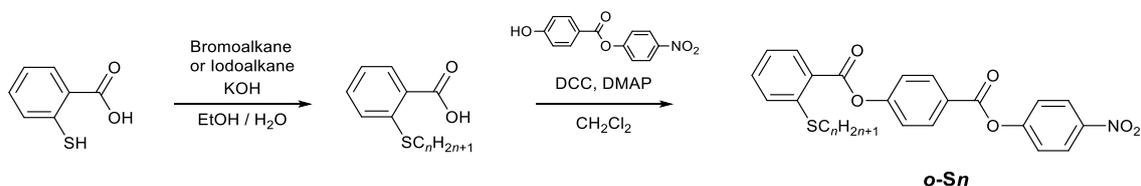
4-((4-Nitrophenoxy)carbonyl)phenyl 2-nonyloxybenzoate (***o*-O9**)

Yield: 36.9%. ¹H NMR (500 MHz, CDCl₃) δ 8.34 (d, *J* = 9.0 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 8.5 Hz, Ar-*H*, 2H), 8.01 (d, *J* = 7.5 Hz, Ar-*H*, 1H), 7.56 (t, *J* = 7.3 Hz, Ar-*H*, 1H), 7.42 (q, *J* = 7.0 Hz, Ar-*H*, 4H), 7.05 (d, *J* = 7.8 Hz, Ar-*H*, 2H), 4.10 (t, *J* = 6.5 Hz, O-CH₂, 2H), 1.85 (tt, *J* = 7.0 Hz, O-CH₂-CH₂, 2H), 1.49 (tt, *J* = 7.0 Hz, O-CH₂-CH₂-CH₂, 2H), 1.33-1.24 (m, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂, 10H), 0.86 (t, *J* = 6.5 Hz, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 164.0, 163.6, 159.6, 155.9, 155.7, 145.4, 134.7, 132.3, 132.0×2, 125.8, 125.3×2, 122.6×2, 122.4×2, 120.1, 118.5, 113.2, 68.9, 31.9, 29.5, 29.3, 29.2×2, 26.0, 22.6, 14.1 ppm. HRMS (ESI, *m/z*): [M+Na]⁺ calcd. for C₂₉H₃₁NNaO₇, 528.1993; found, 528.1987.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-decyloxybenzoate (***o*-O10**)

Yield: 67.7%. ¹H NMR (500 MHz, CDCl₃) δ 8.34 (d, *J* = 9.0 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 8.0 Hz, Ar-*H*, 2H), 8.01 (d, *J* = 6.0 Hz, Ar-*H*, 1H), 7.55 (t, *J* = 7.3 Hz, Ar-*H*, 1H), 7.42 (q, *J* = 6.8 Hz, Ar-*H*, 4H), 7.05 (d, *J* = 7.5 Hz, Ar-*H*, 2H), 4.09 (t, *J* = 6.3 Hz, O-CH₂, 2H), 1.85 (tt, *J* = 7.0 Hz, O-CH₂-CH₂, 2H), 1.49 (tt, *J* = 7.6 Hz, O-CH₂-CH₂-CH₂, 2H), 1.34-1.24 (m, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂, 12H), 0.86 (t, *J* = 7.0 Hz, O-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 164.0, 163.5, 159.5, 155.9, 155.6, 145.4, 134.7, 132.3, 132.0×2, 125.7, 125.3×2, 122.6×2, 122.3×2, 120.1, 118.5, 113.2, 68.9, 31.8, 29.5, 29.5, 29.3, 29.3, 29.2, 26.0, 22.6, 14.1 ppm. HRMS (ESI, *m/z*): [M+Na]⁺ calcd. for C₃₀H₃₃NNaO₇, 542.2149; found, 542.2150.

1.2 Synthesis of *o*-Sn



Scheme S2. Synthesis of *o*-Sn.

General procedure for benzoic acid intermediates

2-Mercaptobenzoic acid (600.0 mg, 3.891 mmol), *n*-bromoalkane (1.2 eq, 4.670 mmol), ethanol (5 mL), and KOH (437 mg, 7.78 mmol) dissolved in distilled water (1 mL) were put in a round flask and the mixture was stirred at room temperature for 2h. 2M Hydrochloric acid was added into the flask for neutralization, giving colorless solids. The precipitated solids were collected by filtration, washed with distilled water and dried under reduced pressure, to afford for the shorter chain homologs.

2-Ethylthiobenzoic acid

Yield: 82.4%. ¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 8.0 Hz, Ar-*H*, 1H), 7.50 (t, *J* = 8.2 Hz, Ar-*H*, 1H), 7.36 (d, *J* = 8.0 Hz, Ar-*H*, 1H), 7.21 (t, *J* = 7.5 Hz, Ar-*H*, 1H), 2.98 (q, *J* = 7.5 Hz, S-CH₂, 2H), 1.41 (t, *J* = 7.5 Hz, S-CH₂-CH₃, 3H) ppm.

2-Propylthiobenzoic acid

Yield: 85.6%. ¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, *J* = 6.5 Hz, Ar-*H*, 1H), 7.49 (t, *J* = 7.5 Hz, Ar-*H*, 1H), 7.35 (d, *J* = 8.5 Hz, Ar-*H*, 1H), 7.20 (t, *J* = 7.5 Hz, Ar-*H*, 1H), 2.92 (t, *J* = 7.3 Hz, S-CH₂, 2H), 1.78 (m, S-CH₂-CH₂, 2H), 1.10 (t, *J* = 7.2 Hz, S-CH₂-CH₂-CH₃, 3H) ppm.

2-Butylthiobenzoic acid

Yield: 90.3%. ¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 9.5 Hz, Ar-*H*, 1H), 7.49 (t, *J* = 8.5 Hz, Ar-*H*, 1H), 7.37 (d, *J* = 8.0 Hz, Ar-*H*, 1H), 7.21 (t, *J* = 7.5 Hz, Ar-*H*, 1H), 2.94 (t, *J* = 7.5 Hz, S-CH₂, 2H), 1.73 (tt, *J* = 7.5 Hz, S-CH₂-CH₂, 2H), 1.52 (tt, *J* = 7.4 Hz, S-CH₂-CH₂-CH₂, 2H), 0.96 (t, *J* = 7.3 Hz, S-CH₂-CH₂-CH₂-CH₃, 3H) ppm.

