

Supplementary information

Liquid Crystalline PEDOT Derivatives Exhibiting Reversible Anisotropic Electrochromism and Linearly and Circularly Polarized Dichroism

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Experimental

Synthesis of another kinds of monomers and polymers

6-((4'-Cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl 2,5-dibromobenzoate (M2)

M2 was prepared using a method similar to that described for **M1**. Quantity used: triphenylphosphine (2.62 g, 20 mmol), DEAD (4.31 g, 40 wt% in toluene 20 mmol), 2,5-dibromobenzoic acid (2.68 g, 10 mmol), CB06OH (4.04 g, 10 mmol) and THF (50 ml). The crude product was passed through a column chromatograph (chloroform) and recrystallized from ethanol to give 2.6 g as a white solid (yield: 48%). ¹H NMR (270 MHz, CDCl₃, δ, from TMS): δ 7.8 (s, 1H), 7.6 (s, 2H), 7.5 (s, 2H), 7.4(s, 1H), 7.3 (s, 1H), 7.1 (s, 2H), 6.9 (s, 2H), 4.3 (t, 2H), 4.0 (t, 2H), 1.8~1.4 (m, 8H) ppm. ¹³C NMR (270 MHz, CDCl₃, δ, from TMS): δ 165.3, 160.3, 146.5, 139.1, 138.0, 129.5, 128.4, 127.3, 121.8, 118.5, 114.2, 111.2, 68.7, 64.1, 29.6, 29.1, 25.4 ppm

Bis(6-(4-(4-pentylcyclohexyl)phenoxy)hexyl) terephthalate (M3)

This compound was prepared using a method similar to that described for **M1**. Quantity used: triphenylphosphine (2.62 g, 10 mmol), DEAD (1.74 g, 40 wt% in toluene 10 mmol), 2,5-dibromoterephthalic acid (1.62 g, 5 mmol), PCH506OH (3.40 g, 10 mmol) and THF (50 ml). The crude product was passed through a column chromatograph (chloroform) and recrystallized from ethanol to give 2.2 g as a white solid (yield: 57%). ¹H NMR (270 MHz, CDCl₃, δ, from TMS): δ 7.9 (s, 4H), 7.8 (s, 4H), 7.6 (s, 4H), 7.4 (s, 4H) 6.9 (d, 2H), 4.3 (t, 4H), 4.1 (t, 4H), 2.8 (m, 4H), 2.0~1.4 (m, 58H) ppm. ¹³C NMR (270 MHz, CDCl₃, δ, from TMS): δ 158.3, 147.3, 145.1, 141.0, 138.1, 132.5, 132.2, 130.1, 129.8, 128.0 127.7, 120.6, 118.5, 114.9, 111.6, 111.3, 72.0, 68.7, 68.3, 32.0, 31.1, 29.6, 29.4, 25.9 ppm.

Bis(6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl) 2,5-dibromoterephthalate (M4)

This compound was prepared using a method similar to that described for **M1**. Quantity used: triphenylphosphine (2.62 g, 10 mmol), diethyl azodicarboxylate, DEAD (1.74 g, 40 wt% in toluene 20 mmol) 2,5-dibromoterephthalic acid (1.62 g, 5 mmol) and CB06OH (2.95 g, 10 mmol) and THF (50 ml). The crude product was passed through a column chromatograph (chloroform) and recrystallised from

ethanol to give 0.84 g as a white solid (yield: 26%). ^1H NMR (270 MHz, CDCl_3 , δ , from TMS): δ 8.2 (s, 2H), 7.8 (s, 4H), 7.7 (s, 4H), 7.4 (s, 4H), 6.9 (s, 4H), 4.3 (t, 4H), 4.0 (t, 4H), 2.7 (m, 4H), 1.7~1.2 (m, 16H) ppm. ^{13}C NMR (270 MHz, CDCl_3 , δ , from TMS): δ 167.3, 158.3, 145.5, 141.7, 138.0, 129.2, 128.6, 127.7, 121.3, 118.6, 114.9, 111.3, 68.7, 64.0, 35.6, 35.0, 29.6, 29.1, 25.9, 25.1 ppm

1,4-Dibromo-2,5-bis(pentylcyclohexylphenoxy-1-hexyl)benzene (M5)

To a solution of triphenylphosphine (1.12 g, 4.3 mmol) and DEAD (1.85 g, 40 wt% in toluene, 4.3 mmol) in THF (3 mL) was added and stirred for 1 hour at room temperature. Then, 2,5-dibromohydroquinone (0.52 g, 1.93 mmol) and PCH506OH (1.44 g, 4.3 mmol) in THF (10 mL) were very slowly added via pressure equalized dropping funnel. The reaction mixture was stirred at room temperature overnight under an argon atmosphere. Thin layer chromatography (TLC) indicated completion of the reaction. The solution was extracted with dichloromethane, washed with water thoroughly, and dried over anhydrous sodium sulfate. The dichloromethane layer was removed by evaporation and was purified by column chromatography (silica gel, dichloromethane). The solvent was removed in vacuum and the residue was further purified through vacuum distillation to give 1.02 g as a white solid (Yield: 42%). ^1H NMR (270 MHz, CDCl_3 , δ , from TMS): δ 7.3 (s, 4H), 7.0 (s, 2H), 6.9 (s, 4H), 4.3 (t, 4H), 4.0 (t, 4H), 2.7 (m, 4H), 1.8~0.8 (m, 58H) ppm. ^{13}C NMR (270 MHz, CDCl_3 , δ , from TMS): δ 156.3, 147.3, 138.5, 120.7, 114.0, 110.8, 68.7, 68.0, 43.6, 37.0, 32.1, 31.1, 29.5, 28.9, 27.1, 25.9, 22.5, 14.0 ppm.

1,4-Dibromo-2,5-bis[1,6-dioxy-6-(4'-cyano-4-biphenyl)hexyloxy]benzene (M6)

This compound was synthesized using a method similar to that described for **M5**. Quantity used: triphenylphosphine (1.12 g, 4.25 mmol), DEAD (1.85 g, 40 wt% in toluene 4.25 mmol), 2,5-dibromohydroquinone (0.52 g, 1.93 mmol), CB06OH (1.25 g, 4.25 mmol) and THF (13 mL). The crude product was passed through a column chromatograph (dichloromethane) and recrystallised from ethanol to give 1.16 g as a white solid (yield: 42%). ^1H NMR (270 MHz, CDCl_3 , δ , from TMS): δ 8.2 (s, 2H), 7.7~7.5 (m, 8H), 7.5~7.4 (m, 6H), 7.0 (m 2H), 4.3 (t, 4H), 4.00 (t, 4H), 1.84~0.85 (m, 16H) ppm. ^{13}C

NMR (270 MHz, CDCl_3 , δ , from TMS): δ 158.3, 147.8, 145.5, 132.7, 132.4, 132.1, 129.7, 129.1, 127.7, 120.5, 118.8, 114.8, 111.5, 68.6, 29.7, 25.8 ppm.

