Molecular redesign unlocks 99.89% light-driven control of azobiphenyl liquid crystals

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1. Materials and reagents

All chemicals and analytical-grade solvents were purchased from Sigma-Aldrich (India), Spectrochem (India), Hyma (India), Finar (India), and BLD (India) and used as received. Standard procedures were followed to dry the solvents whenever necessary. The progress of the synthesis was monitored using thin-layer chromatography (TLC) on pre-coated plates, which were visualized using 5% phosphomolybdic acid in water. The crude products were purified by gravity column chromatography using 100–200 mesh silica and subsequently recrystallized. The purity and structures of the compounds were confirmed using spectroscopic techniques.

2. Instruments and methods

Structural characterization: All structural characterizations have been performed in the masked area, about 5 mg of the compound was dissolved in 10 mL of deuterated chloroform ($CDCl_3$) for proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy. Tetramethylsilane (TMS) was used as the internal standard, and the spectra were recorded on a Bruker Varian Unity 400 and a Varian Unity 500 spectrometer. Elemental analysis was performed through a Microselect CHN analyser instrument for selected compounds. Functional groups were identified using FTIR with the KBr pellet method on a Bruker ALPHA II spectrometer equipped with a Platinum Diamond ATR accessory (Bruker Optics, Germany) and analyzed using OPUS software.

3. Mesophase characterization

Differential Scanning Calorimetry: Enthalpy changes were determined from DSC thermograms recorded on a PerkinElmer DSC-7, with heating and cooling performed at a rate of 10 °C/min. A

second heating/ cooling cycle was used for precise evaluation of the phase transition temperature, which was calibrated using indium as a standard.

Polarized Optical Microscopy: All textural observations are performed with a Nikon Optiphot-2 polarizing microscope equipped with a Mettler FP-82 HT hot stage and control unit (Controlled Liquid Nitrogen Accessory)

2D X-ray diffraction: X-ray studies were carried out using an Incoatec (Geesthacht, Germany) IμS microfocus source with a monochromator for CuKα radiation (λ = 0.154 nm), calibration with the powder pattern of $Pb(NO_3)_2$, 3 mg of sample placed on a glass plate on a Linkam hot stage HFS-X350-GI (rate: 1 K/min). Exposure time was 5 min; the sample-detector distance was 9.00 cm for WAXS and 26.80 cm for SAXS. The diffraction patterns were recorded with a Vantec 500 area detector (Bruker AXS, Karlsruhe) and transformed into 1D plots using GADDS software.2

4. Photo Physical studies:

Photoisomerization measurements for all dimer molecules were carried out in a dark room at controlled temperature using a 1 cm quartz cuvette containing 0.1 μM solutions of the dimers in chloroform. The samples were irradiated with an OmniCure Series 2000 UV light source equipped with a heat filter and a 365 nm band-pass filter, providing an intensity of 1 mW cm^{-2} at the cuvette. Absorbance spectra were recorded as a function of irradiation time for photoisomerization and as a function of relaxation time for thermal back-relaxation.

5. DFT Calculations:

Thermal and kinetic parameters of dimer molecules were calculated using Gaussian 09 software using B3LYP-6311G (d,p) basis set.

6. Aggregation studies:

UV-Visible absorption spectra were recorded using a GENESYS 50 spectrophotometer, software version 3.0.0.18.

7. Electrochemical studies:

We conducted electrochemical characterization studies using a CHI 6194 B potentiostat in a three-electrode configuration at room temperature (27 ± 2 °C). We used a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl (saturated KCl) electrode as the reference electrode. Before the electrochemical measurements, we degassed all solutions with pure nitrogen for 15 minutes. We used 0.1 M $(Bu)_4NPF_6$ as the supporting electrolyte and performed all measurements at room temperature. We estimated the bandgap by adding 4.7 eV to the onset oxidation and reduction potentials (vs. Ag/Ag^+).

8. Experimental section:

Procedure to synthesize ethyl 4-aminobenzoate (2a): *p*-Aminobenzoic acid (3.0 g, 14 mmol) was dissolved in ethyl alcohol (25 mL), and concentrated H_2SO_4 (3 mL) was added dropwise. The reaction mixture was refluxed at 90 °C for two hours with constant stirring, and its progress was monitored by TLC until the starting material was consumed. The mixture was then cooled to room temperature and neutralized to pH 8 with 10% Na_2CO_3 to form a precipitate, which was filtered, washed with water, and dried under vacuum overnight.

2a: Ethyl 4-aminobenzoate [$C_9H_{11}NO_2$]: white solid, Rf = 0.55 (15 % EtOAc-hexanes): yield: 90%: *v* max in cm^{-1}(KBr) 3416, 3335 (NH), 1678 (C=O), 1308, 1272(C-O); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.86 - 7.84 (dd, *J* = 8.0 Hz, 2Hz, 2H), 6.64-6.62 (dd, *J* = 8.0 Hz, 2.0 Hz, 2H), 4.33-4.28 (dd, *J* = 8.0 Hz, 6Hz, 2H), 1.35-1.33 (t, *J* = 8.0 Hz, 3H)

General procedure to synthesize Ethyl (E)-4-((4-hydroxyphenyl) diazenyl) benzoate (3a).

Benzocaine (4.0 g, 14.8 mmol) was dissolved in 3N HCl, and a solution of sodium nitrite (1.22 g, 17.7 mmol) in a small amount of water was added dropwise to obtain a transparent solution. The reaction mixture was then slowly added to a phenol solution (2.78 g, 29.6 mmol) dissolved in 10% NaOH at 0 °C, and the mixture was stirred for 1 hour before being acidified to pH 4–5 with 1N HCl to form an orange precipitate. The resulting solid was filtered, washed with 50% methanol–water, and dried under vacuum to afford a pure orange amorphous compound.

3a: Ethyl (E)-4-((4-hydroxyphenyl) diazenyl) benzoate [$C_{15}H_{14}N_2O_3$]: orange solid, R*f* = 0.60 (20 % EtOAc-hexanes); yield: 75%; ν_{max} in cm^{-1} (KBr) 3350-3065 (O-H), 2230 (C≡N), 1495 (N=N); ^{1}H NMR (400 MHz, CDCl3) δ: 7.98-7.93 (dd, *J* = 8.0 Hz, 4.0 Hz, 4H), 7.83-7.81 (d, *J* = 8.0 Hz, 2H), 7.03-7.01 (d, *J* = 8.0 Hz, 2H), 5.51 (s, 1H, -OH).

3b: (E)-4-((4-hydroxyphenyl)diazenyl)benzonitrile [$C_{13}H_9N_3O$]: orange solid R*f* = 0.50 (10 % EtOAc-hexanes); yield:75%; ν_{max} in cm^{-1} (KBr) 3350-3065 (O-H), 2230 (C≡N), 1495 (N=N); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98-7.93 (dd, *J* = 8.0 Hz, 4.0 Hz, 4H), 7.83-7.81 (d, *J* = 8.0 Hz, 2H), 7.03-7.01 (d, *J* = 8.0 Hz, 2H), 5.51 (s, 1H, -OH).

General procedure to synthesize: Cholesteryl (n+1)-bromobutanoate (5 a-g; n = 3,4,5,6,7,8,9).

A mixture of ω-bromoalkanoic acid (n = 3, 0.5 g, 2.99 mmol), DCC (0.92 g, 4.49 mmol), and DMAP (0.38 g, 0.299 mmol) was stirred in DCM at 0 °C for 30 minutes. Cholesterol (1.15 g, 2.99 mmol) was then added slowly, and the reaction mixture was brought to room temperature and stirred for five hours, while the progress was monitored by TLC. After the reaction was completed, the reaction mixture was filtered through a Celite and silica gel bed to remove the byproduct (DCU) and then washed with DCM. The filtrate was concentrated under controlled pressure to obtain a white, waxy crude. The crude was purified through a 100-200 mesh silica gel column chromatogram, eluted with 2% ethyl acetate-hexane. The product fractions were collected and concentrated under controlled pressure. Final product obtained is white solid (**5a**).

Similar procedure followed for other spacer length intermediates (5b-g; n=4, 5, 6, 7, 8, 9)

5a: Cholesteryl 4-bromobutanoate [$C_{31}H_{51}BrO_2$]: R*f* = 0.6 (3% EtOAc: hexanes); White solid; yield: 78%; ^{1}H NMR (400MHz, CDCl3) δ: 5.31(brd, 1H), 4.5-4.49 (m, 1H), 3.34 (t, *J* = 8.0Hz, 2H), 2.24 (m, 4H), 1.91-0.61 (m, 43H).

5b: Cholesteryl 5-bromopentanoate [$C_{32}H_{53}BrO_2$]: R_f = 0.6 (3% EtOAc: hexanes); White solid; yield: 76%; ^{1}H NMR (400MHz, $CDCl_3$) δ: 5.28 (brd, 1H), 4.61-4.51 (m, 1H), 3.32 (t, 2H, *J* = 8.0Hz), 2.24-2.20(m, 4H,), 1.93-0.61 (m, 45H).

5c: Cholesteryl 6-bromohexanoate [$C_{33}H_{55}BrO_2$]: R_f = 0.6 (3% EtOAc: hexanes); White solid; yield: 76%; ^{1}H NMR (400MHz, $CDCl_3$) δ: 5.32 (brd, 1H), 4.59-4.51 (m, 1H), 3.33 (t, 2H, *J* = 8.0Hz), 2.23-2.19 (m, 4H), 1.91-0.59 (m, 47H).

5d: Cholesteryl 7-bromoheptanoate [$C_{34}H_{57}BrO_2$]: R_f = 0.6 (3% EtOAc: hexanes); White solid; yield: 76%; ^{1}H NMR (400MHz, $CDCl_3$) δ: 5.30(brd, 1H), 4.60-4.52 (m, 1H), 3.35 (t, 2H, *J* = 8.0Hz), 2.24-2.20(t, 4H), 1.92-0.60 (m, 49H).

5e: Cholesteryl 8-bromooctanoate [$C_{35}H_{59}BrO_2$]: R_f = 0.6 (3% EtOAc: hexanes); White solid; yield: 76%; ^{1}H NMR (400MHz, $CDCl_3$) δ: 5.31(brd, 1H), 4.56-4.48 (m, 1H), 3.32 (t, 2H, *J* = 8.0Hz), 2.22-2.18 (t, 4H), 1.92-0.63 (m, 51H).

5f: Cholesteryl 9-bromononoate [$C_{36}H_{61}BrO_2$]: R_f = 0.6 (3% EtOAc: hexanes); White solid; yield: 76%; ^{1}H NMR (400MHz, $CDCl_3$) δ: 5.32 (brd, 1H), 4.61-4.51 (m, 1H), 3.33 (t, 2H, *J* = 8.0Hz), 2.25-2.21 (m, 4H), 1.91-0.60 (m, 53H).

5g: Cholesteryl 10-bromodecanoate [$C_{37}H_{63}BrO_2$]: R_f = 0.6 (3% EtOAc: hexanes); White solid; yield: 76%; ^{1}H NMR (400MHz, $CDCl_3$) δ: 5.31 (brd, 1H), 4.59-4.51 (m, 1H), 3.34 (t, 2H, *J* = 8.0Hz), 2.25-2.21 (m, 4H), 1.94-0.60 (m, 55H).

Synthesis of ACN-*n* series.

A solution of **3b** (50 mg, 0.224 mmol) in butanone (10 mL) was charged with potassium carbonate (46 mg, 0.336 mmol) and a catalytic amount of potassium iodide (2 mg), and Cholesteryl ω-bromoalkanoate (n = 3, 119 mg, 0.224 mmol) was then added to the reaction mixture, which was refluxed for 16 hours. After filtration, the solid obtained was washed with DCM and dried under controlled vacuum to yield an orange-colored compound. The crude product was purified by column chromatography on 100–200 mesh silica gel using 5% ethyl acetate–hexane as the eluent, and the collected fractions were concentrated under reduced pressure to afford a pure compound, which was further purified by recrystallization from 5% DCM–ethanol.

ACN-3: Cholesteryl 4-((E)-4-((4-hydroxyphenyl)diazenyl)benzonitrile)butanoate: Orange solid; R*f* = 0.3 (20% EtOAc: hexanes); yield: 92%; ν_{max} in cm^{-1}(KBr) 2942 (ν_{CH}), 2221 (ν_{CN}), 1730 ($\nu_{C=O}$), 1602 ($\nu_{C=C}$), 1242 (ν_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) 7.94-7.80 (dd, *J* = 4.8, 6.8 Hz, 4H), 7.27 (d, *J*= 4.0 Hz, 2H), 7.01 (d, *J* = 8.8Hz, 2H), 5.31(brd, 1H), 4.51-4.49 (m, 1H), 4.11 (t, *J* = 8.0Hz, 2H), 2.31-2.18 (m, 4H), 1.91-0.61 (m, 43H); Elemental analysis calcd for $C_{44}H_{59}N_3O_3$ (%): C,77.95; H, 8.77; N, 6.20; found, C 77.62; H 8.65; N 6.10.

ACN-4: cholesteryl 5-((E)-4-((4-hydroxyphenyl)diazenyl)benzonitrile)pentanoate: Orange solid, R_f = 0.3 (20% EtOAc: hexanes); yield: 93%; v_{max} in cm^{-1}(KBr) 2940 (v_{CH}), 2225 (v_{CN}), 1725 ($v_{C=O}$), 1597 ($v_{C=C}$), 1246 (v_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) δ: 7.92-7.80 (d, *J* =4.8, 6.8 Hz, 4H), 7.7 (d, *J* = 4.0 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 5.32 (brd, 1H), 4.58-4.50 (m, 1H), 4.06 (t, 2H, *J* = 6.4 Hz), 2.35-2.29 (m, 4H), 1.98-0.66 (m, 45H); Elemental analysis calcd for $C_{45}H_{61}N_3O_3$ (%):C,78.11; H, 8.89; N, 6.07; found, C 77.98; H 8.75; N 6.10.