2-Pentylthiobenzoic acid

Yield: 95.0%. ¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 9.5 Hz, Ar-*H*, 1H), 7.49 (t, *J* = 8.5 Hz, Ar-*H*, 1H), 7.36 (d, *J* = 8.0 Hz, Ar-*H*, 1H), 7.21 (t, *J* = 7.7 Hz, Ar-*H*, 1H), 2.93 (t, *J* = 7.2 Hz, S-CH₂, 2H), 1.74 (tt, *J* = 7.6 Hz, S-CH₂-CH₂, 2H), 1.47 (tt, *J* = 5.9 Hz, S-CH₂-CH₂-CH₂, 2H), 1.37 (tt, *J* =

CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 170.1, 142.6, 133.1, 132.6, 126.4, 126.4, 124.1, 32.6, 31.9, 29.5, 29.5, 29.3, 29.2, 29.2, 28.2, 22.7, 14.1.

o-Sn were synthesized in similar manners to *o-On* through the Steglich esterification.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-ethylthiobenzoate (*o-S2*)

Yield: 30.0%. ¹H NMR (500 MHz, CDCl₃) δ 8.34 (d, *J* = 9.5 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 8.5 Hz, Ar-*H*, 2H), 8.24 (d, *J* = 6.5 Hz, Ar-*H*, 1H), 7.56 (t, *J* = 7.0 Hz, Ar-*H*, 1H), 7.44 (d, *J* = 9.0 Hz, Ar-*H*, 4H), 7.41 (d, *J* = 8.5 Hz, Ar-*H*, 1H), 7.26 (t, *J* = 7.3 Hz, Ar-*H*, 1H), 3.02 (q, *J* = 7.3 Hz, S-CH₂, 2H), 1.42 (t, *J* = 7.3 Hz, S-CH₂-CH₃, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 164.0, 163.5, 155.6, 155.5, 145.4, 144.2, 133.3, 132.0, 131.9×2, 125.9, 125.6×2, 125.3×2, 123.7, 122.6×2, 122.4×2, 21.7, 13.9 ppm. HRMS (ESI, *m/z*): [M+Na]⁺ calcd. for C₂₂H₁₇NNaO₆S, 446.0669; found, 446.0668.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-propylthiobenzoate (*o-S3*)

Yield: 62.0%. ¹H NMR (500 MHz, CDCl₃) δ 8.35 (d, *J* = 9.0 Hz, Ar-*H*, 2H), 8.29 (d, *J* = 8.5 Hz, Ar-*H*, 2H), 8.24 (d, *J* = 6.5 Hz, Ar-*H*, 1H), 7.56 (t, *J* = 7.0 Hz, Ar-*H*, 1H), 7.45 (d, *J* = 8.5 Hz, Ar-*H*, 4H), 7.42 (d, *J* = 8.0 Hz, Ar-*H*, 1H), 7.26 (t, *J* = 6.3 Hz, Ar-*H*, 1H), 2.97 (t, *J* = 7.5 Hz, S-CH₂, 2H), 1.84-1.75 (m, S-CH₂-CH₂, 2H), 1.10 (t, *J* = 7.3 Hz, S-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (164.0, 163.5, 155.6, 155.5, 145.4, 144.2, 133.3, 132.0, 131.9×2, 125.9, 125.6×2, 125.3×2, 123.7, 122.5×2, 122.4×2, 34.1, 21.7, 13.9 ppm. HRMS (ESI, *m/z*): [M+Na]⁺ calcd. for C₂₃H₁₉NNaO₆S, 460.0825; found, 460.0828.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-butylthiobenzoate (*o-S4*)

Yield: 30.6%. ¹H NMR (500 MHz, CDCl₃) δ 8.34 (d, *J* = 9.5 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 7.0 Hz, Ar-*H*, 2H), 8.23 (d, *J* = 6.5 Hz, Ar-*H*, 1H), 7.55 (t, *J* = 6.8 Hz, Ar-*H*, 1H), 7.44 (d, *J* = 7.5 Hz, Ar-*H*, 4H), 7.40 (d, *J* = 8.5 Hz, Ar-*H*, 1H), 7.25 (t, *J* = 6.8 Hz, Ar-*H*, 1H), 2.98 (t, *J* = 7.5 Hz, S-CH₂, 2H), 1.75 (tt, *J* = 7.5 Hz, S-CH₂-CH₂, 2H), 1.57-1.49 (m, S-CH₂-CH₂-CH₂, 2H), 0.97 (t, *J* = 7.5 Hz, S-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 164.0, 163.5, 155.6, 155.5, 145.4, 144.2, 133.3, 132.0, 131.9×2, 125.9, 125.6×2, 125.3×2, 123.7, 122.6×2, 122.4×2, 31.7, 30.1, 22.3, 13.7 ppm. HRMS (ESI, *m/z*): [M+Na]⁺ calcd. for C₂₄H₂₁NNaO₆S, 474.0982; found, 474.0984.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-pentylthiobenzoate (*o-S5*)

Yield: 46.0%. ¹H NMR (400 MHz, CDCl₃) δ 8.35 (d, *J* = 7.2 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 8.8 Hz, Ar-*H*, 2H), 8.23 (d, *J* = 6.4 Hz, Ar-*H*, 1H), 7.55 (t, *J* = 6.8 Hz, Ar-*H*, 1H), 7.44 (d, *J* = 8.4 Hz,

Ar-H, 4H), 7.40 (d, $J = 8.0$ Hz, Ar-H, 1H), 7.25 (t, $J = 7.0$ Hz, Ar-H, 1H), 2.97 (t, $J = 7.6$ Hz, S-CH₂, 2H), 1.77 (tt, $J = 7.5$ Hz, S-CH₂-CH₂, 2H), 1.49 (tt, $J = 7.4$ Hz, S-CH₂-CH₂-CH₂, 2H), 1.42-1.33 (m, S-CH₂-CH₂-CH₂-CH₂, 2H), 0.92 (t, $J = 7.4$ Hz, S-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 155.5, 145.4, 144.2, 133.3, 132.0×2, 126.0, 125.6, 125.3×2, 124.8, 123.7, 122.6×2, 122.4×2, 32.0, 31.3, 27.8, 22.3, 13.9 ppm. HRMS (ESI, m/z): [M+Na]⁺ calcd. for C₂₅H₂₃NNaO₆S, 488.1138; found, 488.1135.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-hexylthiobenzoate (*o*-S6)