Poly[1-oxy-(6-(4'-cyano-4-biphenyl)-hexyl)-3,4-ethylenedioxythiophene benzoate] (P2)

This polymer was synthesized using a method similar to that described for **P1**. Quantity used: **M2** (545 mg, 1.0 mmol), 2,5-bis(tributylstannyl-3,4-ethylenedioxythiophene) (720 mg, 1.0 mmol), $\text{Pd}(\text{PPh}_3)\text{Cl}_2$ (15 mg, 0.02 mmol) and toluene (5 ml). The resulting precipitate was collected by filtration and dissolved in minimum amount of THF (5 mL) and stirred in methanol (300 mL) for 24 h. After filtration, the product was dried under vacuum to give 0.78 g as a yellow powder (yield: 62%). FT-IR (KBr, cm^{-1}): 2935 (s, $\nu_{\text{CH}_2\text{CH}_3}$) 2224 (s, $\nu_{\text{C}\equiv\text{N}}$) 1718 (s, $\nu_{\text{C=O}}$) 1602 (s, $\nu_{\text{C=C}}$) 1507 (s, ν_{CH}) 1250 (m, $\nu_{\text{C-O-C}}$) 824 (s, $\delta_{\text{C=O}}$). ^1H NMR (270 MHz, CDCl_3 , δ , from TMS): δ 7.8 (s, 1H), 7.6 (s, 2H), 7.5 (s, 2H), 7.4 (s, 1H), 7.3 (s, 1H), 7.1 (s, 2H), 6.9 (s, 2H), 4.6 (t, 2H), 4.3 (t, 2H), 4.0 (t, 2H), 1.8~1.4 (m, 8H) ppm. ^{13}C NMR (270 MHz, CDCl_3 , δ , from TMS): δ 168.3, 158.3, 146.5, 139.1, 138.1, 132.1, 130.8, 130.1, 129.5, 128.4, 127.3, 121.8, 118.5, 114.2, 111.2, 68.7, 65.2, 64.1, 29.6, 29.3, 28.5, 27.4, 25.5, 10.1 ppm

Poly[1,4-(bis(4-pentylcyclohexylphenoxy)hexyl)-3,4-ethylenedioxythiophene terephthalate] (P3)

This polymer was synthesized using a method similar to that described for **P1**. Quantity used: **M3** (327 mg, 0.33 mmol), 2,5-bis(tributylstannyl-3,4-ethylenedioxythiophene) (240 mg, 0.33 mmol), $\text{Pd}(\text{PPh}_3)\text{Cl}_2$ (5 mg, 0.007 mmol) and toluene (2 ml). The resulting precipitate was collected by filtration and dissolved in minimum amount of THF (3 mL) and stirred in methanol (300 mL) for 24 h. After filtration, the product was dried under vacuum to give 0.25 g as a yellow-green powder (yield: 44%). FT-IR (KBr, cm^{-1}): 2935 (s, $\nu_{\text{CH}_2\text{CH}_3}$) 2922 (s, $\nu_{\text{C=O}}$) 1718 (s, ν_{CH}) 1510 (s, ν_{CH}) 1242 (m, $\nu_{\text{C-O-C}}$) 826 (s, $\delta_{\text{C=O}}$). ^1H NMR (270 MHz, CDCl_3 , δ , from TMS): δ 7.9 (s, 4H), 7.8 (s, 4H), 7.6 (s, 4H), 7.4 (s, 4H), 6.9 (d, 2H), 4.3 (t, 4H), 4.1 (t, 4H), 3.9 (t, 4H), 2.8 (m, 4H), 2.0~1.4 (m, 58H) ppm. ^{13}C NMR (270 MHz, CDCl_3 , δ , from TMS): δ 158.3, 147.3, 145.1, 141.0, 138.1, 132.5, 132.2, 130.1, 129.8, 128.0, 127.7, 120.6, 118.5, 114.9, 111.6, 111.3, 72.0, 68.7, 68.3, 32.0, 31.1, 29.6, 29.4, 25.9, 15.5, 10.2 ppm.

Poly[1,4-bis-oxy-(6-(4'-cyano-4-biphenyl)hexyl)-3,4-ethylenedioxythiophene terephthalate] (P4)

This polymer was synthesized using a method similar to that described for **P1**. Quantity used: **M4** (293 mg, 0.33 mmol), 2,5-bis(tributylstannyl-3,4-ethylenedioxythiophene) (240 mg, 0.33 mmol), Pd(PPh₃)Cl₂ (5 mg, 0.007 mmol) and toluene (2 ml). The resulting precipitate was collected by filtration and dissolved in minimum amount of THF (3 mL) and stirred in methanol (300 mL) for 24 h. After filtration, the product was dried under vacuum to give 0.29 g as a yellow-green powder (yield: 55%). FT-IR (KBr, cm⁻¹): 2938 (s, $\nu_{\text{CH}_2\text{CH}_3}$) 2225 (s, $\nu_{\text{C}\equiv\text{N}}$) 1725 (s, $\nu_{\text{C=O}}$) 1494 (s, ν_{CH}) 1245 (m, $\nu_{\text{C-O-C}}$) 822 (s, $\delta_{\text{C=O}}$). ¹H NMR (270 MHz, CDCl₃, δ , from TMS): δ 7.8 (s, 2H), 7.7 (s, 4H), 7.6 (s, 4H), 7.4 (s, 4H), 6.9 (s, 4H), 4.2 (t, 4H), 4.0 (t, 4H), 3.9 (t, 4H), 1.7~1.2 (m, 16H) ppm. ¹³C NMR (270 MHz, CDCl₃, δ , from TMS): δ 167.3, 158.3, 145.5, 141.7, 138.0, 129.2, 128.6, 127.7, 121.3, 118.6, 114.9, 111.3, 68.7, 64.0, 35.6, 35.0, 29.6, 29.1, 25.9, 25.1 ppm

Poly[2,5-bis(4-pentylcyclohexylphenoxy-1-hexyl)-3,4-ethylenedioxythiophene phenylene] (P5)

This polymer was synthesized using a method similar to that described for **P1**. Quantity used: **M5** (308 mg, 0.33 mmol), 2,5-bis(tributylstannyl-3,4-ethylenedioxythiophene) (240 mg, 0.33 mmol), Pd(PPh₃)Cl₂ (5 mg, 0.007 mmol) and toluene (2 ml). The resulting precipitate was collected by filtration and dissolved in minimum amount of THF (3 mL) and stirred in methanol (300 mL) for 24 h. After filtration, the product was dried under vacuum to give 0.32 g as a yellow powder (yield: 59%). FT-IR (KBr, cm⁻¹): 3433 (s, $\nu_{\text{O-H}}$) 2920 (s, $\nu_{\text{CH}_2\text{CH}_3}$) 2851 (s, $\nu_{\text{C=O}}$) 1611 (s, ν_{CH}) 1510 (s, ν_{CH}) 1244 (m, $\nu_{\text{C-O-C}}$) 827 (s, $\delta_{\text{C=O}}$). ¹H NMR (270 MHz, CDCl₃, δ , from TMS): δ 7.3 (s, 4H), 7.0 (s, 2H), 6.9 (s, 4H), 4.3 (t, 4H), 4.0 (t, 4H), 3.8 (t, 4H), 2.7 (m, 4H), 1.8~0.8 (m, 58H) ppm. ¹³C NMR (270 MHz, CDCl₃, δ , from TMS): δ 156.3, 151.3, 147.3, 146.5, 138.5, 125.4, 120.7, 115.5, 114.0, 112.2, 110.8, 68.7, 68.0, 43.6, 37.0, 32.1, 31.1, 29.5, 28.9, 27.1, 25.9, 22.5, 14.0, 10.0 ppm.

