Supporting Information

Photo-responsive Liquid Crystals Derived From Azobenzene Centered Cholesterol-based Tetramers

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1. Experimental Section

1.1 Materials and Reagents

Chemicals and solvents were all of AR quality and were used without further purification. Cholesterol, n-bromoalkanoic acids, dicyclohexyl carbodiimide, 4-dimethylaminopyridine, 5-nitroisophthalic acid, sodium hydroxide, potassium hydroxide, dextrose, hydrochloric acid, n-butanone and tetraoctyl ammonium bromide were all purchased from Sigma–Aldrich (Bangalore, India). Column chromatographic separations were performed on silica gel (60-120 & 230-400 mesh). Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel 60, F254).

1.2 Instrumental

Structural characterization. Structural characterization of the compound was carried out through a combination of infrared spectroscopy (Perkin Elmer Spectrum AX3), ^{1}H NMR and ^{13}C NMR (Bruker Biospin Switzerland Avance-iii 400 MHz and 100 MHz spectrometers respectively) and UV-VIS-NIR spectrophotometer (Agilent Technologies UV-vis-NIR Spectrophotometer). NMR spectra were recorded using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as an internal standard.

Differential Scanning Calorimetry. DSC measurements were performed on Perkin Elmer DSC 8000 coupled to a Controlled Liquid Nitrogen Accessory (CLN 2) with a scan rate of 5 °C/min.

Polarized Optical Microscopy. Textural observations of the mesophase were performed with Nikon Eclipse LV100POL polarising microscope provided with a Linkam heating stage (LTS 420). All images were captured using a Q-imaging camera.

X-ray Diffraction. X-ray diffraction (XRD) was carried out on powder samples using Cu Kα (λ=1.54 Å) radiation from a source (GeniX 3D, Xenocs) operating at 50 kV and 0.6 mA. The diffraction patterns were collected on a two module Pilatus detector.

1.3 Synthesis of oligomers 5

Synthesis of compounds **2** and **4** has been described in the earlier reports (Scheme 2).[38-42] For the synthesis of the target compound **5**, compound **4** (1 equivalent) was dissolved in aqueous

KOH (1.1 equivalent) solution. To that solution, compound **2** (6 equivalents) was added followed by the addition of tetraoctylammonium bromide in catalytic amounts. The reaction mixture was refluxed under vigorous stirring for 5 hours & was then cooled to room temperature. The compound was extracted with dichloromethane. The organic layer was washed with brine & dried over anhydrous sodium sulphate. The chloroform was removed by rotary evaporation and the resulting residue was purified by column chromatography over silica gel using hexane & ethyl acetate as eluent. The synthesized compounds **5a-h** were characterized by ^{1}H NMR, ^{13}C NMR, IR, UV-vis and elemental analysis as shown below:

Compound **5a**

FT-IR (cm^{-1}): 2946.1, 2869.4, 1730.2, 1467.2, 1380.1, 1331.9, 1314.1, 1240.6, 1174.5, 1106.1, 1029.8, 1009.8, 923.2, 840.7, 801.3, 757.1, 738.0, 704.4, 685.2, 593.8.

UV-vis (nm): 236, 315.6, 332.8, 347.5, 448.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ 8.83 (s, 2H), 8.80 (s, 4H), 5.36 (d, 4H, J = 4 Hz), 4.60 (m, 4H), 4.45 (t, 8H, J = 4, 8 Hz), 2.41 (t, 8H, J = 8, 4 Hz), 2.32 (m, 8H), 1.90 (m, 28H), 1.31 (m, 104H), 0.90 (m, 36H), 0.68 (s, 12H).

^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm): 172.62, 172.52, 165.11, 152.32, 139.58, 133.00, 132.10, 131.86, 128.00, 122.66, 73.98, 65.34, 56.66, 56.12, 49.98, 42.30, 39.71, 39.52, 38.14, 36.97, 36.57, 36.19, 35.81, 34.10, 31.90, 31.83, 28.25, 28.16, 28.02, 27.81, 24.29, 23.85, 22.86, 22.59, 21.56, 21.43, 21.03, 19.32, 18.73, 11.86.

MS (MALDI): *m/z* for $C_{144}H_{218}N_2O_{16}$ 2232.6340; found 2232.6825.