Yield: 58.4%. ¹H NMR (500 MHz, CDCl₃) δ 8.35 (d, $J = 9.0$ Hz, Ar-H, 2H), 8.28 (d, $J = 8.5$ Hz, Ar-H, 2H), 8.23 (d, $J = 8.0$ Hz, Ar-H, 1H), 7.55 (t, $J = 7.0$ Hz, Ar-H, 1H), 7.44 (d, $J = 8.0$ Hz, Ar-H, 4H), 7.40 (d, $J = 8.0$ Hz, Ar-H, 1H), 7.25 (t, $J = 6.5$ Hz, Ar-H, 1H), 2.97 (t, $J = 7.5$ Hz, S-CH₂, 2H), 1.76 (tt, $J = 7.5$ Hz, S-CH₂-CH₂, 2H), 1.55-1.47 (m, S-CH₂-CH₂-CH₂, 2H), 1.34-1.31 (m, S-CH₂-CH₂-CH₂-CH₂-CH₂, 4H), 0.90 (t, $J = 7.0$ Hz, S-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 164.0, 163.5, 155.6, 155.5, 145.4, 144.2, 133.3, 132.0, 131.9×2, 126.0, 125.6×2, 125.3×2, 123.7, 122.6×2, 122.4×2, 32.0, 31.4, 28.8, 28.0, 22.5, 14.0 ppm. HRMS (ESI, m/z): [M+Na]⁺ calcd. for C₂₆H₂₅NNaO₆S, 502.1295; found, 502.1270.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-heptylthiobenzoate (*o*-S7)

Yield: 31.8%. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, $J = 8.8$ Hz, Ar-H, 2H), 8.28 (d, $J = 8.8$ Hz, Ar-H, 2H), 8.24 (d, $J = 6.4$ Hz, Ar-H, 1H), 7.55 (t, $J = 7.0$ Hz, Ar-H, 1H), 7.44 (d, $J = 8.4$ Hz, Ar-H, 4H), 7.40 (d, $J = 8.4$ Hz, Ar-H, 1H), 7.25 (t, $J = 7.4$ Hz, Ar-H, 1H), 2.97 (t, $J = 7.4$ Hz, S-CH₂, 2H), 1.76 (tt, $J = 7.5$ Hz, S-CH₂-CH₂, 2H), 1.49 (tt, $J = 7.4$ Hz, S-CH₂-CH₂-CH₂, 2H), 1.38-1.24 (m, S-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂, 6H), 0.89 (t, $J = 6.8$ Hz, S-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 163.5, 155.6, 155.5, 145.4, 144.2, 133.3, 132.0, 131.9×2, 125.9, 125.6×2, 125.3×2, 123.7, 122.6×2, 122.4×2, 32.0, 31.7, 29.1, 28.9, 28.1, 22.6, 14.1 ppm. HRMS (ESI, m/z): [M+Na]⁺ calcd. for C₂₇H₂₇NNaO₆S, 516.1451; found, 516.1451.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-octylthiobenzoate (*o*-S8)

Yield: 17.0%. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, $J = 8.8$ Hz, Ar-H, 2H), 8.28 (d, $J = 8.8$ Hz, Ar-H, 2H), 8.24 (d, $J = 6.8$ Hz, Ar-H, 1H), 7.55 (t, $J = 7.2$ Hz, Ar-H, 1H), 7.44 (d, $J = 8.8$ Hz, Ar-H, 4H), 7.40 (d, $J = 8.0$ Hz, Ar-H, 1H), 7.25 (t, $J = 7.4$ Hz, Ar-H, 1H), 2.97 (t, $J = 7.2$ Hz, S-CH₂, 2H), 1.76 (tt, $J = 7.5$ Hz, S-CH₂-CH₂, 2H), 1.49 (tt, $J = 7.3$ Hz, S-CH₂-CH₂-CH₂, 2H), 1.35-1.27 (m, S-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂, 8H), 0.88 (t, $J = 6.8$ Hz, S-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 163.5, 155.6, 155.5, 145.4, 144.2, 133.3, 132.0, 132.0×2, 126.0, 125.6×2, 125.3×2, 123.7, 122.7×2, 122.4×2,

32.0, 31.8, 29.2, 29.1×2, 28.9, 28.1, 22.6, 14.1 ppm. HRMS (ESI, m/z): [M+Na]⁺ calcd. for C₂₈H₂₉NNaO₆S, 530.1608; found, 530.1597.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-nonylthiobenzoate (*o*-S9)

Yield: 26.4%. ¹H NMR (500 MHz, CDCl₃) δ 8.34 (d, *J* = 8.5 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 8.5 Hz, Ar-*H*, 2H), 8.23 (d, *J* = 8.0 Hz, Ar-*H*, 1H), 7.55 (t, *J* = 7.0 Hz, Ar-*H*, 1H), 7.44 (d, *J* = 8.0 Hz, Ar-*H*, 4H), 7.40 (d, *J* = 8.0 Hz, Ar-*H*, 1H), 7.25 (t, *J* = 6.8 Hz, Ar-*H*, 1H), 2.97 (t, *J* = 7.5 Hz, S-CH₂, 2H), 1.76 (tt, *J* = 7.5 Hz, S-CH₂-CH₂, 2H), 1.49 (tt, *J* = 7.4 Hz, S-CH₂-CH₂-CH₂, 2H), 1.35-1.27 (m, S-CH₂-CH₂-CH₂-CH₂-C H₂-C H₂-C H₂-CH₂, 10H), 0.88 (t, *J* = 6.8 Hz, S-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 164.0, 163.5, 155.6, 155.5, 145.4, 144.2, 133.3, 132.0, 132.0×2, 126.0, 125.6×2, 125.3×2, 123.7, 122.6×2, 122.4×2, 32.0, 31.8, 29.4, 29.2×2, 29.2, 28.1, 22.6, 14.1 ppm. HRMS (ESI, m/z): [M+Na]⁺ calcd. for C₂₉H₃₁NNaO₆S, 544.1764; found, 544.1760.

4-((4-Nitrophenoxy)carbonyl)phenyl 2-decylthiobenzoate (*o*-S10)

Yield: 43.9%. ¹H NMR (500 MHz, CDCl₃) δ 8.34 (d, *J* = 9.5 Hz, Ar-*H*, 2H), 8.28 (d, *J* = 8.5 Hz, Ar-*H*, 2H), 8.23 (d, *J* = 8.0 Hz, Ar-*H*, 1H), 7.55 (t, *J* = 7.8 Hz, Ar-*H*, 1H), 7.44 (d, *J* = 8.5 Hz, Ar-*H*, 4H), 7.40 (d, *J* = 8.0 Hz, Ar-*H*, 1H), 7.25 (t, *J* = 7.3 Hz, Ar-*H*, 1H), 2.97 (t, *J* = 7.5 Hz, S-CH₂, 2H), 1.76 (tt, *J* = 7.5 Hz, S-CH₂-CH₂, 2H), 1.49 (tt, *J* = 7.4 Hz, S-CH₂-CH₂-CH₂, 2H), 1.35-1.27 (m, S-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂, 12H), 0.88 (t, *J* = 7.0 Hz, S-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₃, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ 164.0, 163.5, 155.6, 155.5, 145.4, 144.2, 133.3, 132.0, 132.0×2, 126.0, 125.6×2, 125.3×2, 123.7, 122.6×2, 122.4×2, 32.0, 31.9, 29.5×2, 29.3, 29.2×2, 28.1, 22.7, 14.1 ppm. HRMS (ESI, m/z): [M+Na]⁺ calcd. for C₃₀H₃₃NNaO₆S, 558.1921; found, 558.1937.