ACN-5: cholesteryl 6-((E)-4-((4-hydroxyphenyl)diazenyl)benzonitrile)hexanoate; Orange solid, R_f = 0.3 (20% EtOAc: hexanes); yield: 93%; v_{max} in cm^{-1}(KBr) 2941 (v_{CH}), 2224 (v_{CN}), 1725 ($v_{C=O}$), 1594 ($v_{C=C}$), 1236 (v_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) δ: 7.91-7.79 (d, *J* =4.8, 6.8 Hz, 4H), 7.72 (d, *J* = 4.0 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 5.35(brd, 1H), 4.57-4.51 (m, 1H), 4.04 (t, 2H, *J* = 6.4 Hz), 2.34-2.28 (m, 4H), 1.98-0.66 (m, 47H); Elemental analysis calcd for $C_{46}H_{63}N_3O_3$ (%): C,78.26; H, 8.99; N, 5.95; found, C 78.44; H 8.79; N 6.04.

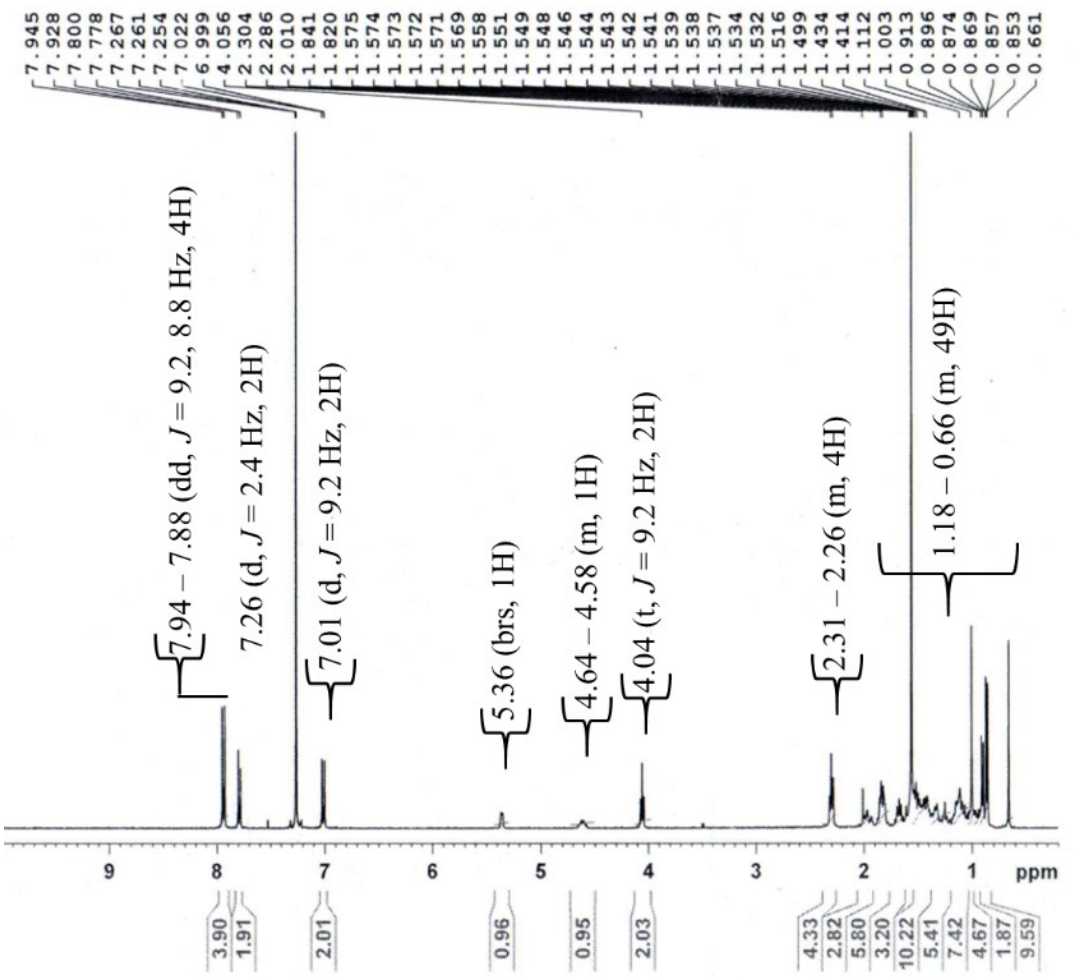
ACN-6: cholesteryl 7-((E)-4-((4-hydroxyphenyl)diazenyl)benzonitrile)heptanoate: Orange solid, R_f = 0.3 (20% EtOAc: hexanes); yield: 92%; v_{max} in cm^{-1}(KBr) 2941 (v_{CH}), 2225 (v_{CN}),1734 ($v_{C=O}$), 1595 ($v_{C=C}$), 1245 (v_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) δ: 7.93 (d, *J* = 6.8 Hz 4H), 7.78 (d, *J* = 8.8 Hz, 2***H***), 7.01 (d, *J* = 9.2 Hz, 2***H***), 5.35 (brd, 1H), 4.58-4.50 (m, 1H), 4.05 (t, 2H, *J* = 8.0 Hz), 2.30-2.01 (m, 4H), 1.84-0.66 (m, 49H) ; ^{13}C NMR (100MHz, $CDCl_3$): 173.36, 162.97, 155.10, 147.02, 139.39, 133.51, 133.40, 125.73, 124.75, 123.33, 122.89, 120.34, 118.88, 115.15, 114.61, 113.43, 77.47, 77.26, 77.04, 74.06, 68.53, 56.96, 56.43, 50.31, 42.58, 40.00, 39.78, 38.44, 37.25, 36.86, 36.45, 36.04, 34.82, 32.16, 32.13, 29.94, 29.18, 28.99, 28.47, 28.27, 28.10, 25.93, 25.18, 24.53, 24.10 ; Elemental analysis calcd for $C_{47}H_{65}N_3O_3$ (%): C,78.40; H, 9.10; N, 5.84; found, C 78.21, H 9.21; N 5.72.

ACN-7: cholesteryl 8-((E)-4-((4-hydroxyphenyl)diazenyl)benzonitrile)octanoate: Orange solid, R_f = 0.3 (20% EtOAc: hexanes); yield: 95%; v_{max} in cm^{-1}(KBr) 2937 (v_{CH}), 2229 (v_{CN}),1735 ($v_{C=O}$), 1602,($v_{C=C}$), 1255 (v_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) δ: 7.92 (d, *J* = 4.8 Hz, 4***H***), 7.78 (d, *J* = 8.4 Hz, 2***H***), 7.01 (d, *J* = 9.2 Hz, 2H), 5.35 (brd, 1H), 4.57-4.50 (m, 1H), 4.05 (t, 2H, *J* = 8.0 Hz), 2.30-2.01 (m, 4H), 1.82-0.66 (m, 51H) ; Elemental analysis calcd for $C_{48}H_{67}N_3O_3$ (%): C,78.54; H, 9.20; N, 5.72; found, C 78.32; H 9.41; N 5.46.

ACN-8: cholesteryl 9-((E)-4-((4-hydroxyphenyl)diazenyl)benzonitrile)nonanoate: Orange solid, R_f = 0.3 (20% EtOAc: hexanes); yield: 92%; v_{max} in cm^{-1}(KBr) 2933 (v_{CH}), 2225 (v_{CN}), 1725 ($v_{C=O}$), 1601 ($v_{C=C}$), 1601 (v_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) δ: 7.92 (d, *J* = 4.8 Hz, 4***H***), 7.79 (d, *J* = 8.8 Hz, 2***H***), 7.01 (d, *J* = 8.8 Hz, 2***H***), 5.35 (brd, 1H), 4.58-4.50 (m, 1H), 4.05 (t, 2H, *J* = 6.8 Hz, 2H), 2.31-2.26 (m, 4H), 1.98-0.66 (m, 53H); Elemental analysis calcd for $C_{49}H_{69}N_3O_3$ (%): C,78.67; H, 9.30; N, 5.62; found, C 78.53; H 9.25; N 5.43.

ACN-9: cholesteryl 10-((E)-4-((4-hydroxyphenyl)diazenyl)benzonitrile)decanoate: Orange solid, R_f = 0.3 (20% EtOAc: hexanes); yield: 93%; v_{max} in cm^{-1}(KBr) 2947 (v_{CH}), 2349 (v_{CN}),1727 ($v_{C=O}$), 1601($v_{C=C}$), 1292 (v_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) δ: 7.92 (d, *J* = 4.8 Hz, 4***H***), 7.79 (d, *J* = 8.4 Hz, 2***H***), 7.01 (d, *J* = 9.2 Hz, 2***H***), 5.35 (brd, 1H), 4.55-4.52 (m, 1H), 4.04 (t, *J* = 4.8 Hz, 2H), 2.31-2.25 (m, 4H), 1.86-0.66 (m, 55H) ; Elemental analysis calcd for $C_{50}H_{71}N_3O_3$ (%): C,78.80; H, 9.39; N, 5.51;found, C 78.62; H 9.26; N; 5.35

ACN-6 , ^{1}H NMR, $CDCl_3$,



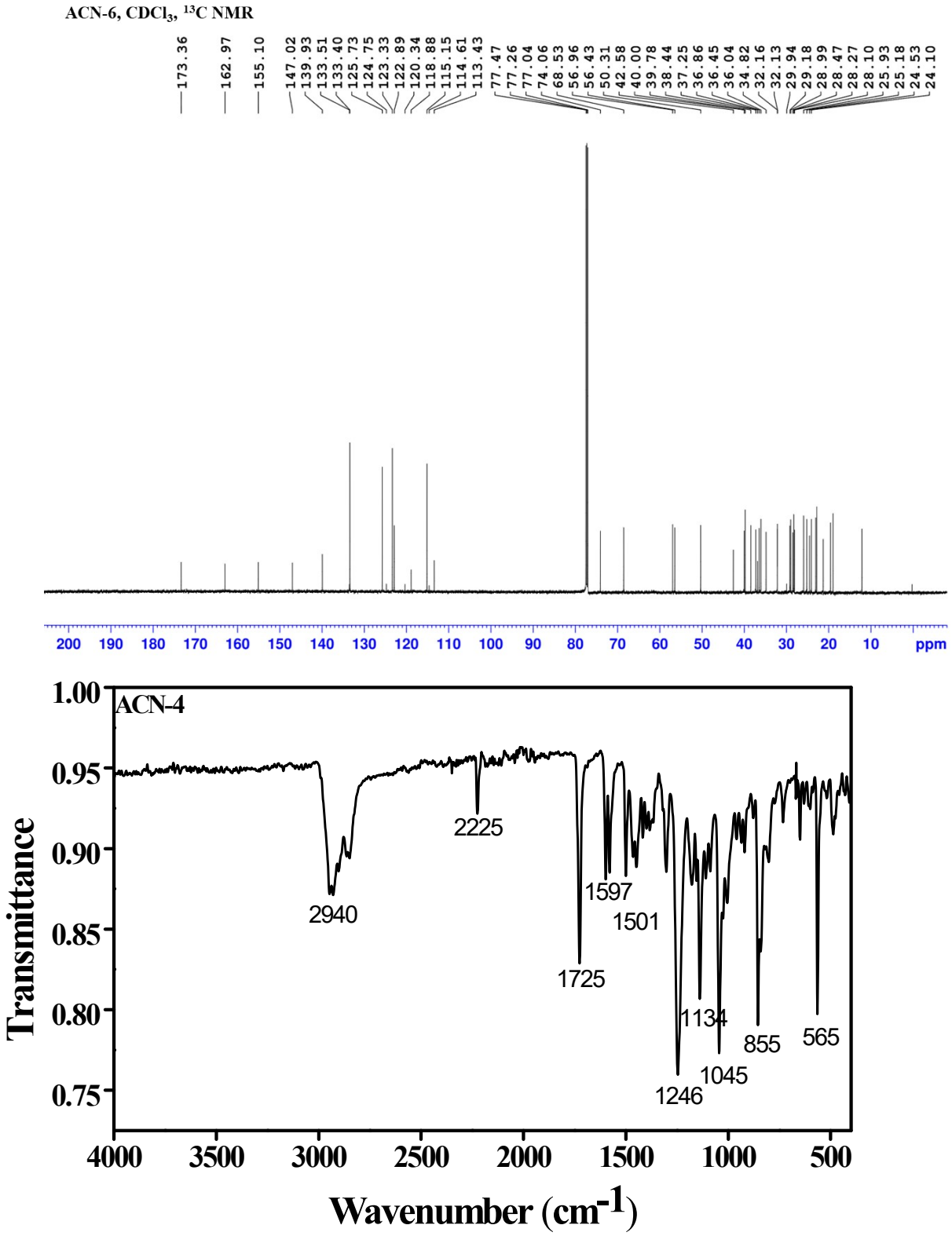


Fig S1: ^{1}H NMR and ^{13}C NMR of **ACN-6;** IR spectra for **ACN-4**

Synthesis of ACEt-*n* series.

A solution of **3a** (50 mg, 0.184 mmol) in butanone (10 mL) was charged with potassium carbonate (38.3 mg, 0.277 mmol) and a catalytic amount of potassium iodide (2 mg), and Cholesteryl ω-bromoalkanoate (n = 3, 99 mg, 0.184 mmol) was then added to the reaction mixture, which was refluxed for 16 hours. After filtration, the solid obtained was washed with DCM and dried under controlled vacuum to yield an orange-colored compound. The crude product was purified by column chromatography on 100–200 mesh silica gel using 5 % ethyl acetate–hexane as the eluent, and the collected fractions were concentrated under reduced pressure to afford a pure compound, which was further purified by recrystallization from 5% DCM–ethanol.