Poly[2,5-bis(1,6-dioxy-6-(4'-cyano-4-biphenyl)hexyloxy)-3,4-ethylenedioxythiophene phenylene] (P6)

This polymer was synthesized using a method similar to that described for **P1**. Quantity used: **M6** (274 mg, 0.33 mmol), 2,5-bis(tributylstannyl-3,4-ethylenedioxythiophene) (240 mg, 0.33 mmol), Pd(PPh₃)Cl₂ (5 mg, 0.007 mmol) and toluene (2 ml). The resulting precipitate was collected by filtration and dissolved in minimum amount of THF (3 mL) and stirred in methanol (300 mL) for 24 h. After filtration, the product was dried under vacuum to give 0.25 g as a yellow powder (yield: 48%). FT-IR (KBr, cm⁻¹): 3431 (s, $\nu_{\text{O-H}}$) 2938 (s, $\nu_{\text{CH}_2\text{CH}_3}$) 2864 (s, $\nu_{\text{C=O}}$) 2224 (s, $\nu_{\text{C}\equiv\text{N}}$) 1602 (s, $\nu_{\text{C=C}}$) 1494 (s, ν_{CH}) 1248 (m, $\nu_{\text{C-O-C}}$) 820 (s, $\delta_{\text{C=O}}$). ¹H NMR (270 MHz, CDCl₃, δ , from TMS): δ 7.6 (s, 2H), 7.7~7.5 (m, 8H), 7.5~7.4 (m, 6H), 7.0 (m 2H), 4.3 (t, 4H), 4.0 (t, 4H), 3.8 (t, 4H), 1.8~0.8 (m, 16H) ppm. ¹³C NMR (270 MHz, CDCl₃, δ , from TMS): δ 159.3, 150.7, 147.8, 146.2, 146.0 145.5, 142.1 141.8, 132.7, 132.4, 132.1, 129.5, 128.1, 120.5, 118.8, 114.8, 112.3, 111.5, 68.6, 68.4, 64.5, 29.7, 25.8, 15.2, 9.8 ppm.

Figure captions

Figure S1. Polarizing optical micrographs (POMs) of the polymers in the cooling process. (a) Schlieren texture of **P3** at 112 °C, (b) Schlieren texture of **P4** at 95 °C, (c) nematic phase of **P5** at 145 °C and (d) nematic phase of **P6** at 155 °C in cooling process.

Figure S2. UV-Vis absorption (upper) and fluorescence (lower) spectra of the polymers in chloroform and as cast films: (a) **P3**, (b) **P4**, (c) **P5** and (d) **P6**. The insets contain photographs of the fluorescent colors of the polymers in chloroform and cast films.

Figure S3. UV-Vis and CD spectra of polymer films on ITO glasses: (a) **P2**, (b) **P3** and (c) **P6**. The polymer films were prepared by adding a chiral inducer, (*R*)- or (*S*)-PCH-BINOL or (*R*)- or (*S*)-CB06-BINOL, to the PEDOT derivatives at the N-LC temperature and cooling the mixtures to room temperature.

Figure S4. UV-Vis and CD spectra of **P4** and **P5** films on ITO glasses. The polymer films were prepared by adding a chiral inducer, (*R*)- or (*S*)-CB06-BINOL, to the PEDOT derivatives at the N-LC temperature and cooling the mixtures to room temperature.

Figure S5. Laue photographs (top) and X-ray diffraction pattern (bottom) of polymers: (a) **P2**, (b) **P3** and (c) **P5**.

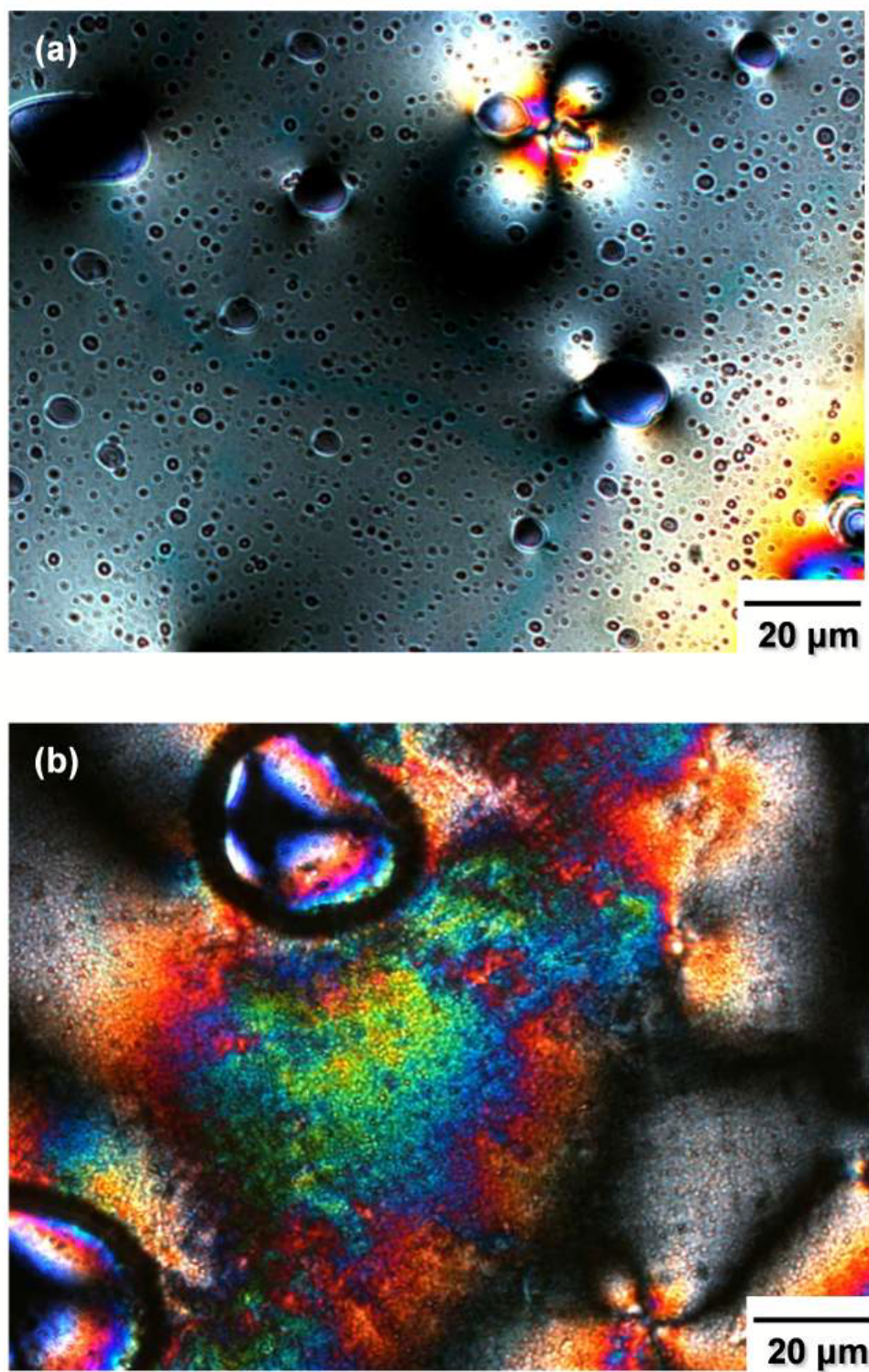


Figure S1. Polarizing optical micrographs (POMs) of the polymers in the cooling process. (a) Schlieren texture of **P3** at 112 °C, (b) Schlieren texture of **P4** at 95 °C, (c) nematic phase of **P5** at 145 °C and (d) nematic phase of **P6** at 155 °C in cooling process. (Continued)