Compound **5b**

FT-IR (cm^{-1}): 2943.3, 2870.2, 1729.9, 1466.3, 1379.3, 1315.0, 1238.4, 1191.8, 1108.8, 1010.8, 927.3, 841.3, 803.8, 757.9, 737.9, 687.8.

UV-vis (nm): 236.3, 315.9, 333.7, 348.4, 448.2.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ 8.83 (t, 2H, J = 1.6 Hz), 8.80 (d, 4H, J = 1.2 Hz), 5.33 (d, 4H, J = 4 Hz), 4.62 (m, 4H), 4.43 (t, 8H, J = 8, 4 Hz), 2.33 (m, 16 H), 1.86 (m, 32 H), 1.30 (m, 108H), 0.89 (m, 36H), 0.68 (s, 12H).

^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm): 172.89, 165.14, 152.28, 139.58, 132.99, 132.16, 127.96, 122.61, 73.82, 65.59, 56.65, 56.11, 49.98, 42.31, 42.28, 39.70, 39.52, 38.14, 36.96, 36.58, 36.55, 36.19, 35.81, 34.51, 31.87, 31.82, 28.45, 28.24, 28.02, 27.80, 25.52, 25.43, 24.69, 24.28, 23.85, 22.85, 22.59, 21.01, 19.32, 18.72, 11.85.

MS (MALDI): *m/z* for $C_{148}H_{226}N_2O_{16}$ 2288.6966; found 2288.7869.

Compound **5c**

FT-IR (cm^{-1}): 2942.3, 2868.5, 1730.9, 1466.9, 1379.6, 1332.5, 1309.8, 1238.9, 1189.0, 1106.8, 1000.7, 922.9, 801.2, 757.9, 737.3, 685.7, 628.6, 592.5.

UV-vis (nm): 237.2, 315.5, 332.8, 348.2, 448.7.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ 8.83 (t, 2H, J = 1.6 Hz), 8.80 (d, 4H, J = 1.2 Hz), 5.53 (d, 4H, J = 4Hz), 4.62 (m, 4H), 4.42 (t, 8H, J = 8, 4 Hz), 2.32 (t, 16H, J = 8Hz), 1.99 (m, 8H), 1.87 (m, 20H), 1.69 (m, 8H), 1.45 (m, 52H), 1.05 (m, 60H), 0.87 (m, 36H), 0.68 (s, 12H).

^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm): 173.08, 165.21, 152.32, 139.64, 132.20, 127.95, 122.62, 73.77, 65.76, 56.67, 56.12, 50.00, 42.30, 39.72, 39.52, 38.15, 36.98, 36.58, 36.19, 35.81, 34.57, 31.90, 31.84, 28.77, 28.56, 28.24, 28.03, 27.81, 25.70, 24.90, 24.29, 23.85, 22.85, 22.59, 21.03, 19.33, 18.72, 11.86.

MS (MALDI): *m/z* for $C_{152}H_{234}N_2O_{16}$ 2344.7592; found 2344.6648.

Compound **5d**

FT-IR (cm^{-1}): 2937.7, 2868.0, 1731.0, 1467.0, 1380.4, 1331.0, 1313.5, 1237.9, 1191.5, 1107.3, 1028.2, 994.8, 959.9, 923.3, 840.6, 801.0, 758.0, 737.9, 685.9, 591.5.

UV-vis (nm): 236.8, 316.0, 332.8, 348.7, 449.0.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ 8.83 (s, 2H), 8.80 (d, 4H, J = 1.6 Hz), 5.37 (d, 4H, J = 4 Hz), 4.62 (m, 4H), 4.42 (t, 8H, J = 8, 4 Hz), 2.30 (t, 16H, J = 8 Hz), 1.99 (m, 8H), 1.84 (m, 20H), 1.49 (m, 60H), 1.09 (m, 68H), 0.90 (m, 36H), 0.68 (s, 12H).

^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm): 173.19, 165.22, 152.31, 139.67, 132.22, 127.93, 122.60, 73.73, 65.86, 56.67, 56.12, 50.00, 42.30, 39.72, 39.52, 38.15, 36.98, 36.58, 36.19,

35.81, 34.64, 31.90, 31.64, 28.99, 28.94, 28.64, 28.24, 28.03, 27.81, 25.82, 24.97, 24.21, 23.85, 22.85, 22.59, 21.03, 19.33, 18.72, 11.86.

MS (MALDI): *m/z* for $C_{156}H_{242}N_2O_{16}$ 2400.8218; found 2400.7816.