A similar procedure has been used for other homologue series (*n* = 4, 5, 6, 7, 8, 9)

ACEt-3: cholesteryl 4-(ethyl (E)-4-((4-hydroxyphenyl)diazenyl)benzoate)butanoate:

R*f* = 0.4 (20% EtOAc: hexanes); Orange solid; yield: 89%; ν_{max} in cm^{-1}(KBr) 2936 (ν_{CH}), 1721 ($\nu_{C=O}$), 1592 ($\nu_{C=C}$), 1274 (ν_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) 8.16 (d, *J* = 2 Hz, 2H), 7.95 – 7.89 (dd, *J*= 8.8, 8.4 Hz, 4H), 7.01 (d, *J* = 9.2 Hz, 2H), 5.35(brd, 1H), 4.51-4.49 (m, 1H), 4.43 – 4.38 (m, 2H), 4.11(t, *J* = 6.0 Hz, 2H), 2.31-2.18 (m, 4H), 1.91-0.67 (m, 46H); Elemental analysis calcd for $C_{46}H_{64}N_2O_5$ (%):C,76.20; H, 8.90; N, 3.86; found, C 75.98, H 8.76; N, 3.74.

ACEt-4: cholesteryl 5-(ethyl (E)-4-((4-hydroxyphenyl)diazenyl)benzoate)pentanoate: Orange solid, R_f = 0.4 (20% EtOAc: hexanes); yield: 90%; ν_{max} in cm^{-1}(KBr) 2933 (ν_{CH}), 1708 ($\nu_{C=O}$), 1602 ($\nu_{C=C}$), 1282 (ν_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) δ: 8.16 (d, J =4.8, Hz, 2H), 7.95 – 7.89 (m, 4H), 7.01 (d, J = 9.2 Hz, 2H), 5.32(brd, 1H),, 4.58-4.50 (m, 1H), 4.42 – 4.40 (m, 2H), 4.07 (t, 2H, *J* = 6.4 Hz), 2.38-2.29 (m, 4H), 1.86 - 0.66 (m, 48H); Elemental analysis calcd for $C_{47}H_{66}N_2O_5$ (%):C,76.38; H, 9.00; N, 3.79; found, C 76.47, H 8.79; N, 3.62.

ACEt-5: cholesteryl 6-(ethyl (E)-4-((4-hydroxyphenyl)diazenyl)benzoate)hexanoate

Orange solid, R_f = 0.4 (20% EtOAc: hexanes); yield: 87%; ν_{max} in cm^{-1}(KBr) 2930 (ν_{CH}), 1725 ($\nu_{C=O}$), 1602 ($\nu_{C=C}$), 1245 (ν_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) δ: 8.16 (d, J = 2 Hz, 2H), 7.94-7.89 (dd, 1H, *J* = 9.2, 8.8 Hz), 7.01 (d, *J* = 8.8 Hz, 2H), 5.35 (brd, 1H), 4.57-4.51 (m, 1H),4.42 – 4.40 (m, 2H), 4.06 (t, 2H, *J* = 6.4 Hz), 2.35-2.29 (m, 4H), 1.87-0.66 (m, 50H); Elemental analysis calcd for $C_{48}H_{68}N_2O_5$ (%):C,76.56; H, 9.10; N, 3.72; found, C 76.41, H 9.23; N, 3.74.

ACEt-6: cholesteryl 7-(ethyl (E)-4-((4-hydroxyphenyl)diazenyl)benzoate)heptanoate

Orange solid, R_f = 0.4 (20% EtOAc: hexanes); yield: 90%; ν_{max} in cm^{-1}(KBr) 2952 (ν_{CH}), 1724 ($\nu_{C=O}$), 1592 ($\nu_{C=C}$), 1224 (ν_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) δ: 8.16 (d, *J* = 2 Hz, 2H), 7.94 – 7.89 (dd, *J* = 8.8, 8.4 Hz, 4H), 7.01 (d, *J* = 8.8 Hz, 2H), 5.35 (brd, 1H), 4.58-4.50 (m, 1H), 4.42 – 4.40 (m, 2H), 4.05 (t, 2H, *J* = 6.4 Hz), 2.32-2.28 (m, 4H), 1.85-0.66 (m, 52H); Elemental analysis calcd for $C_{49}H_{70}N_2O_5$; (%):C,76.72; H 9.20; N; 3.65; found, C 76.60; H 9.10; N 3.51.

ACEt-7: cholesteryl 8-(ethyl (E)-4-((4-hydroxyphenyl)diazenyl)benzoate)octanoate

Orange solid, R_f = 0.4 (20% EtOAc: hexanes); yield: 95%; ν_{max} in cm^{-1}(KBr) 2934 (ν_{CH}), 1734 ($\nu_{C=O}$), 1601 ($\nu_{C=C}$), 1282 (ν_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) δ: 8.16 (d, *J* = 2 Hz, 2H), 7.95-7.88 (dd, *J* = 9.2, 8.8 Hz, 4H), 7.01 (d, *J* = 8.8 Hz, 2H), 5.35 (brd, 1H), 4.57-4.50 (m, 1H), 4.420 - 4.40 (m, 2H), 4.04 (t, 2H, *J* = 6.4 Hz), 2.31-2.26 (m, 4H), 1.85-0.66 (m, 54H) ; Elemental analysis calcd for $C_{50}H_{72}N_2O_5$ (%):C,76.88; H, 9.29; N, 3.59; found, C 76.94, H 9.32; N, 3.64.

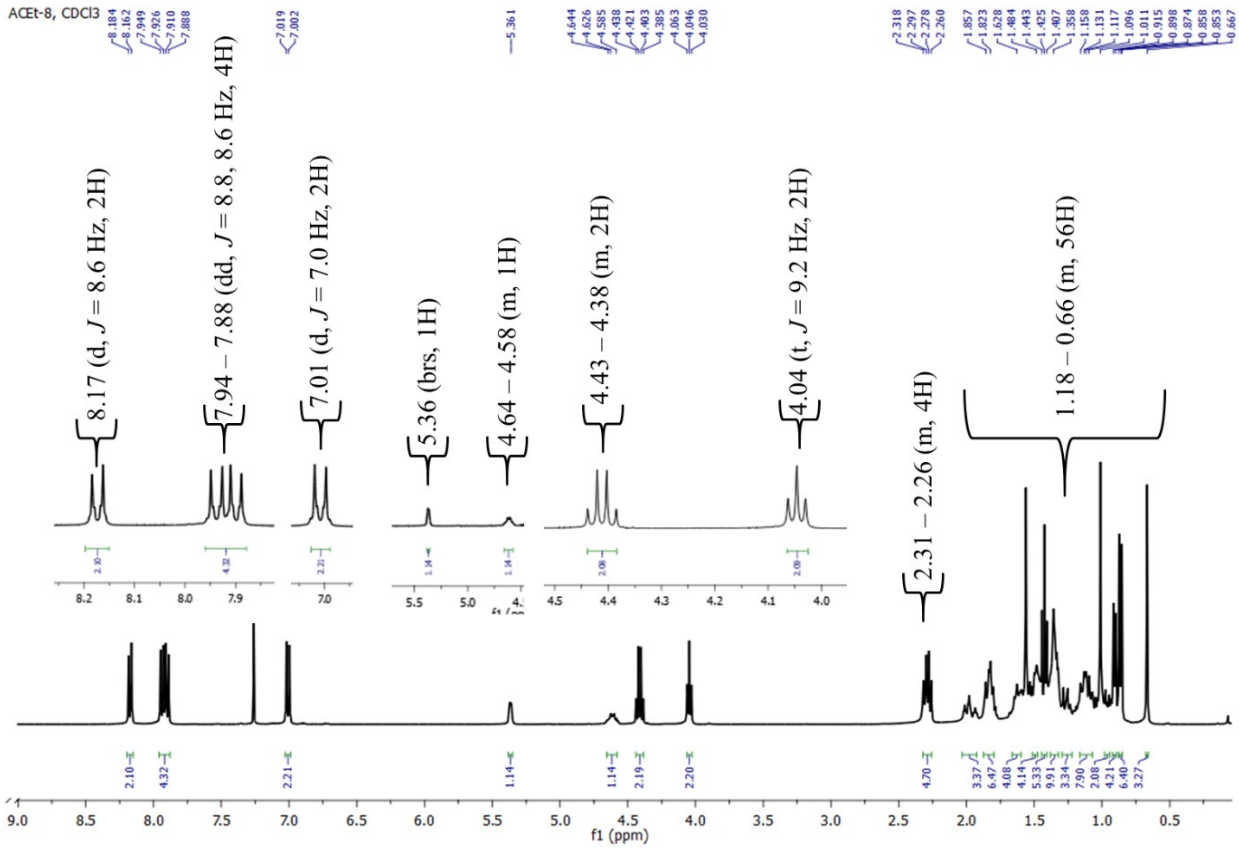
ACEt-8: cholesteryl 9-(ethyl (E)-4-((4-hydroxyphenyl)diazenyl)benzoate)nonanoate

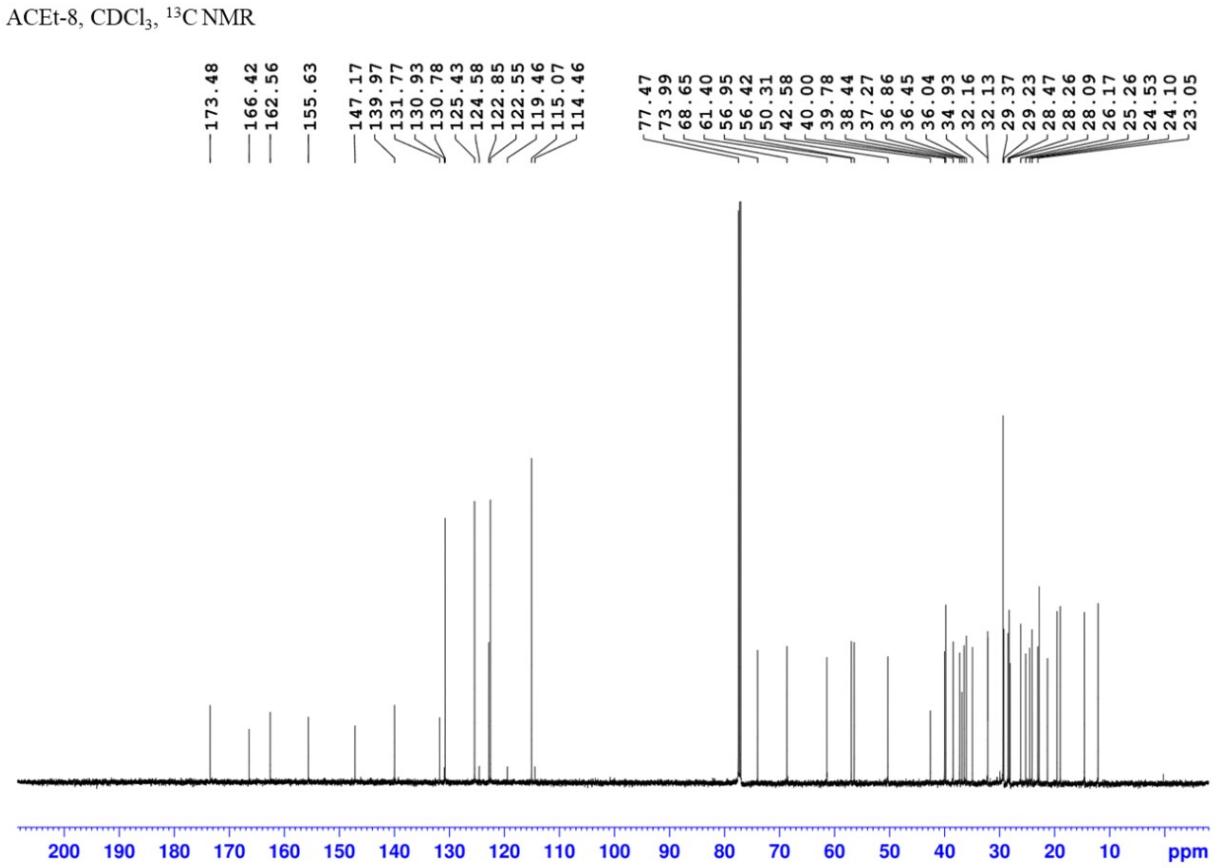
Orange solid, R_f = 0.4 (20% EtOAc: hexanes); yield: 92%; ν_{max} in cm^{-1}(KBr) 2932 (ν_{CH}), 1712 ($\nu_{C=O}$), 1601 ($\nu_{C=C}$), 1281 (ν_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) δ: 8.17 (d, *J* = 8.6 Hz, 2H), 7.94 – 7.88 (dd, *J* = 8.8, 8.6 Hz, 4H), 7.01 (d, *J* = 7.0 Hz, 2H), 5.36 (brs, 1H), 4.64 – 4.58 (m, 1H), 4.43 – 4.38 (m, 2H), 4.04 (t, *J* = 9.2 Hz, 2H), 2.31 – 2.26 (m, 4H), 1.18 – 0.66 (m, 56H); ^{13}C NMR (100MHz, $CDCl_3$): 173,48, 166.42, 162.56, 155.63, 147.17, 139.97, 131.77, 130.93, 130.78, 125.43, 124.58, 122.85, 122.55, 119.46, 115.07, 114.46, 77.47, 73.99, 68.65, 61.40, 56.95, 50.31, 42.58, 40.00, 39.78, 38.44, 37.27, 36.86, 36.45, 36.04, 34.93, 32.16, 32.13, 29.37, 29.23, 28.47, 28.26, 28.09, 26.17, 25.26, 24.53, 24.10, 23.05; Elemental analysis calcd for $C_{51}H_{74}N_2O_5$ (%):C,77.04; H, 9.38; N, 3.52; found, C 77.08, H 9.34; N, 3.63.