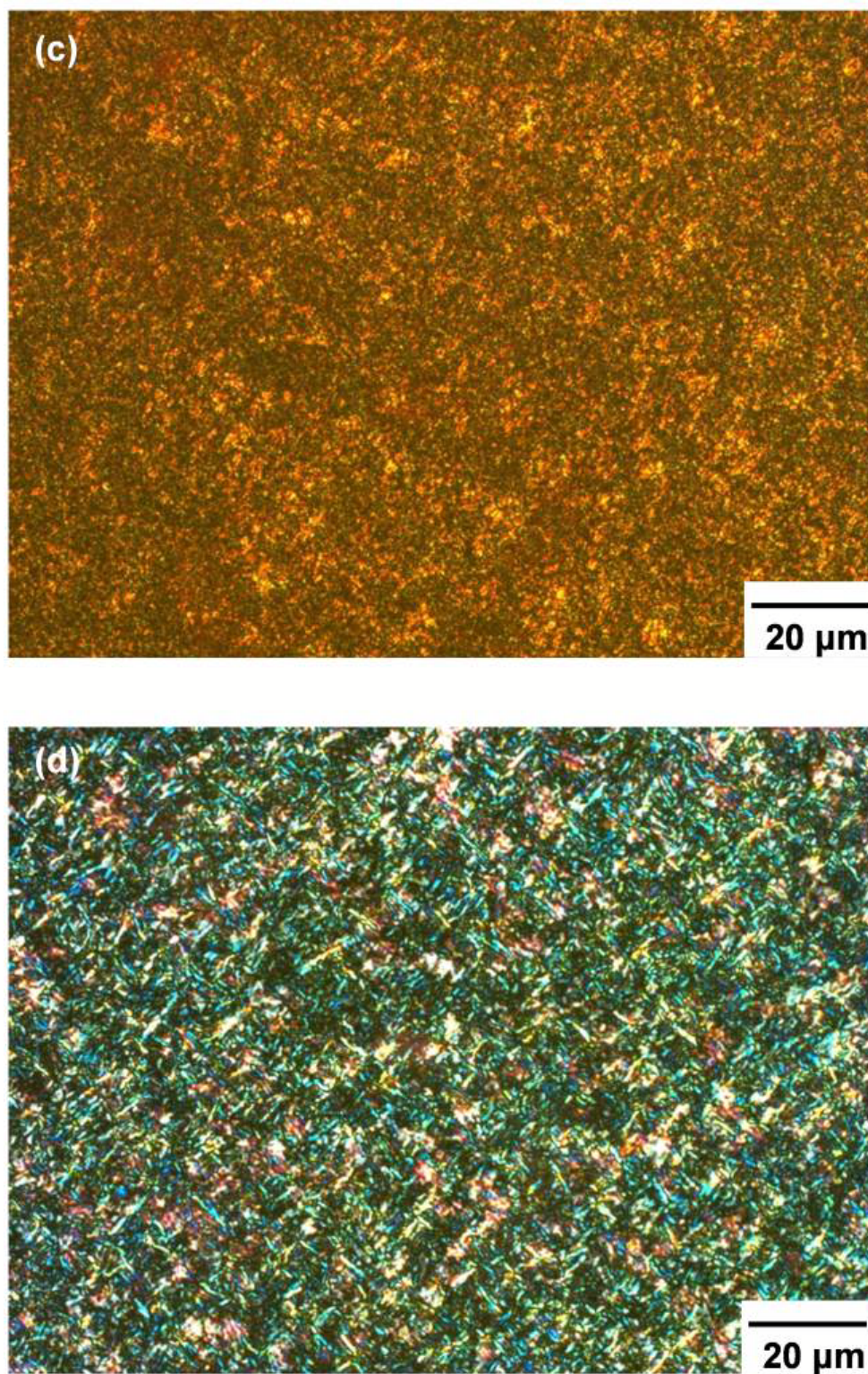


Figure S1

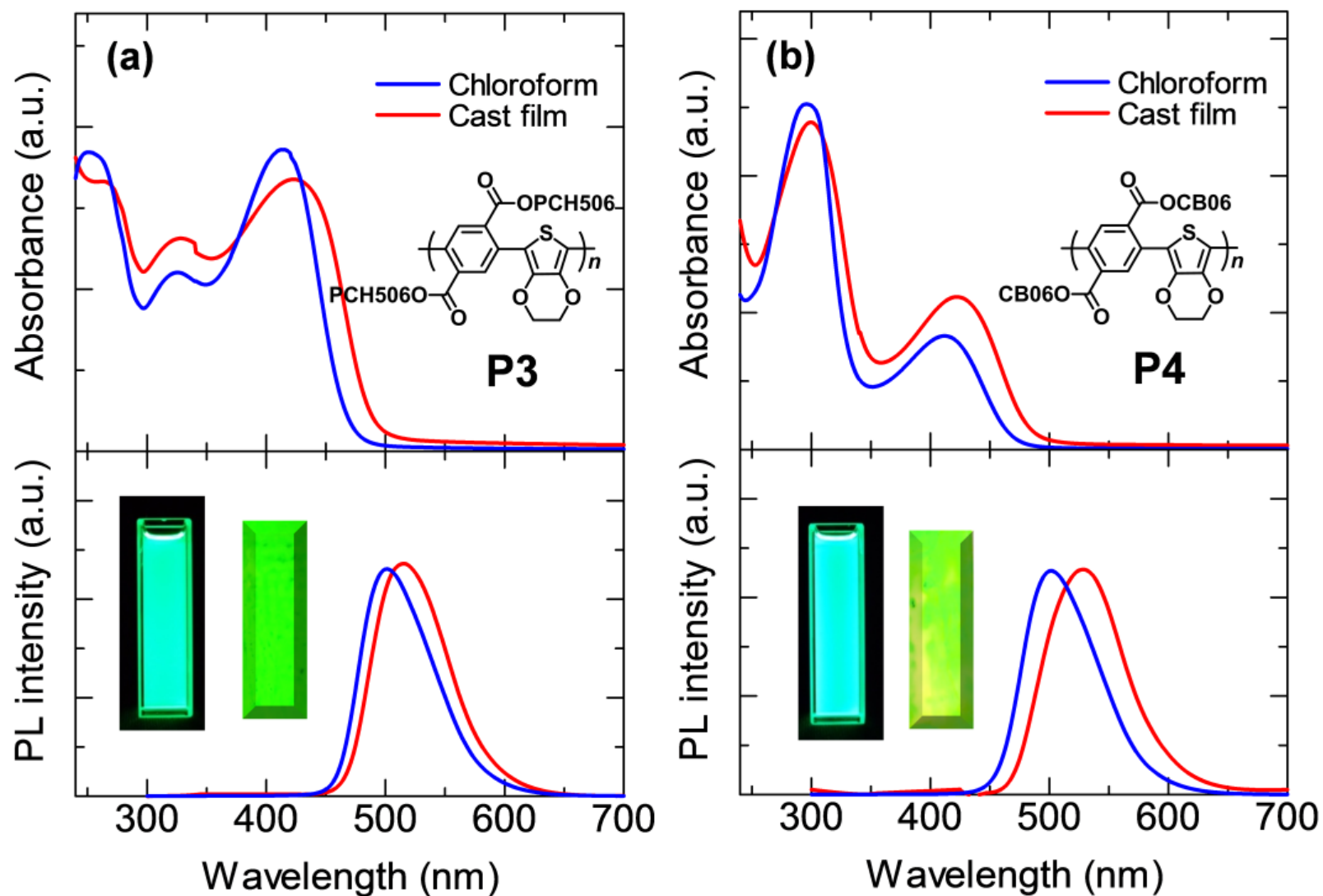


Figure S2. UV-Vis absorption (upper) and fluorescence (lower) spectra of the polymers in chloroform and as cast films: (a) **P3**, (b) **P4**, (c) **P5** and (d) **P6**. The insets contain photographs of the fluorescent colors of the polymers in chloroform and cast films. (Continued)