2. POM images

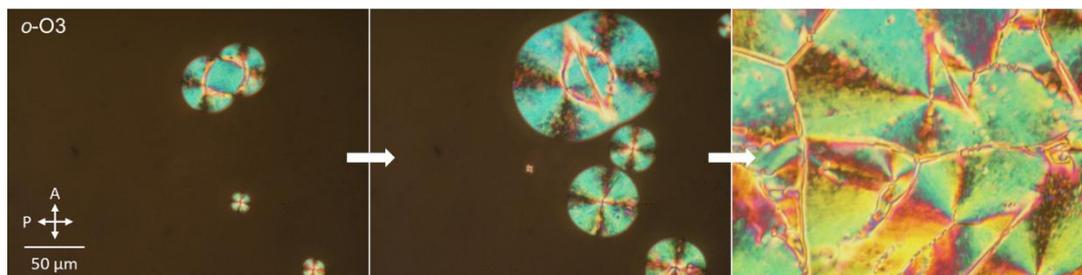


Fig. S1. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-03.

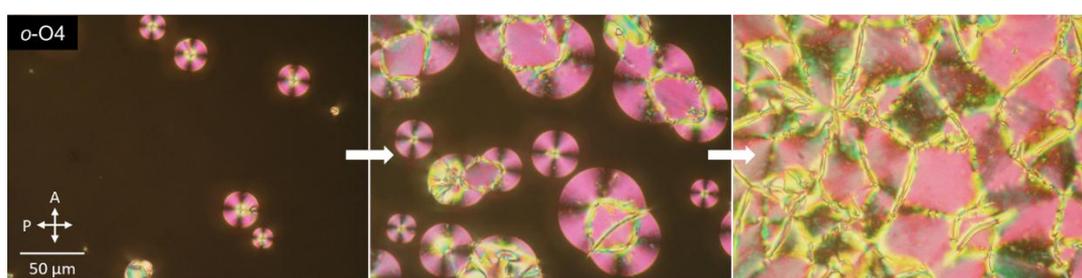


Fig. S2. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-04.

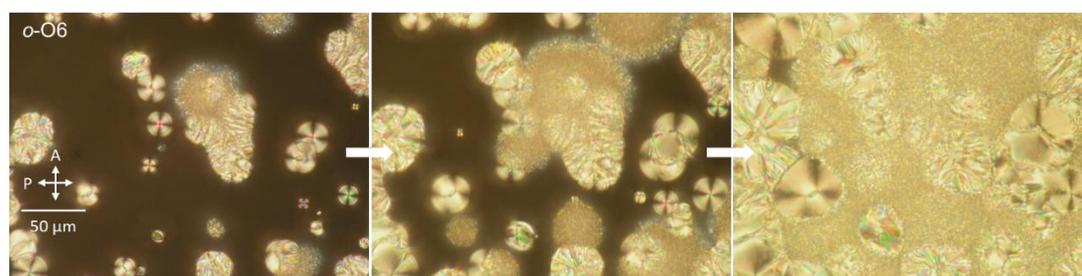


Fig. S3. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-06.

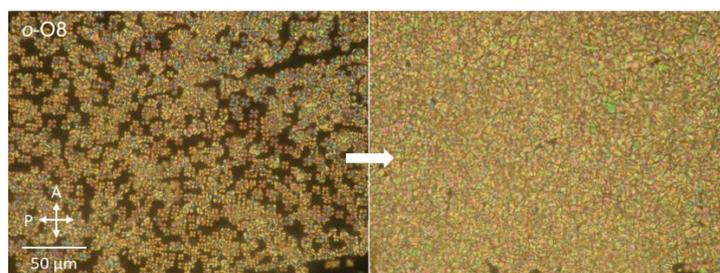


Fig. S4. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-08.

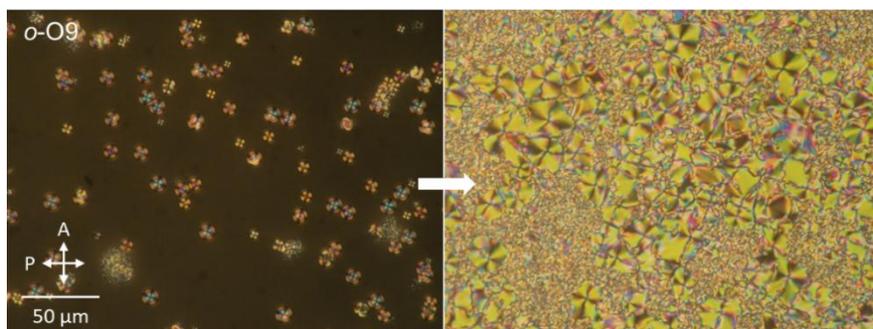


Fig. S5. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-O9.

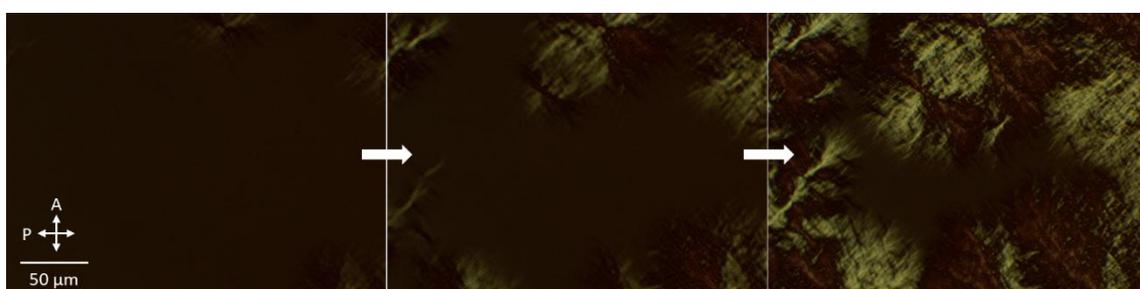


Fig. S6. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-O10.