ACEt-9: cholesteryl 10-(ethyl (E)-4-((4-hydroxyphenyl)diazenyl)benzoate)decanoate

Orange solid, R_f = 0.4 (20% EtOAc: hexanes); yield: 93%; ν_{max} in cm^{-1}(KBr) 2935 (ν_{CH}), 1716 ($\nu_{C=O}$), 1603 ($\nu_{C=C}$), 1252 (ν_{C-O}); ^{1}H NMR (400MHz, $CDCl_3$) δ: 8.46 (d, *J* = 1.6 Hz, 2H), 7.95 – 7.88 (d, *J* = 8.8, 8.8 Hz, 4H), 7.01 (d, *J* = 8.8 Hz, 2H), 5.36 (brd, 1H), 4.55-4.52 (m, 1H), 4.42 –

4.40 (m, 2H), 4.04 (t, J = 6.8 Hz, 2H), 2.31-2.25 (m, 4H), 1.86-0.66 (m, 58H); Elemental analysis calcd for $C_{52}H_{76}N_2O_5$ (%):C,77.18; H, 9.47; N, 3.46; found, C 77.01; H 9.33; N 3.34.





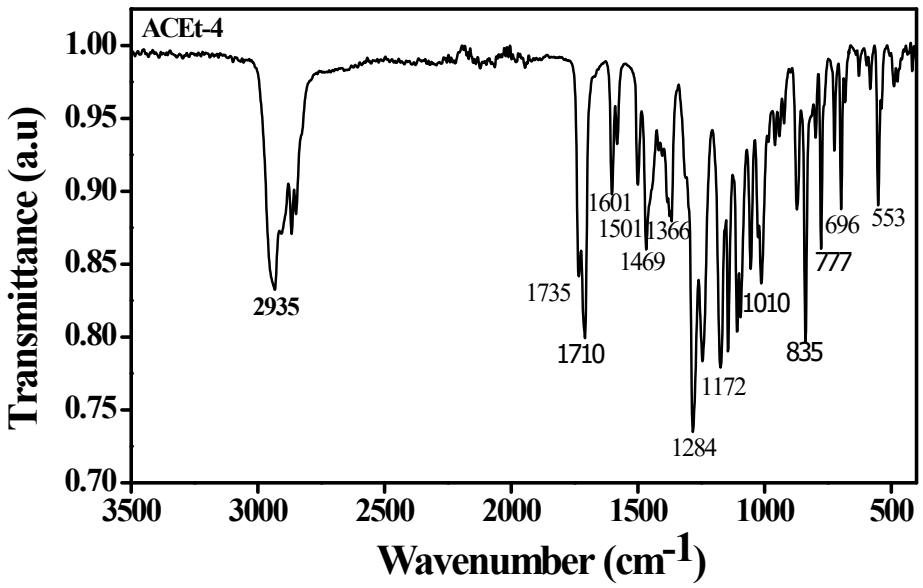


Figure S2: ^{1}H, ^{13}C NMR for **ACEt-8** in $CDCl_3$; IR spectra for **ACEt-4**

9. POM textures:

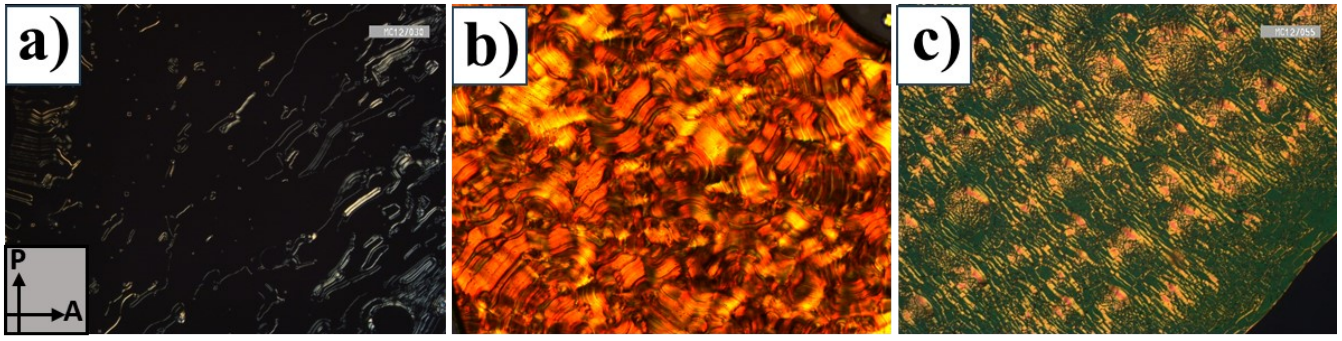


Figure S3: a) Oily streaks texture for N* phase of **ACN-5,** T = 130 °C; b) SmC* phase of **ACN-9**, T = 96 °C and c) N* phase of **ACN-8,** T = 156 °C.

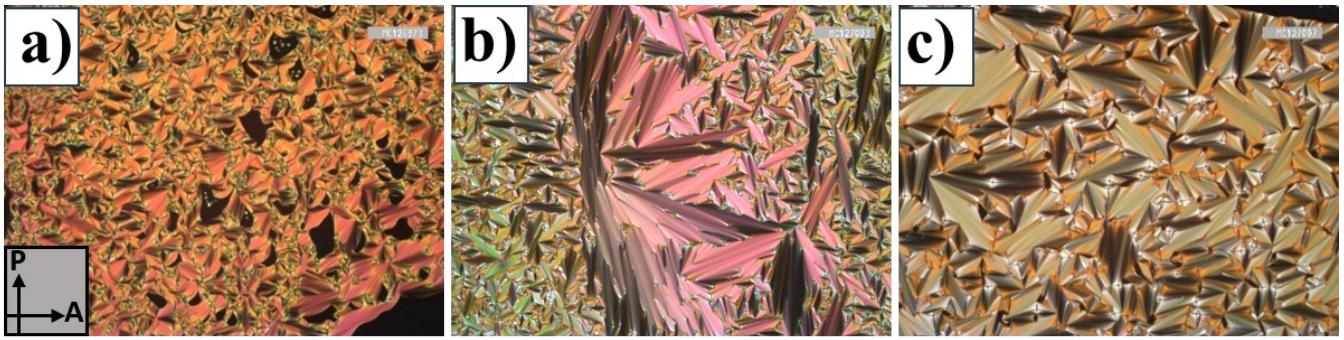


Figure S4: a) SmC* phase of **ACEt-3, T =** 170 °C; b) SmC* phase of **ACEt-7,** T =130 °C**;** c) SmA* phase of **ACEt-9,** T = 163 °C.

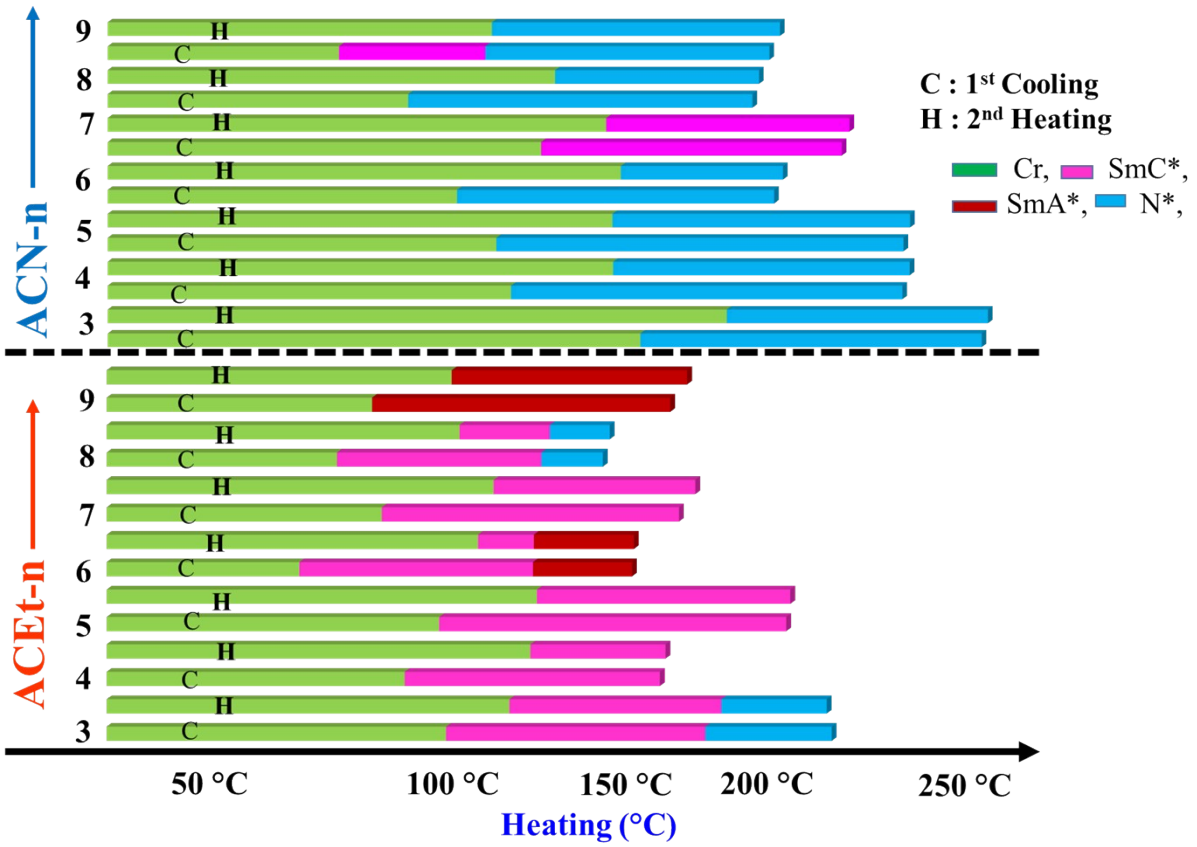
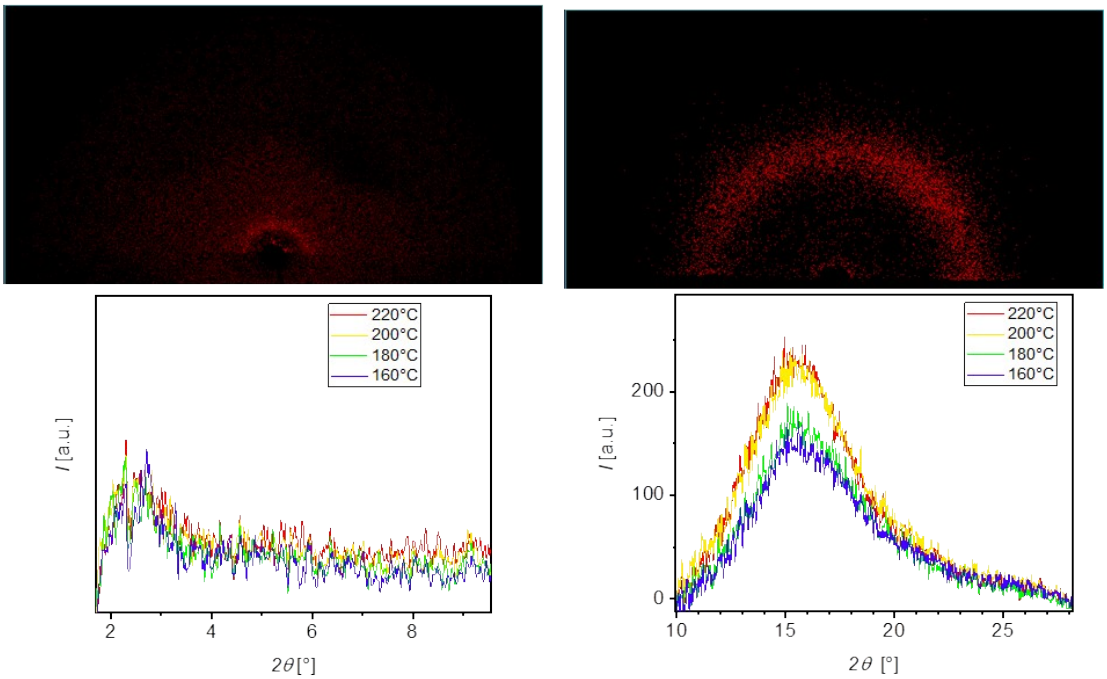


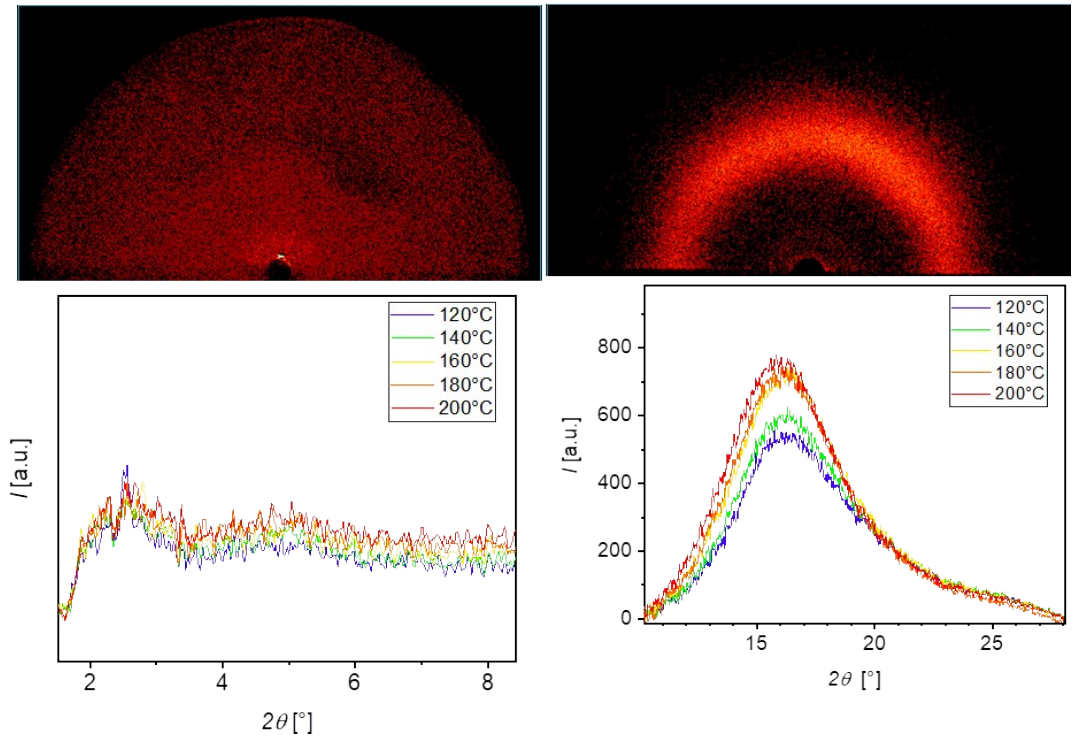
Figure S5: Bar diagram displaying the LC phase and phase transition of the **ACN-*n*** and **ACEt-*n*** series in heating and cooling cycles scanned at 10 °C min^{-1}.