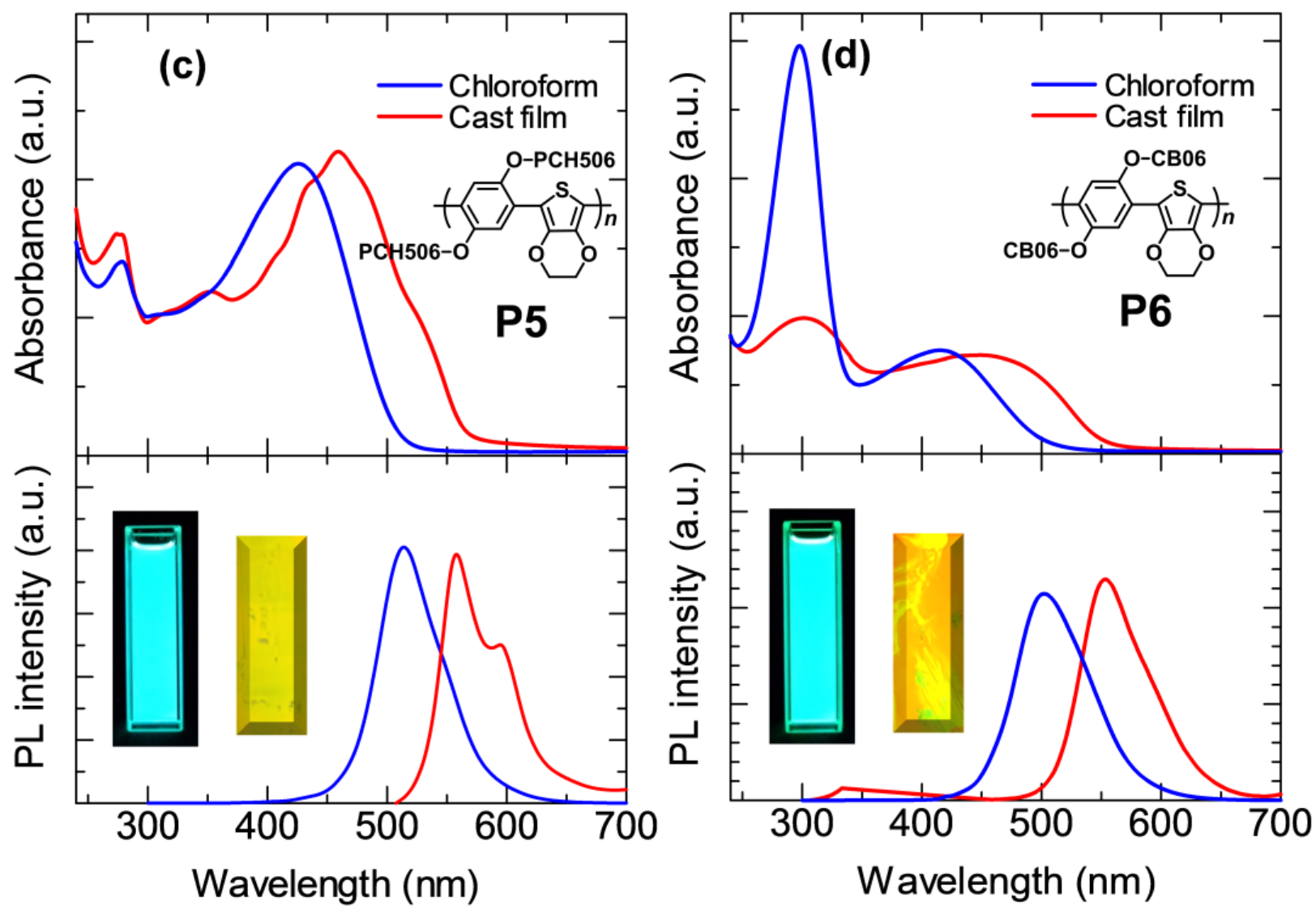


Figure S2.

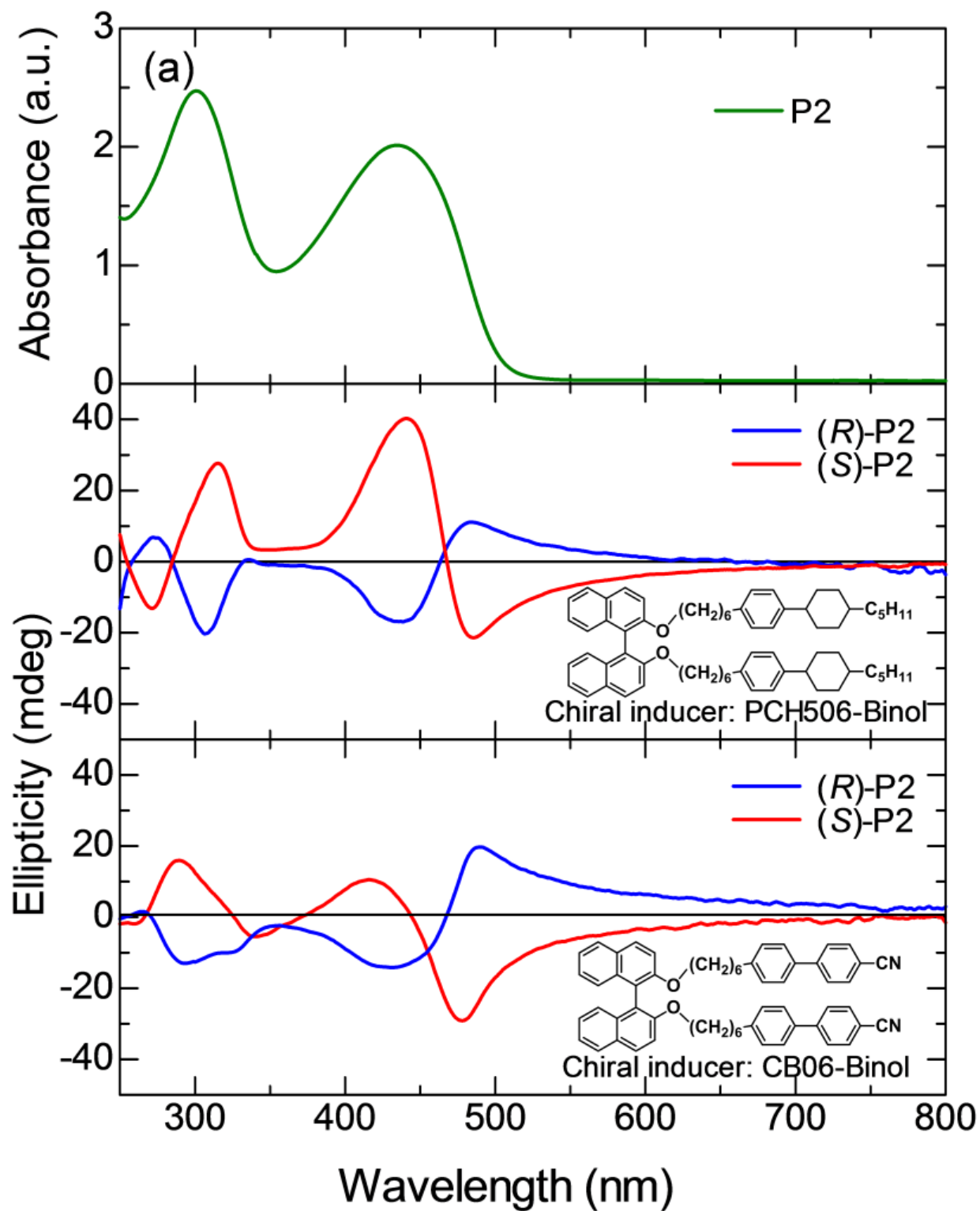


Figure S3. UV-Vis and CD spectra of polymer films on ITO glasses: (a) **P2**, (b) **P3** and (c) **P6**. The polymer films were prepared by adding a chiral inducer, (*R*)- or (*S*)-PCH-BINOL or (*R*)- or (*S*)-CB06-BINOL, to the PEDOT derivatives at the N-LC temperature and cooling the mixtures to room temperature.