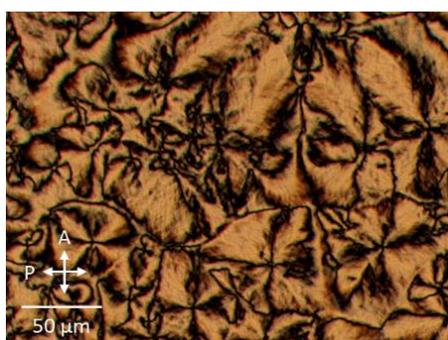


Fig. S7. POM image of a LC phase texture at ambient temperature of *o*-O10.

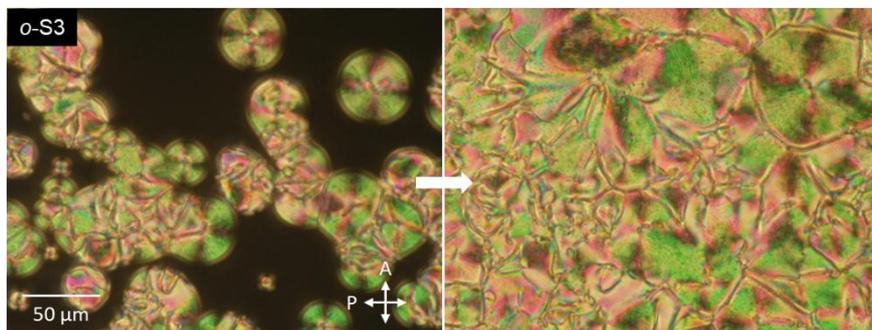


Fig. S8. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-S3.

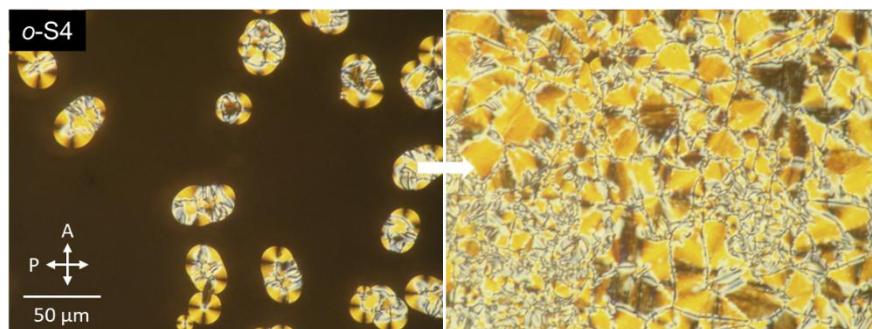


Fig. S9. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-S4.

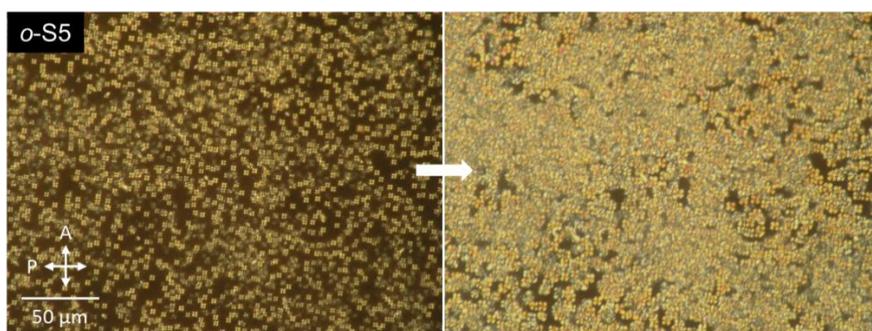


Fig. S10. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-S5.

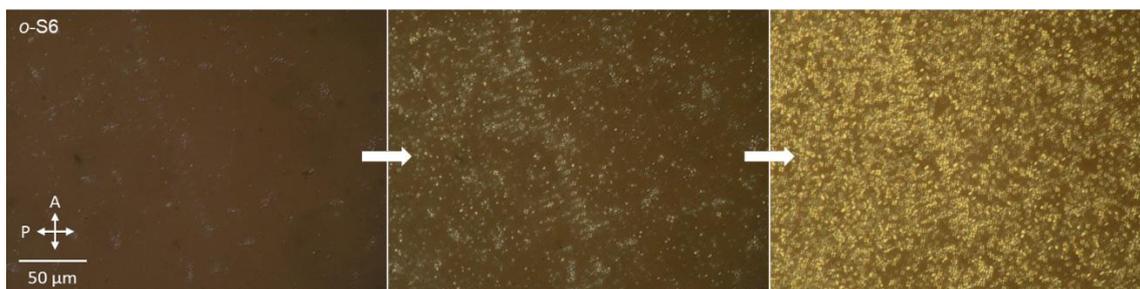


Fig. S11. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-S6.

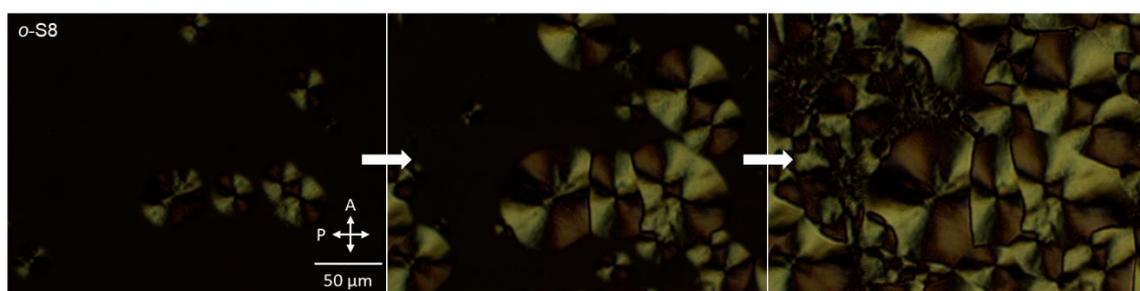


Fig. S12. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-S8.

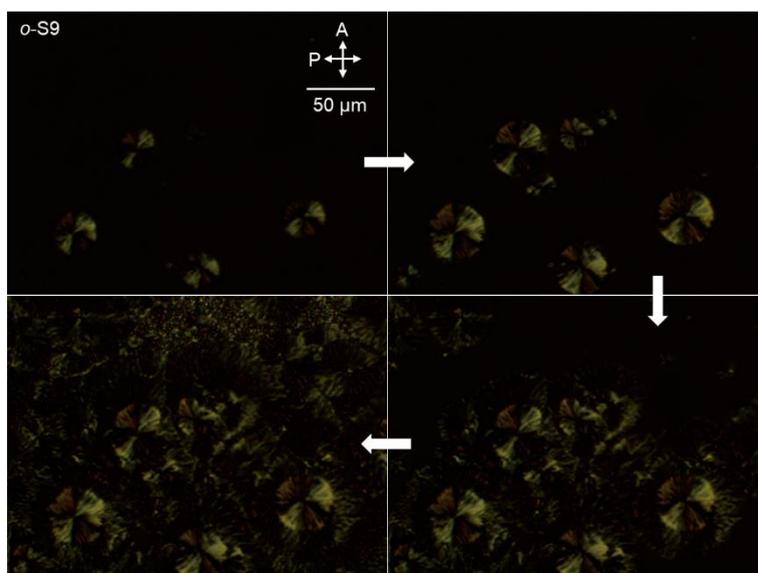


Fig. S13. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-S9.