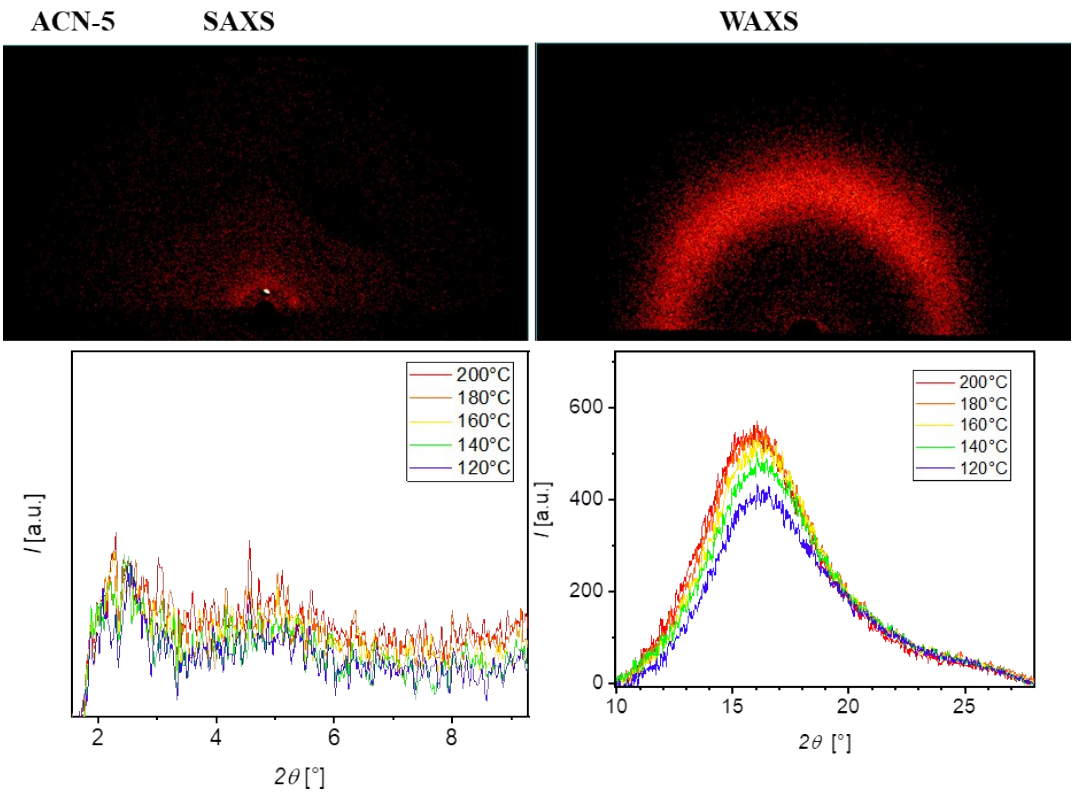
10. XRD Studies:

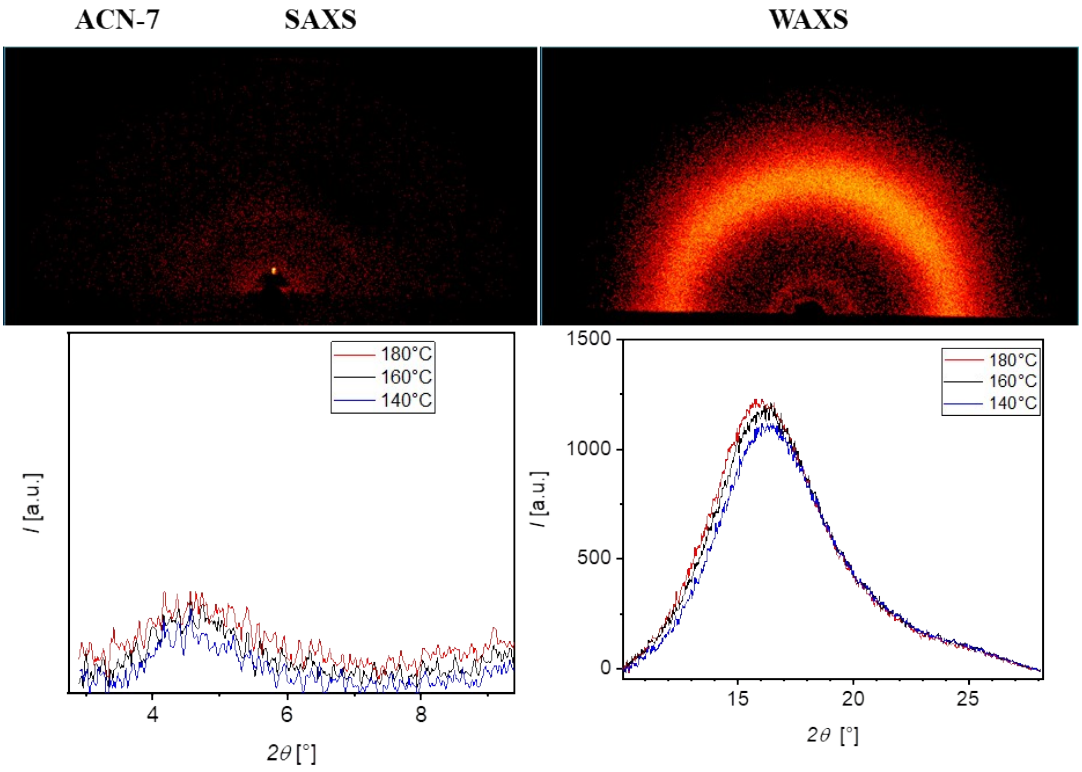
ACN-3 **SAXS** **WAXS**



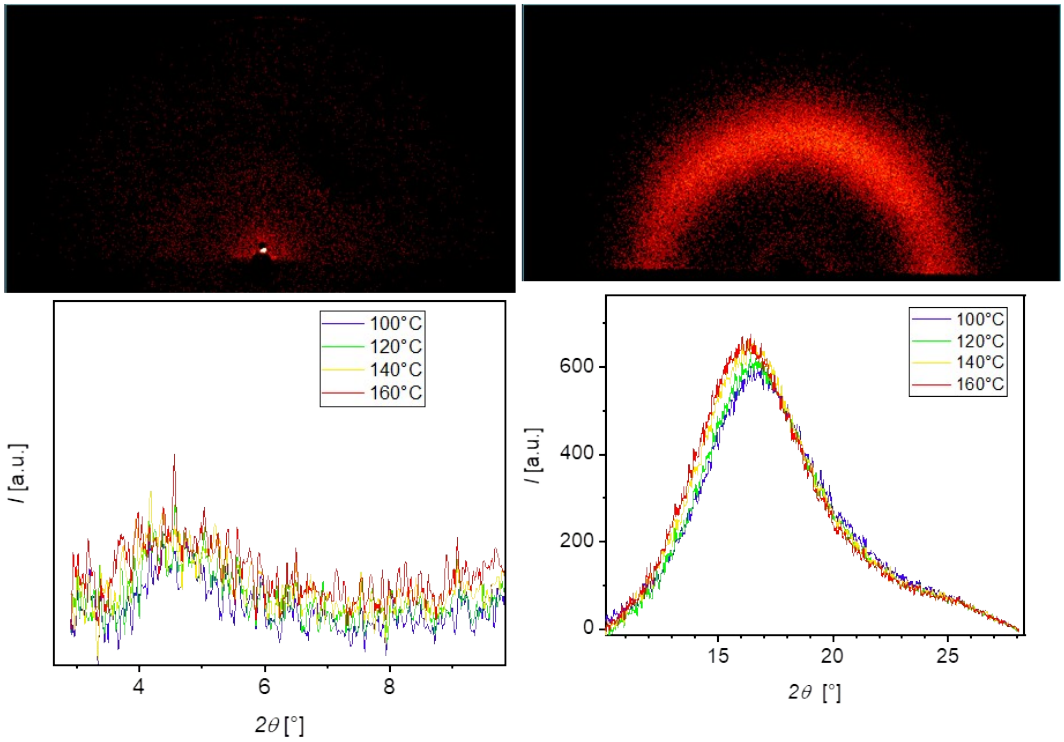
ACN-4 **SAXS** **WAXS**



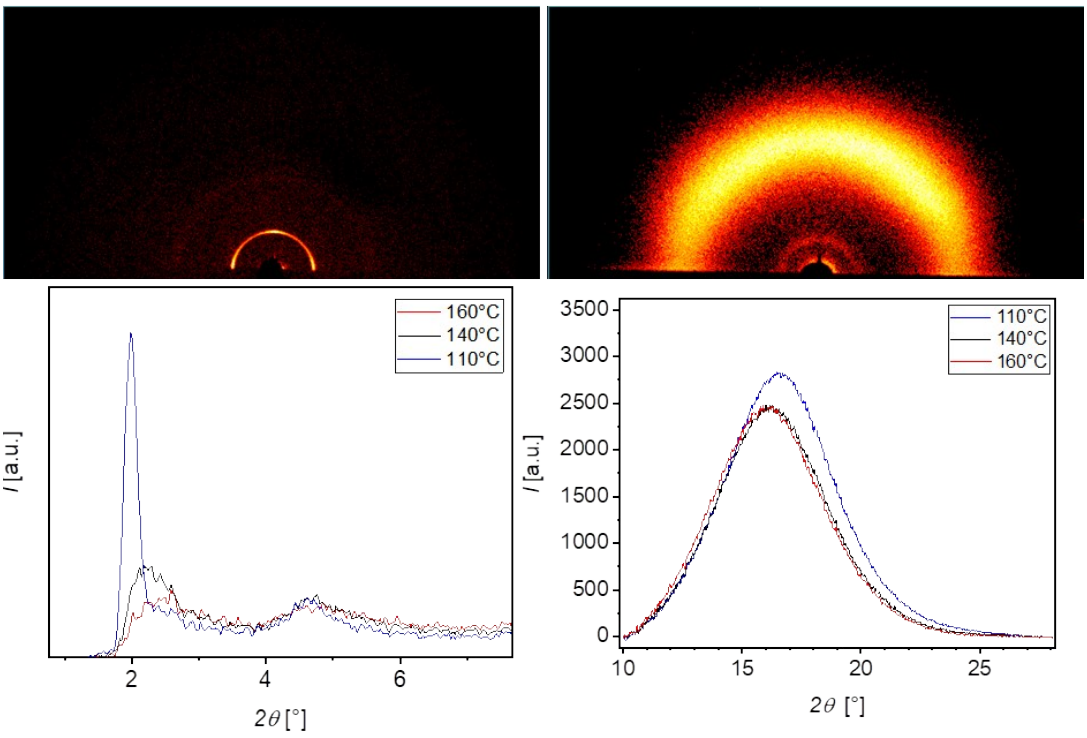

ACN-5
SAXS
WAXS
200°C
180°C
160°C
140°C
120°C
I [a.u.]
2θ [°]