(Continued)

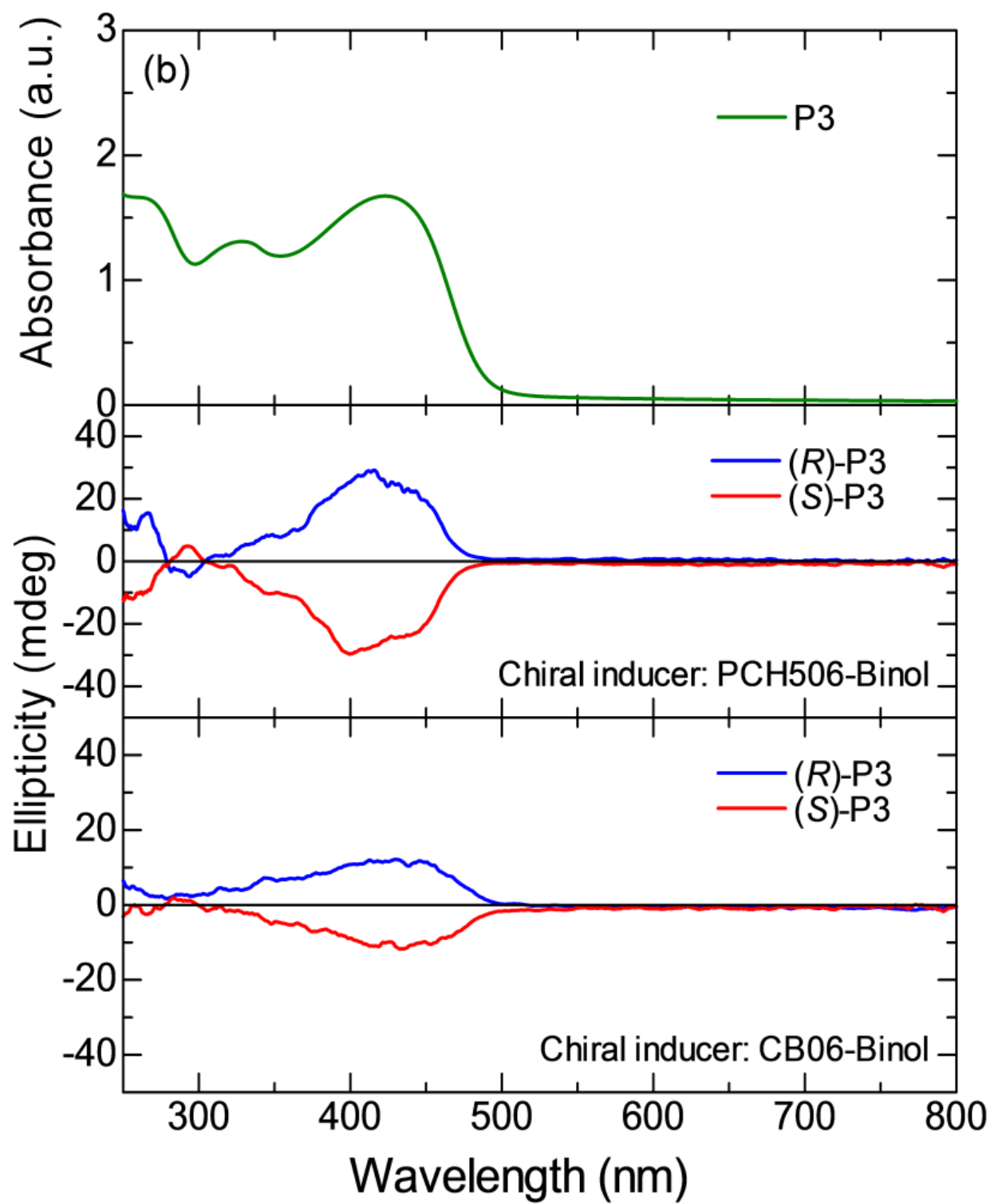


Figure S3

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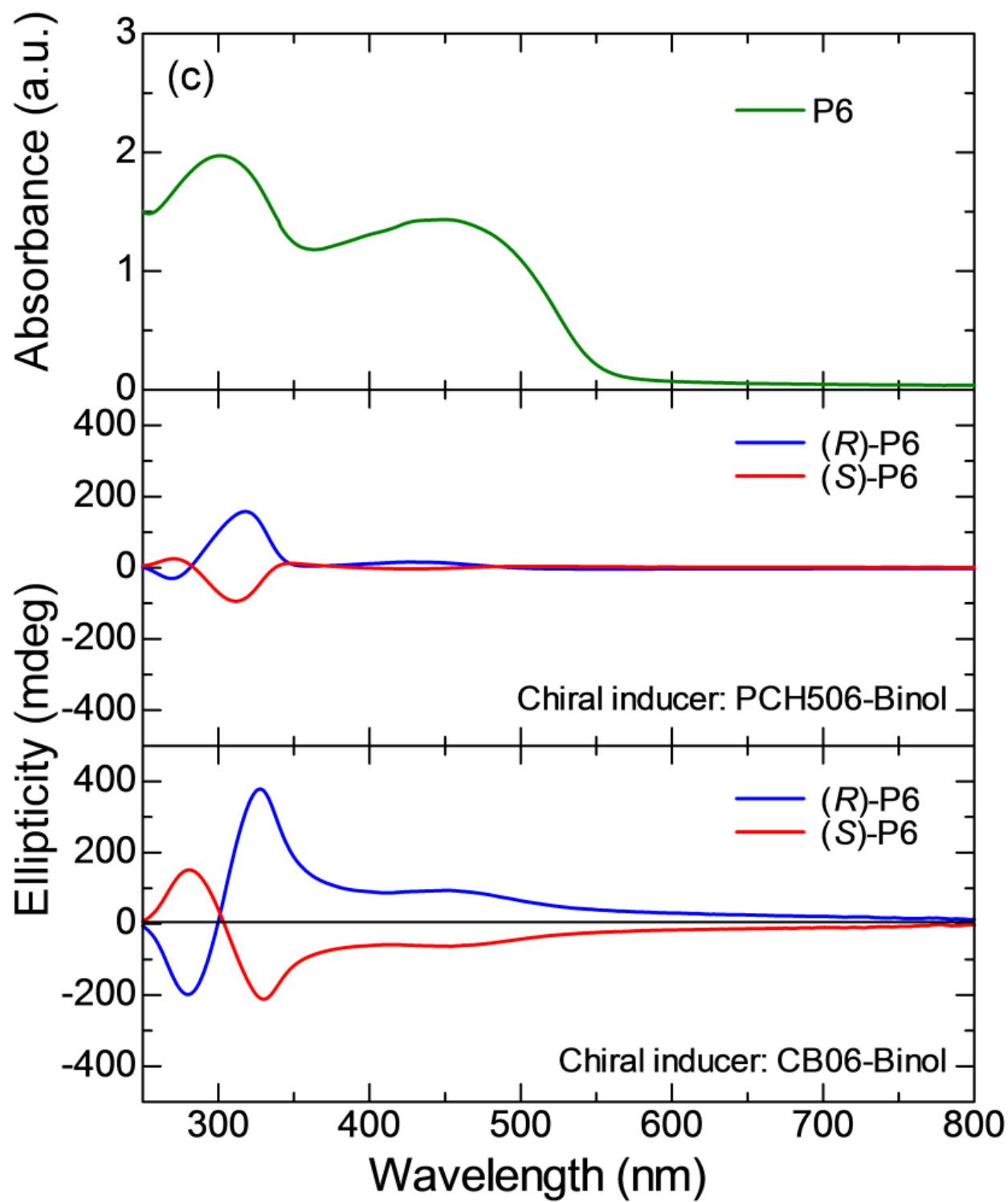


Figure S3.