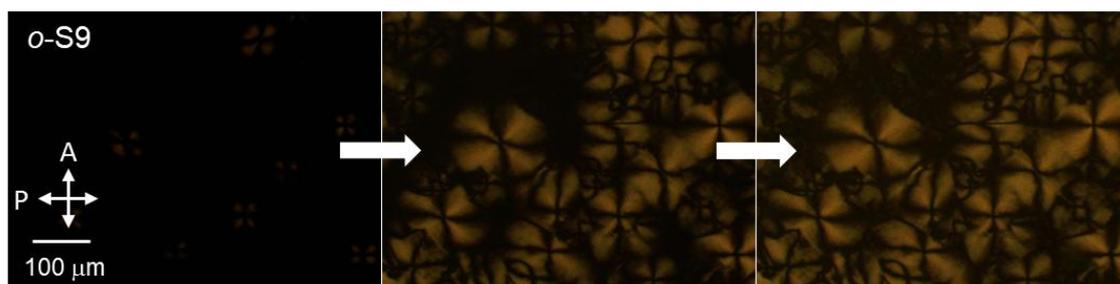


Fig. S14. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-S9.

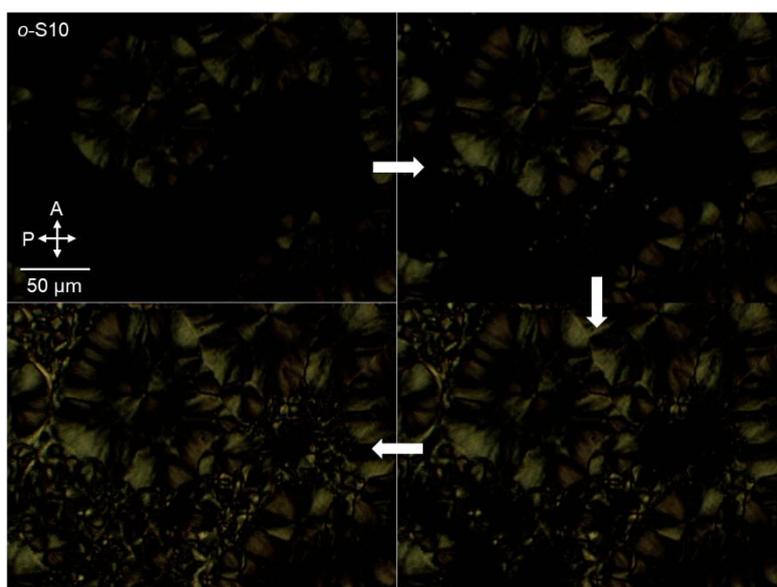


Fig. S15. POM images of the growth in the LC phase texture from the Iso phase upon cooling of *o*-S10.

3. DSC Curves

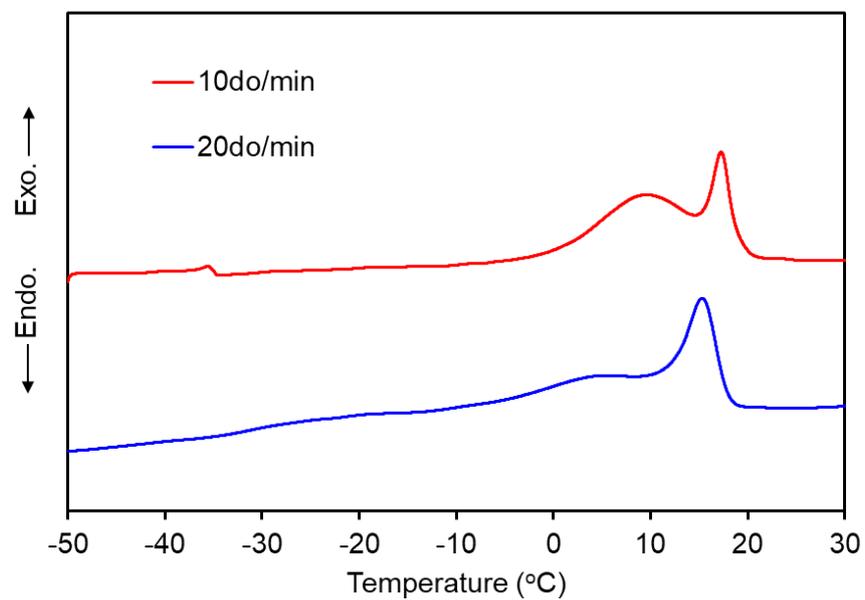


Fig. S16. DSC curves upon cooling of *o*-O10 at different cooling rates.

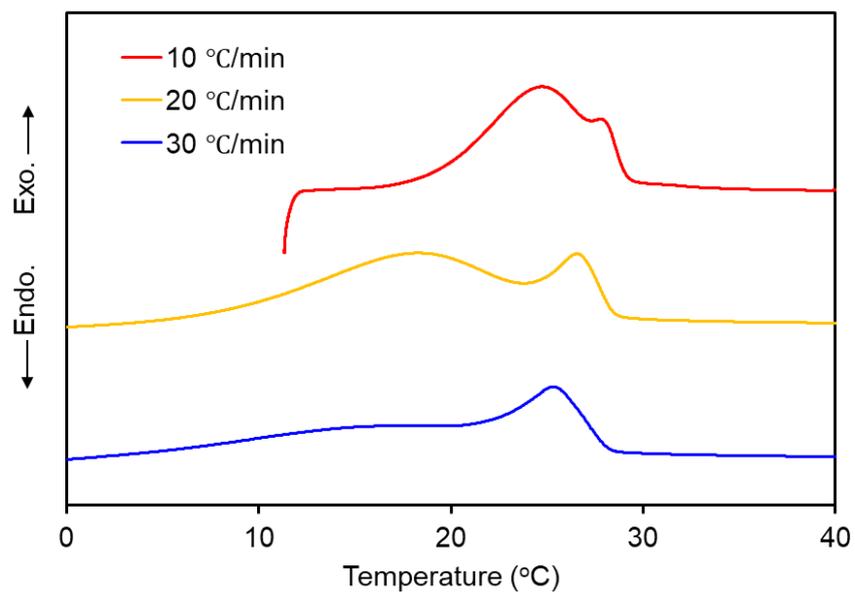


Fig. S17. DSC curves upon cooling of *o*-S8 at different cooling rates.