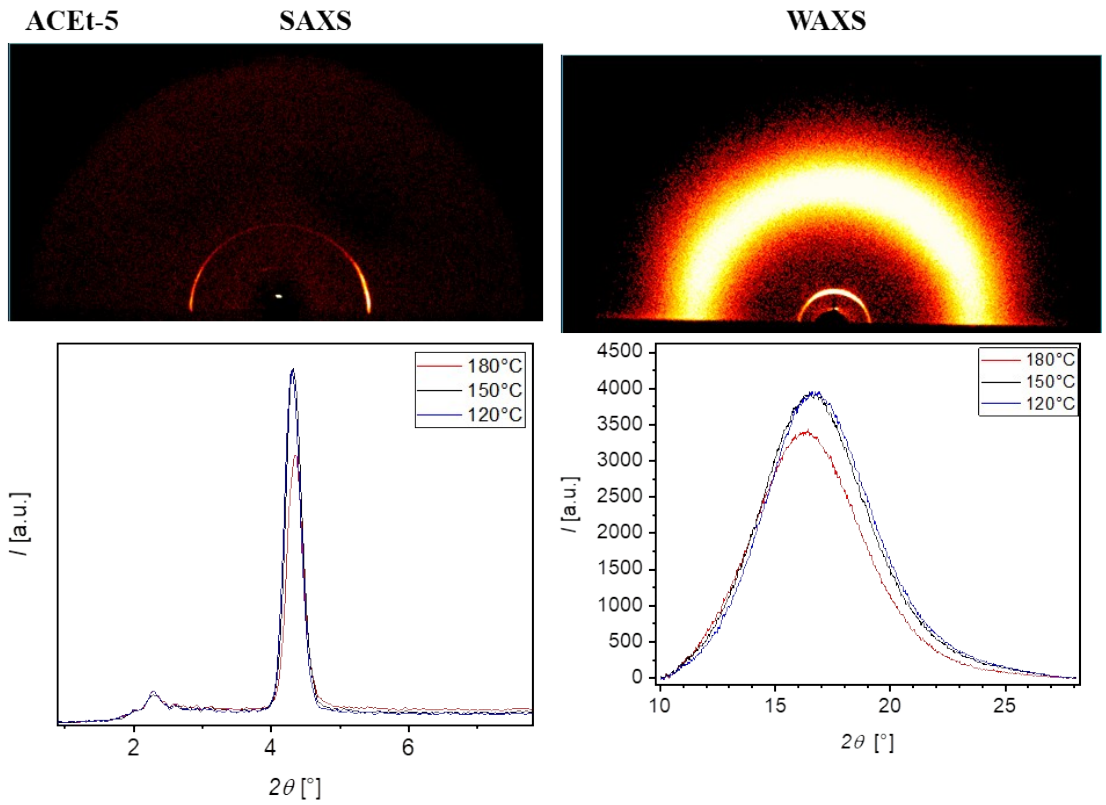

ACN-7
SAXS
WAXS
180°C
160°C
140°C
I [a.u.]
2θ [°]

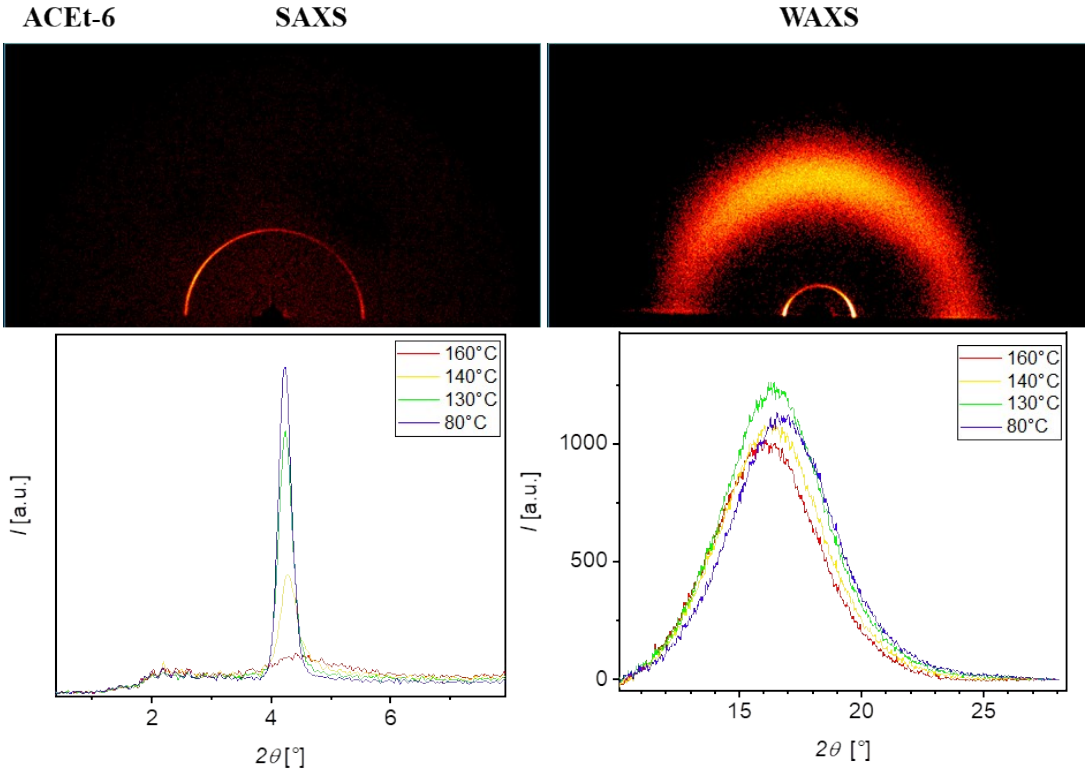
ACN-8 **SAXS** **WAXS**

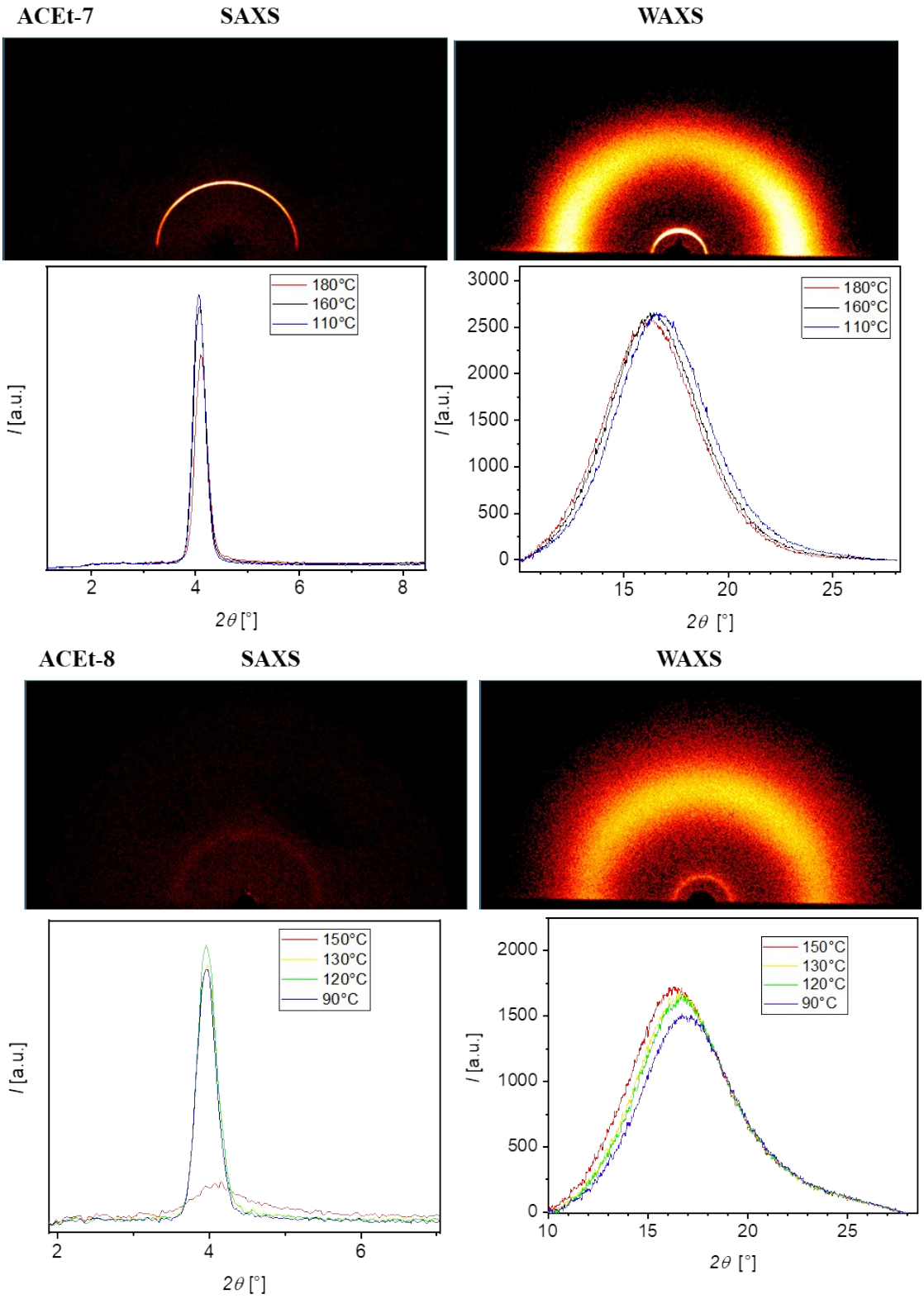


ACEt-4 **SAXS** **WAXS**




ACEt-5
SAXS
WAXS
180°C
150°C
120°C
I [a.u.]
2θ [°]


ACEt-6
SAXS
WAXS
160°C
140°C
130°C
80°C
I [a.u.]
2θ [°]


ACEt-7
SAXS
WAXS
180°C
160°C
110°C
I [a.u.]
2θ [°]
ACEt-8
SAXS
WAXS
150°C
130°C
120°C
90°C
I [a.u.]
2θ [°]

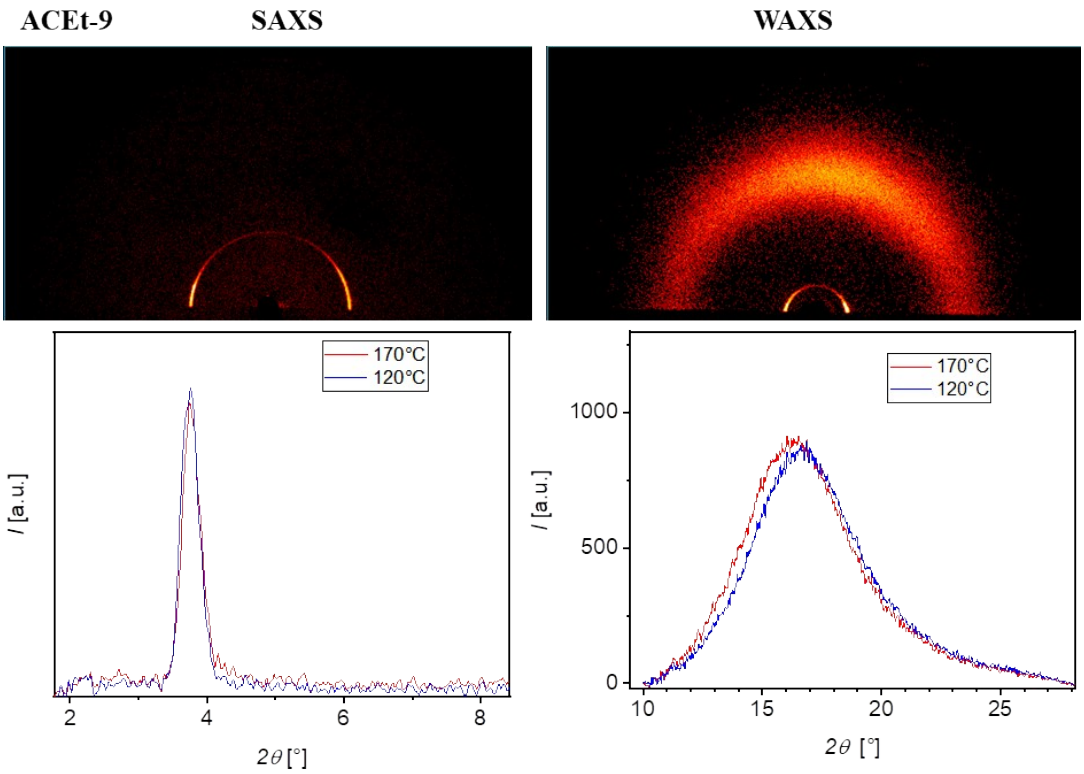


Figure S6: 2D and 1D SAXS and WAXS pattern for **ACN-*n*** and **ACEt-*n*** dimers.