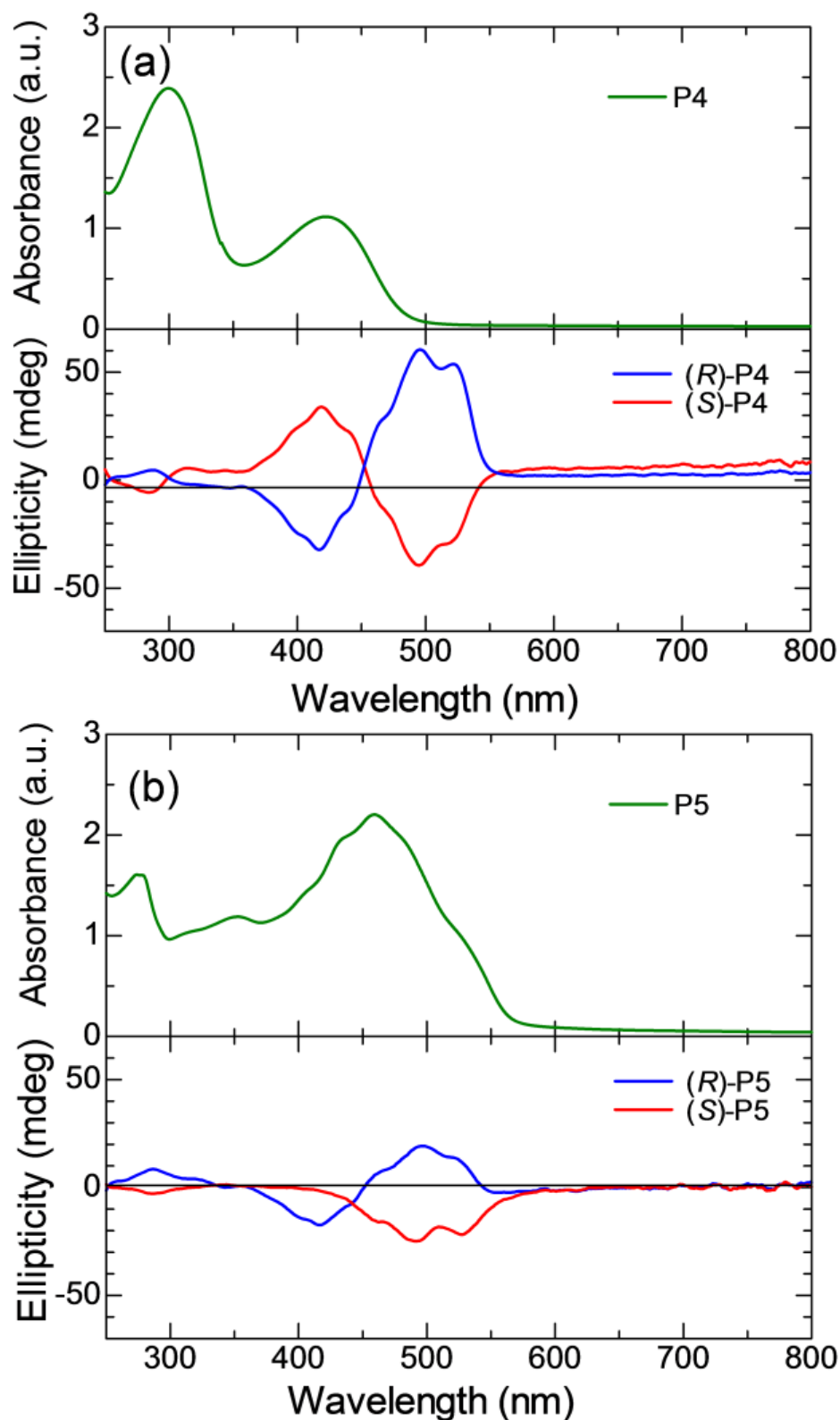


Figure S4. UV-Vis and CD spectra of **P4** and **P5** films on ITO glasses. The polymer films were prepared by adding a chiral inducer, (*R*)- or (*S*)-CB06-BINOL, to the PEDOT derivatives at the N-LC temperature and cooling the mixtures to room temperature.

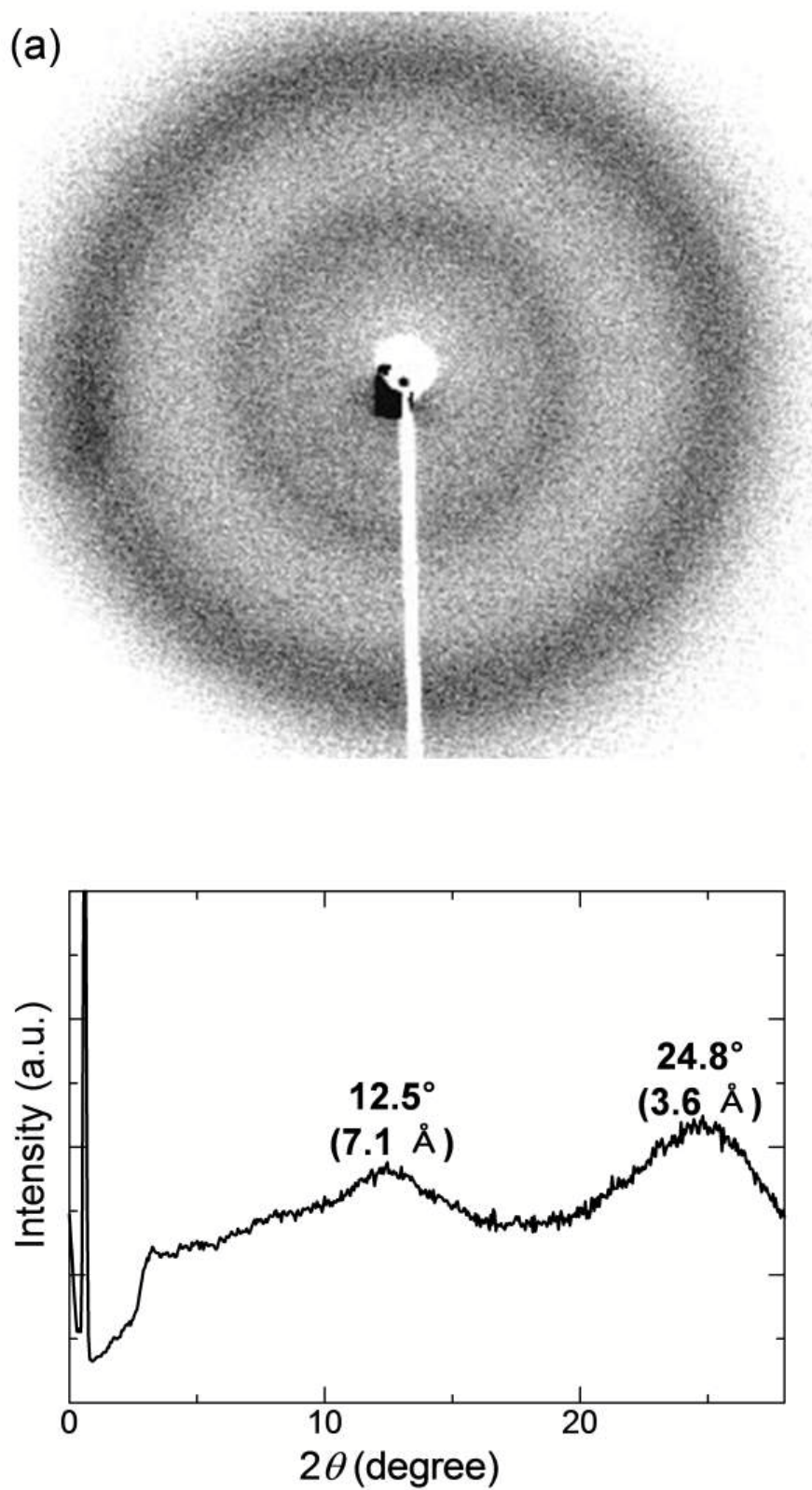


Figure S5. Laue photographs (top) and X-ray diffraction pattern (bottom) of polymers: (a) **P2**, (b) **P3** and (c) **P5**. (Continued)