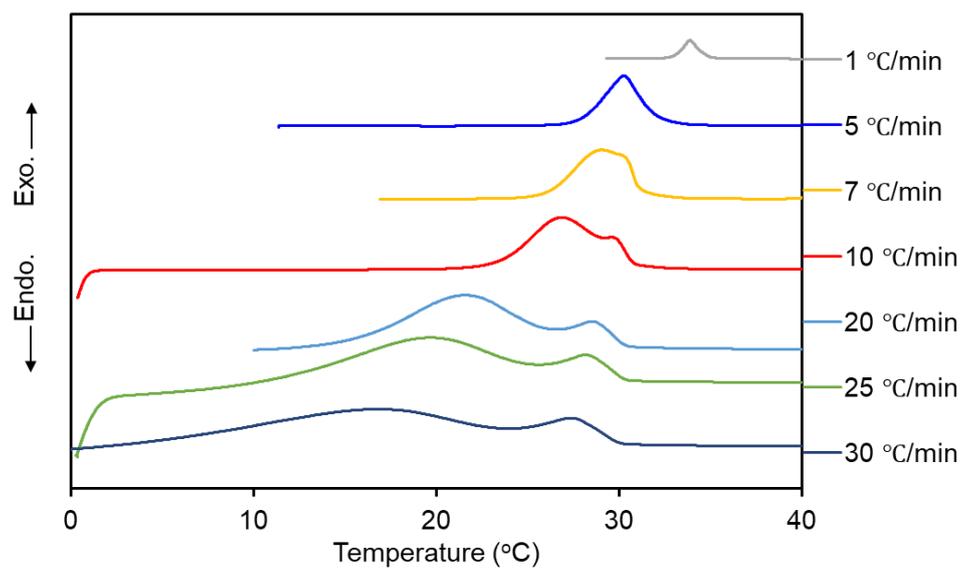


Fig. S18. DSC curves upon cooling of *o*-S9 at different cooling rates.

4. XRD patterns

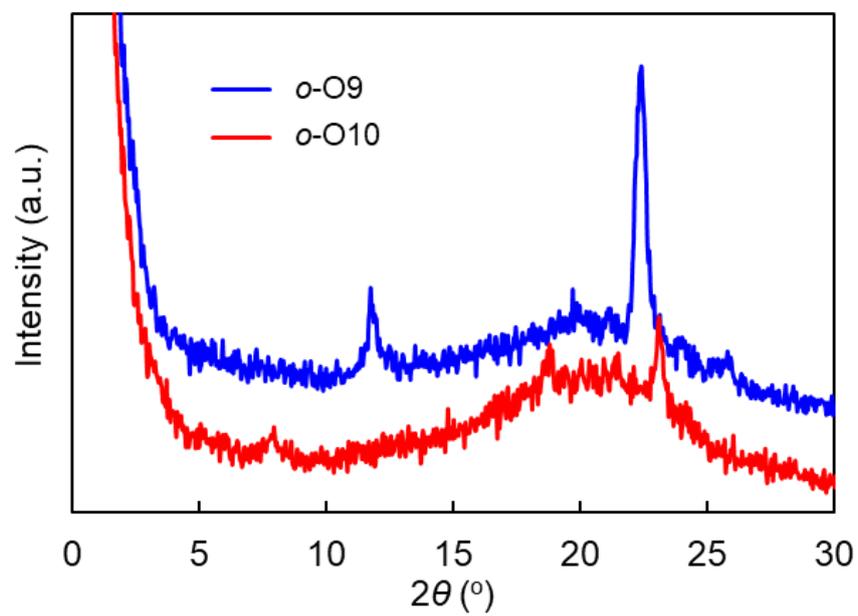


Fig. S19. 1D-XRD patterns of the melt-quenched *o*-O9 and *o*-O10 samples at ambient temperature.

5. P - E hysteresis loop measurements

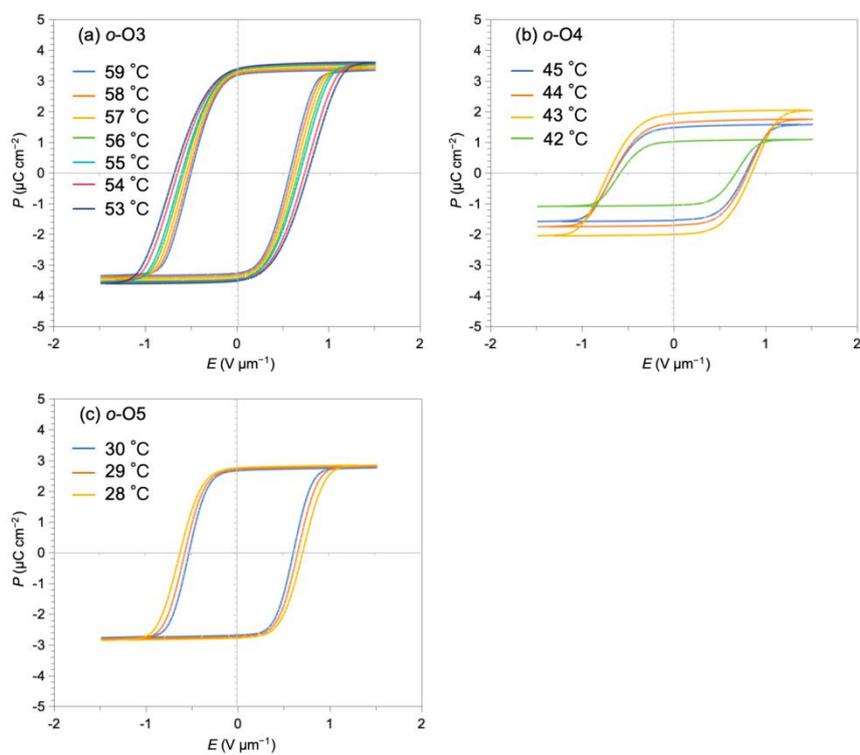


Fig. S20. P - E measurements of (a) o -O3, (b) o -O4, and (c) o -O5 at different temperatures in 20 μm cell. The measurement frequency was 200 Hz, 100 Hz and 20 Hz for o -O3, o -O4 and o -O5, respectively.