11. Photoisomerization

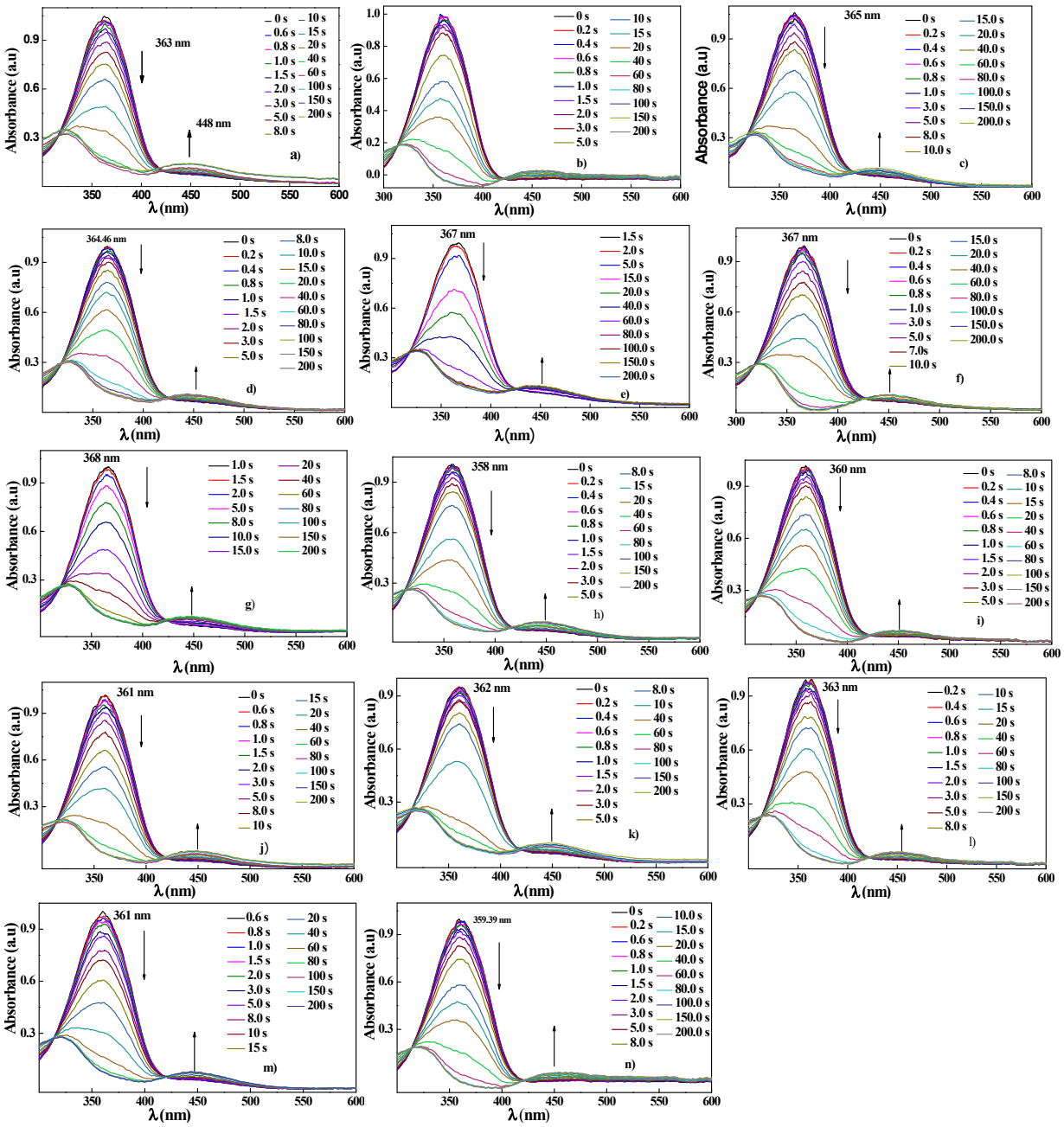


Figure S7: Absorbance spectral plots as a function of UV irradiation for a) to g) for **ACN-*n*** and h) to n) for **ACEt-*n*** series**.** (***n* = 3-9**)

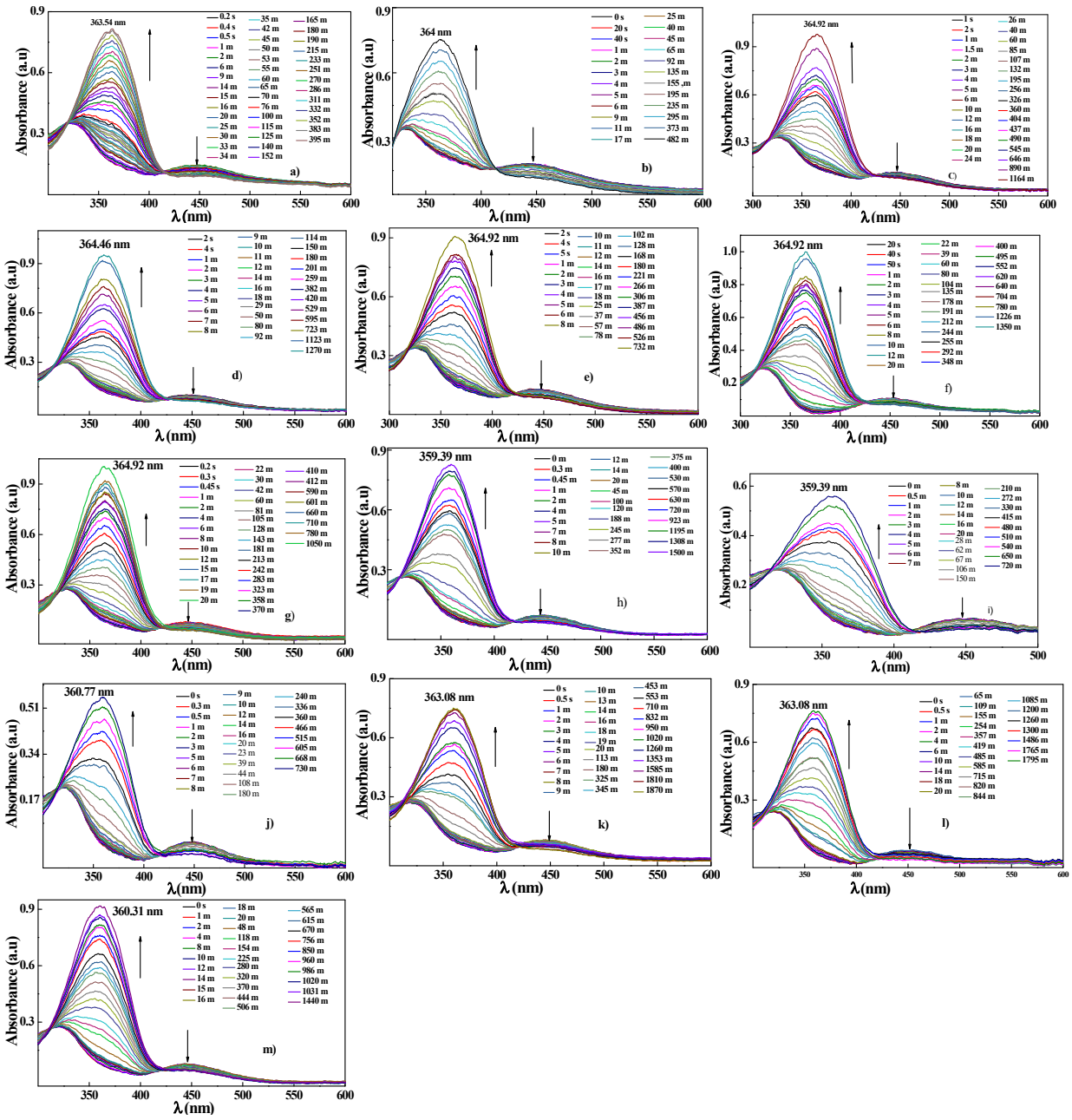


Figure S8: Thermal back relaxation process for the a) to g) for **ACN-*n*** and h) to n) for **ACEt-*n*** series. o) Peak absorbance plots **ACN-*n*** series p) for **ACEt-*n*** series. (***n* = 3-9**).

12. Computational studies:

Optimized geometries:

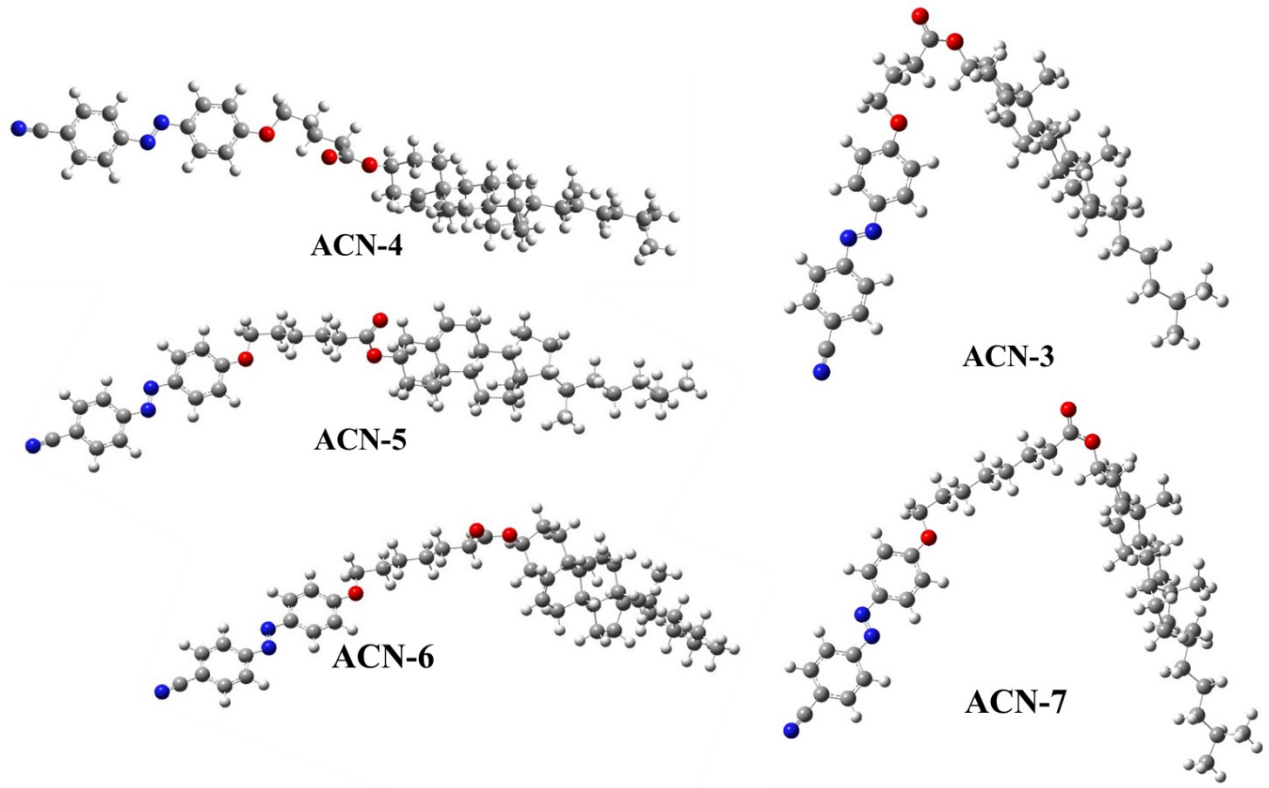


Figure S9a. The DFT optimized structures of **ACN-*n* (*n*= 3-7)** series were calculated using B3LYP/6-311G (d,p)

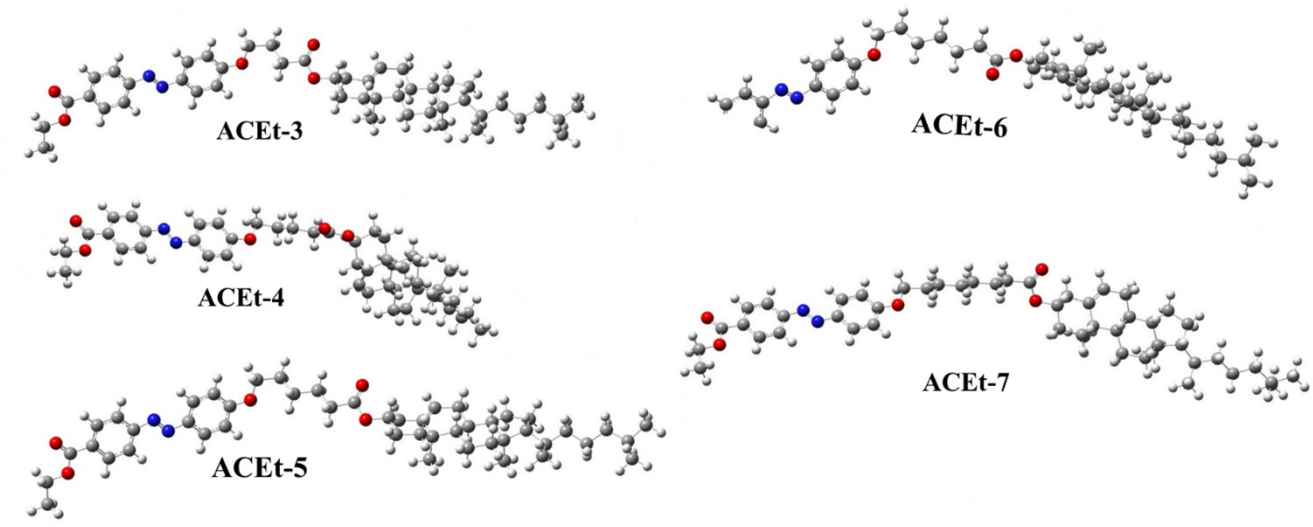


Figure S9b. The DFT optimized structures of **ACEt-*n* (*n*= 3-7)** series calculated using B3LYP/6-311G (d,p)

Electrostatic potential (ESP):