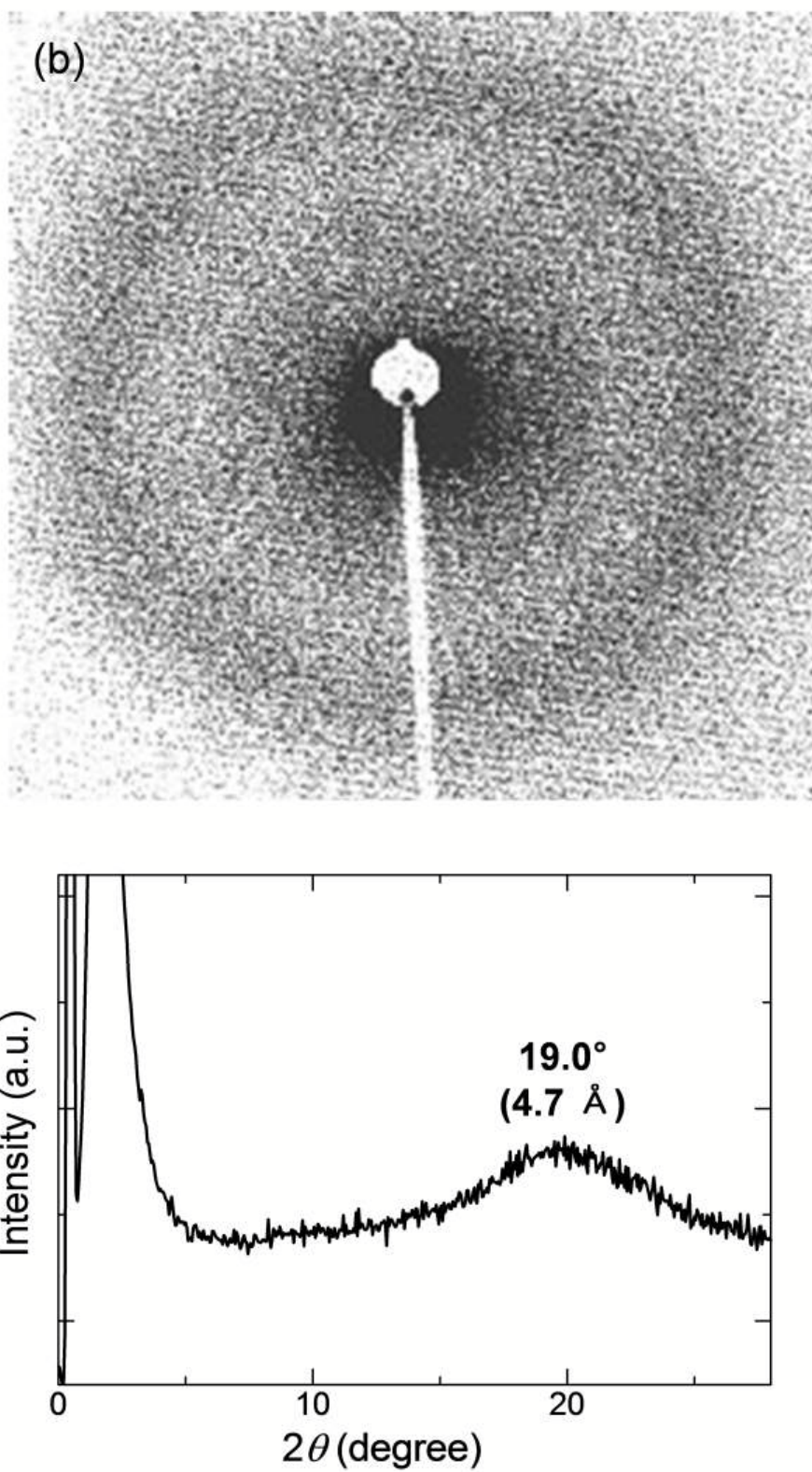


Figure S5.

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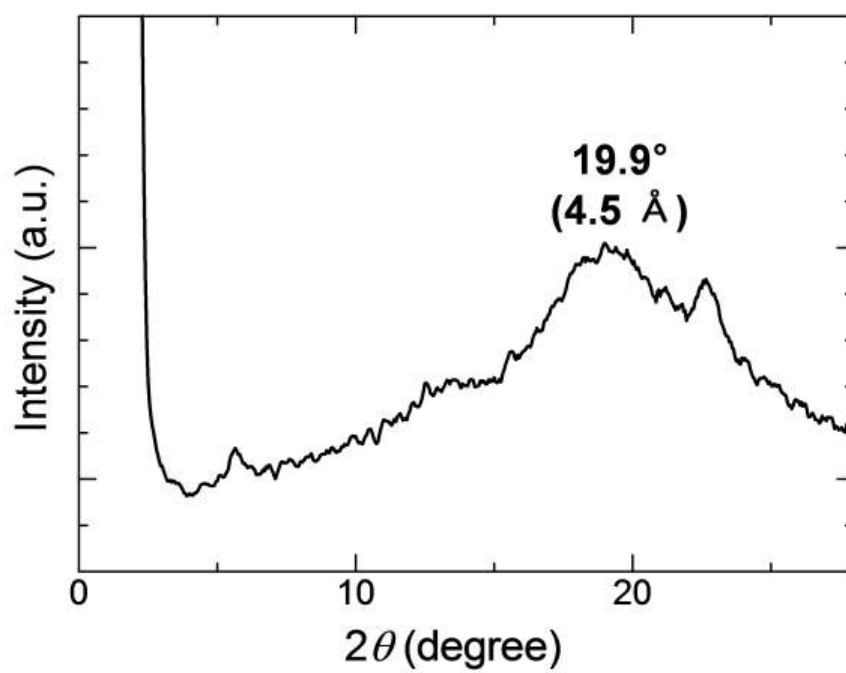
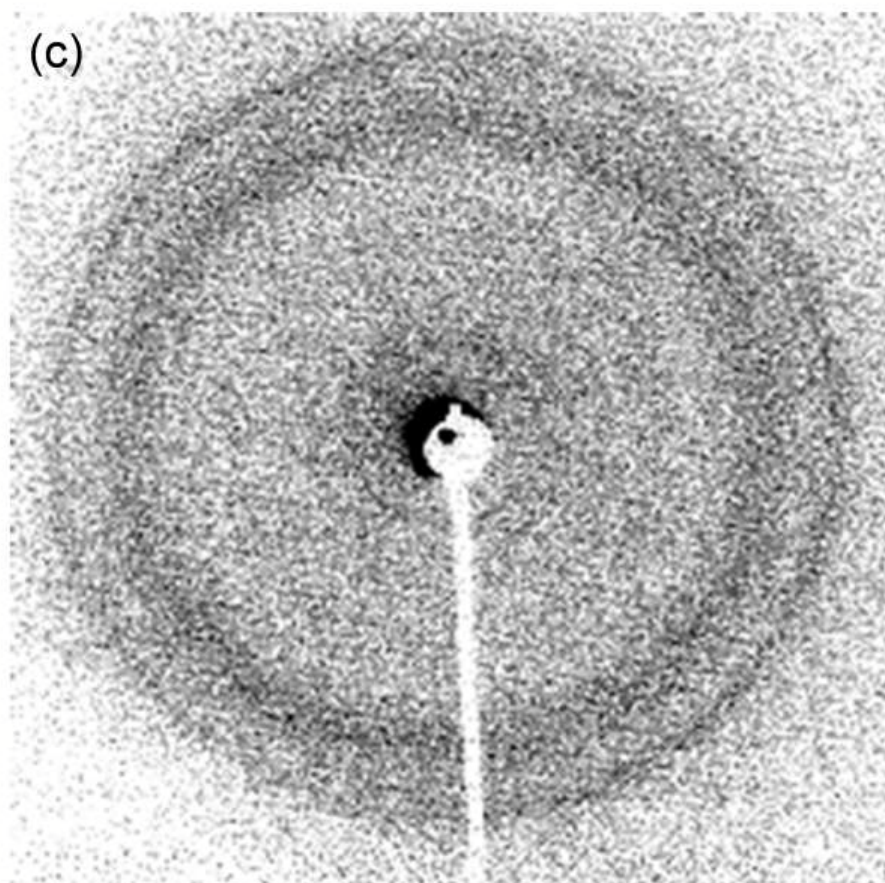


Figure S5.