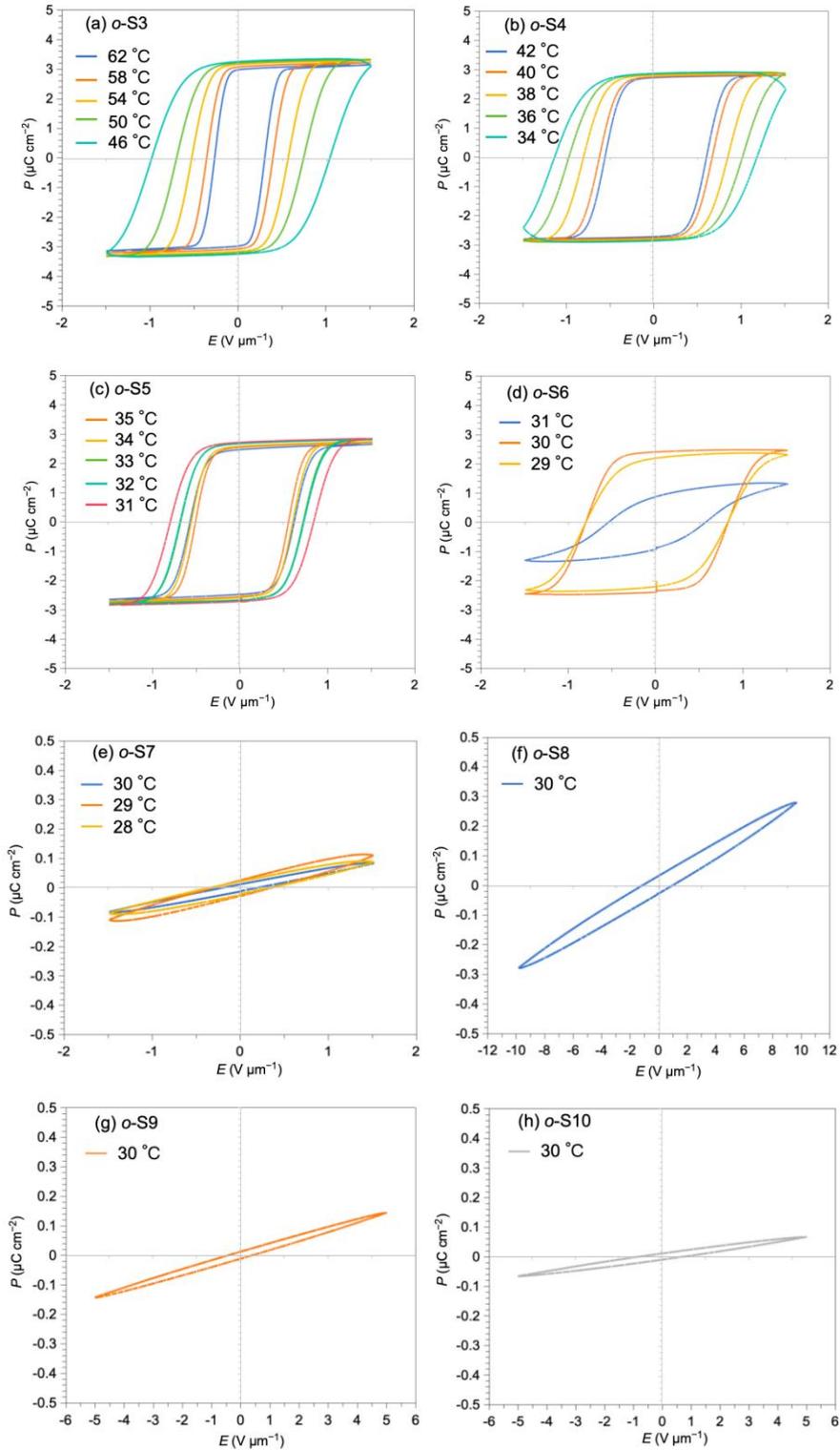


Fig. S21. P - E measurements of (a) o -S3, (b) o -S4, and (c) o -S5, and (d) o -S6, and (e) o -S7, (f) o -S8, (g) o -S9, (h) o -S10 at different temperatures in 20 μm cells. The measurement frequency was 50 Hz, 5 Hz, 3Hz, 2 Hz and 2 Hz, 0.1 Hz, 0.1 Hz, 0.1 Hz for o -S3, o -S4, o -S5, o -S6 and o -S7, o -S8, o -S9, o -S10 respectively.

6. Dielectric constant measurements

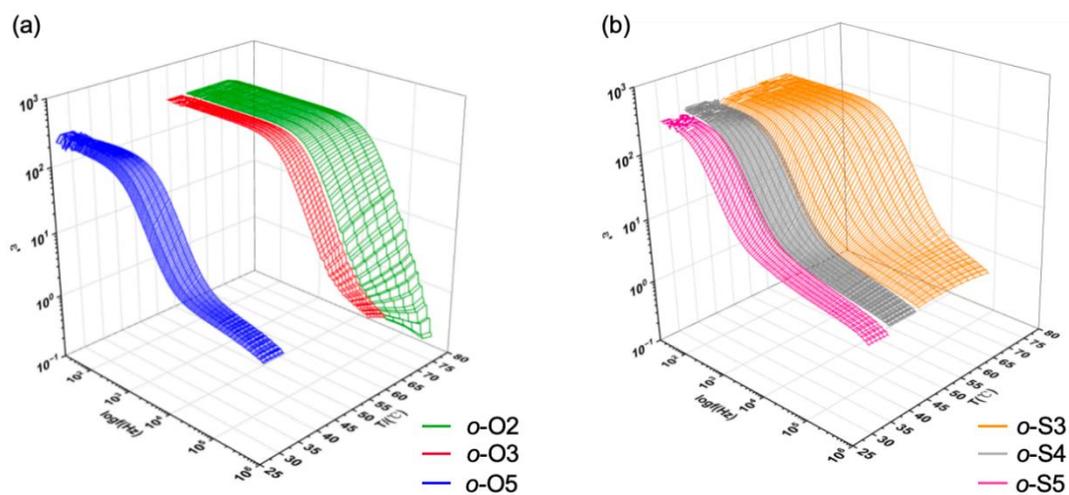


Fig. S22. Dielectric spectrum measurements of (a) *o*-O2, *o*-O3, *o*-O5, and (b) *o*-S3, *o*-S4, *o*-S5 at different temperatures in 9 μm cells. The measurement probe voltage was 0.05 V.

Reference

S1. Y. Arakawa, Q. Ning, S. Karthick and S. Aya, *J. Mater. Chem. C*, 2024, **12**, 16206–16217.