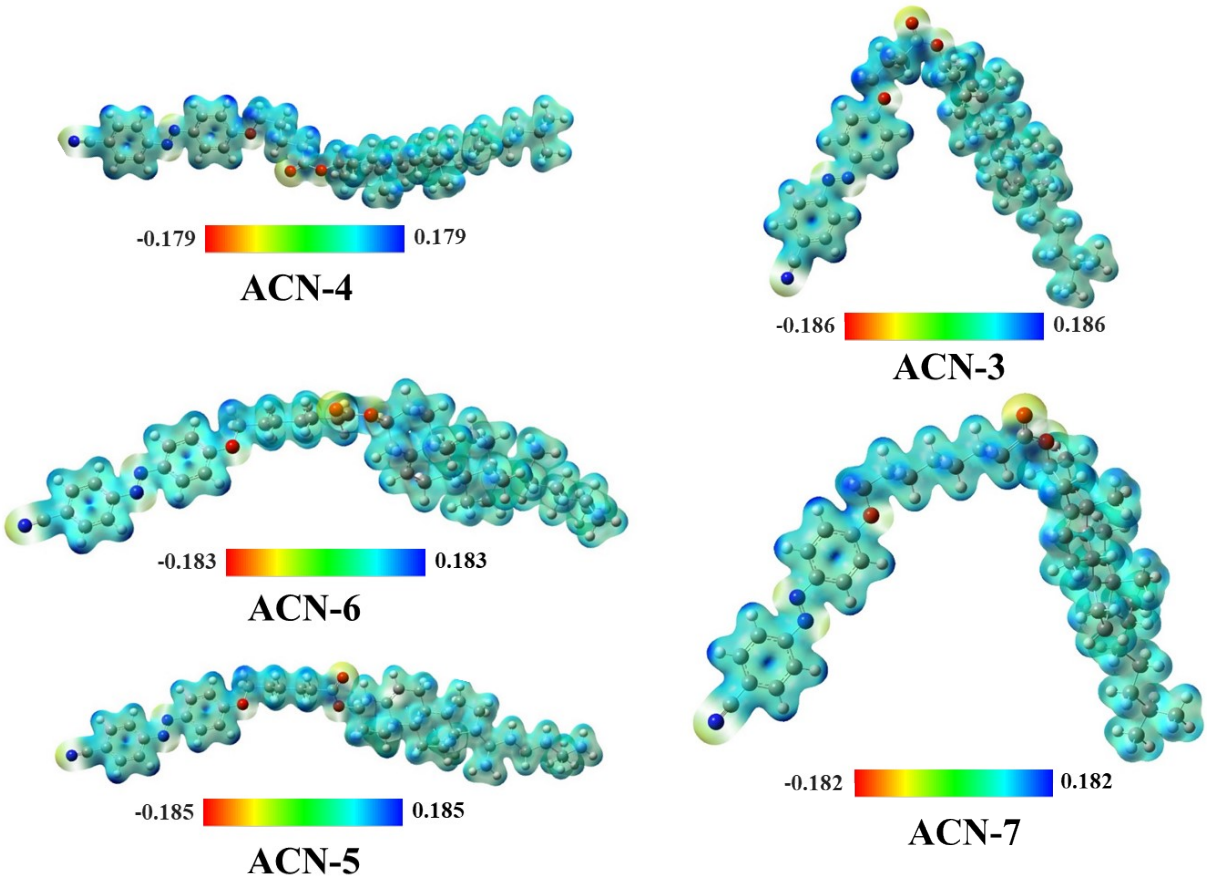


Figure S10a: Electrostatic potential for **ACN-*n*** (*n* = 3-7) dimers

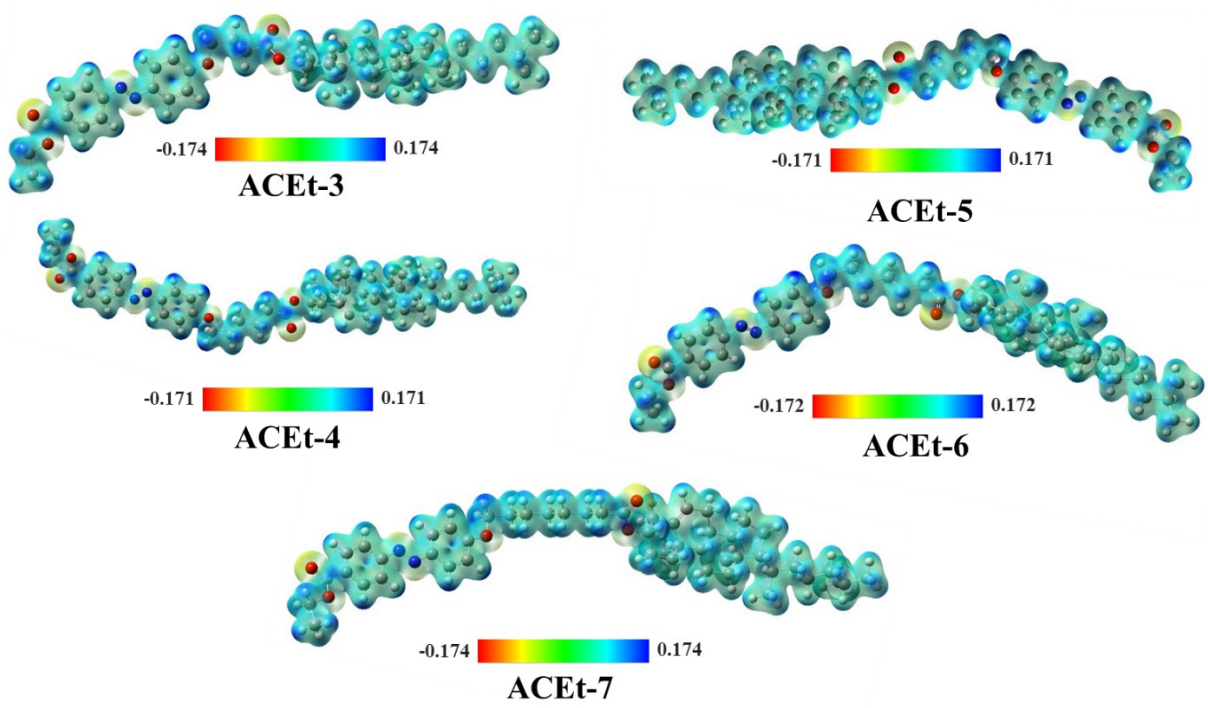
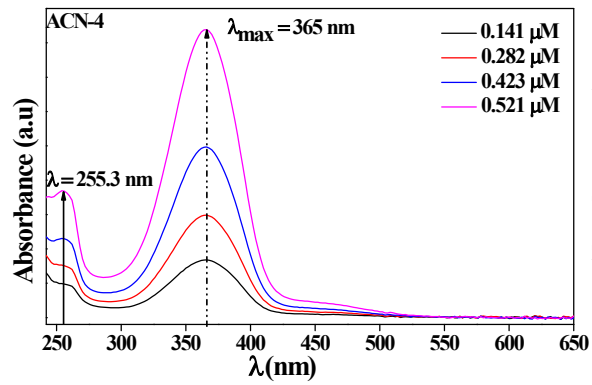
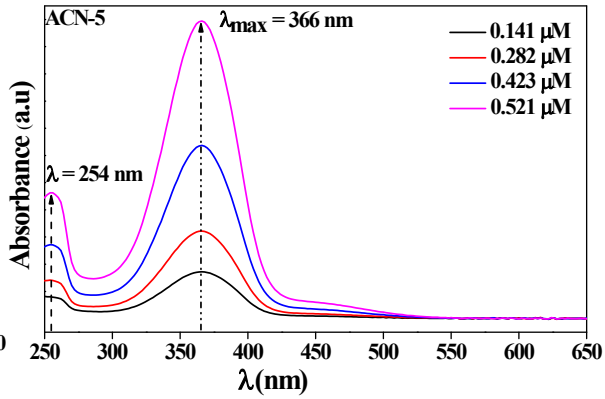
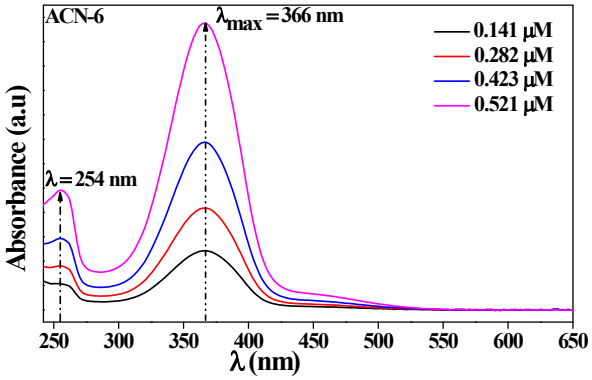


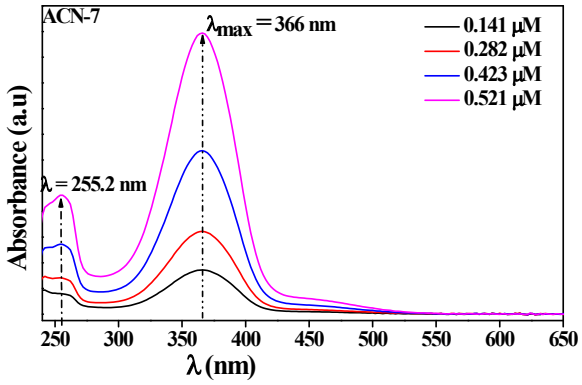
Figure S10b: Electrostatic potential for **ACEt-*n*** (*n* = 3-7) dimers

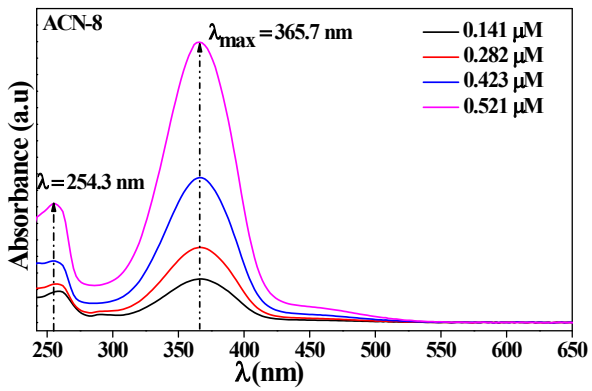
13. Optical studies:

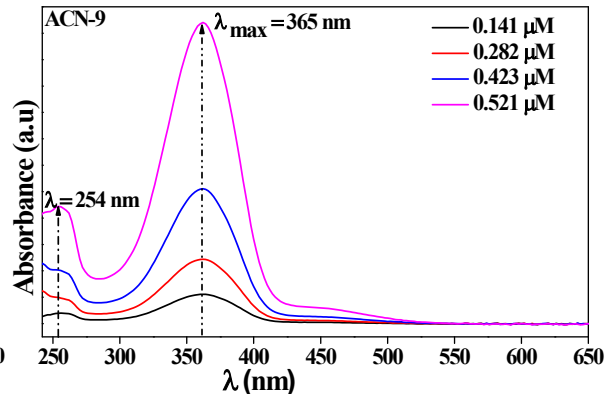


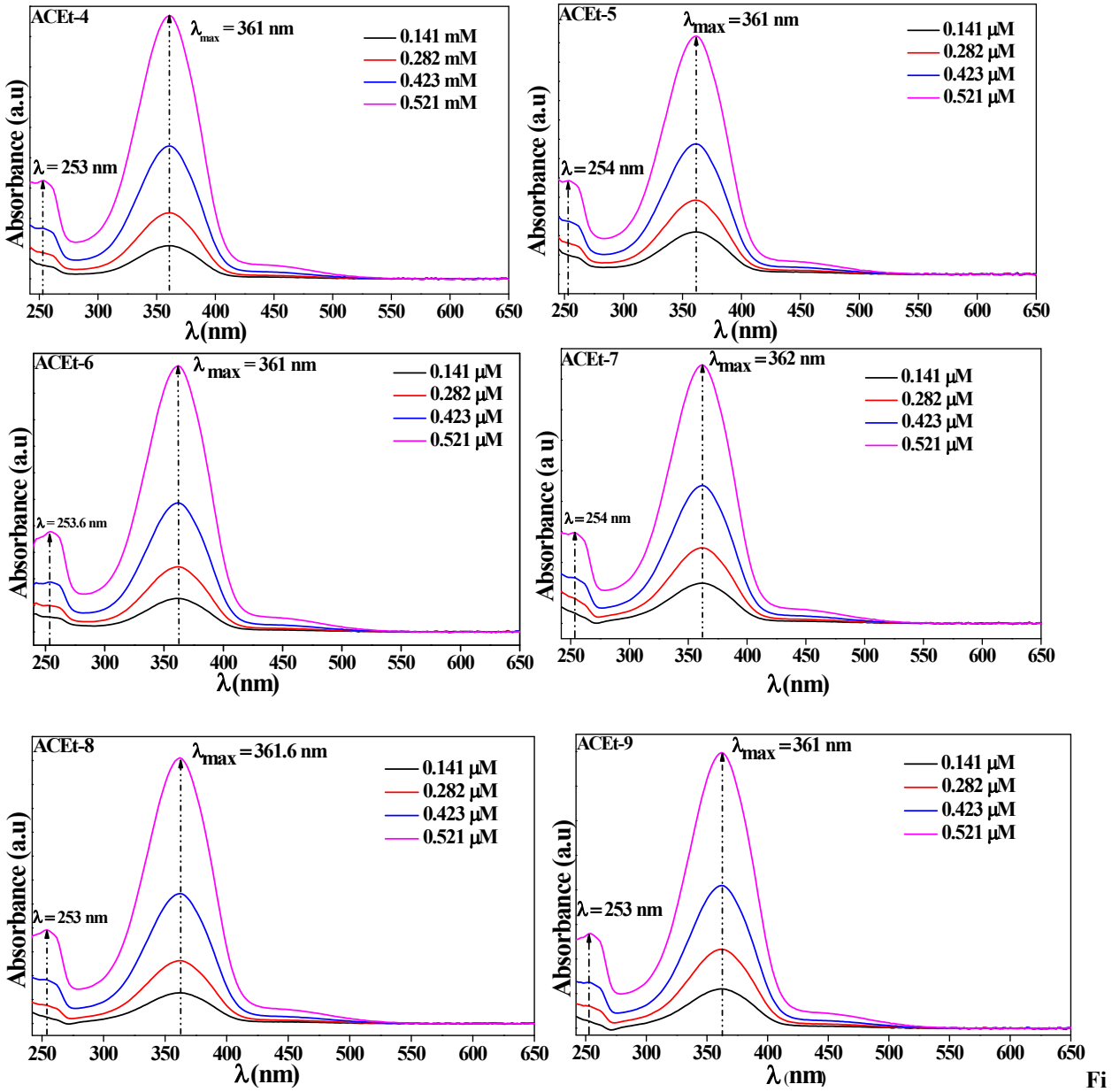












gure S11. SAXS: UV-Visible absorption spectra of **ACN-*n*** and **ACEt-*n*** (*n* = 4 - 9) at room temperature in $CHCl_3$