Compound **5e**

FT-IR (cm^{-1}): 2935.5, 2867.3, 2850.9, 1732.2, 1467.1, 1379.9, 1336.7, 1313.7, 1238.6, 1173.9, 1106.5, 1009.9, 923.6, 842.2, 801.1, 758.7, 738.2, 686.3.

UV-vis (nm): 236.8, 315.5, 332.5, 347.5, 448.3.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ 8.83 (t, 2H, J = 1.2, 2 Hz), 8.80 (d, 4H, J = 1.6 Hz), 5.38 (d, 4H, J = 4 Hz), 4.62 (m, 4H), 4.42 (t, 8H, J = 8 Hz), 2.29 (q, 16H, J = 8, 8, 4 Hz), 1.99 (m, 8H), 1.85 (m, 20H), 1.49 (m, 80H), 1.09 (m, 56H), 0.87 (m, 36H), 0.68 (s, 12H).

^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm): 173.24, 165.24, 152.31, 139.68, 132.24, 122.60, 73.70, 65.91, 56.68, 56.12, 50.00, 42.31, 39.72, 39.52, 38.16, 36.99, 36.59, 36.19, 35.81, 34.67, 31.90, 31.85, 29.18, 29.13, 29.07, 28.68, 28.25, 28.03, 27.81, 25.94, 25.02, 24.29, 23.85, 22.85, 22.59, 21.03, 19.34, 18.72, 11.87.

MS (MALDI): *m/z* for $C_{160}H_{250}N_2O_{16}$ 2456.8844; found 2456.5314.

Compound **5f**

FT-IR (cm^{-1}): 2933.8, 2853.8, 1731.7, 1466.9, 1379.6, 1330.5, 1317.4, 1237.7, 1195.8, 1173.3, 1107.5, 1009.8, 958.2, 924.2, 801.1, 758.2, 736.9, 687.0, 487.4.

UV-vis (nm): 235.5, 315.8, 332.9, 348.3, 448.6.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ 8.84 (s, 2H), 8.80 (d, 4H, J = 1.2 Hz), 5.38 (d, 4H, J = 4 Hz), 4.62 (m, 4H), 4.42 (t, 8H, J = 8 Hz), 2.30 (m, 16H), 2.00 (m, 8H), 1.85 (m, 20H), 1.44 (m, 88H), 1.10 (m, 56H), 0.90 (m, 36H), 0.68 (s, 12H).

^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm): 173.29, 165.25, 161.27, 152.31, 139.69, 135.02, 132.24, 127.91, 122.60, 73.69, 65.93, 56.68, 56.12, 50.01, 42.31, 39.72, 39.52, 38.16, 37.00, 36.59, 36.19, 35.81, 34.70, 31.90, 31.85, 29.35, 29.23, 29.10, 28.69, 28.24, 28.03, 27.81, 25.97, 25.05, 24.29, 23.85, 22.85, 22.59, 21.03, 19.34, 18.72, 11.87.

MS (MALDI): *m/z* for $C_{164}H_{258}N_2O_{16}$ 2512.9470; found 2512.9132.

Compound **5g**

FT-IR (cm^{-1}): 2932.9, 2854.1, 1732.2, 1467.2, 1379.9, 1313.6, 1237.6, 1174.2, 1107.4, 1003.2, 923.8, 801.2, 758.9, 739.1, 686.5.

UV-vis (nm): 236.8, 315.6, 332.6, 347.5, 447.6.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ 8.84 (t, 2H, J = 1.2, 1.6 Hz), 8.80 (d, 4H, J = 1.6 Hz), 5.38 (d, 4H, J = 4 Hz), 4.62 (m, 4H), 4.42 (t, 8H, J = 8 Hz), 2.29 (m, 16H), 2.00 (m, 8H), 1.86 (m, 20H), 1.47 (m, 96H), 1.07 (m, 56H), 0.88 (m, 36H), 0.68 (s, 12H).

^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm): 173.31, 165.25, 152.30, 139.69, 132.24, 127.91, 122.60, 73.68, 65.96, 56.67, 56.11, 49.99, 42.30, 39.72, 39.52, 38.17, 37.00, 36.59, 36.18, 35.82, 34.72, 31.91, 31.84, 29.50, 29.43, 29.29, 29.28, 29.14, 28.71, 28.26, 28.04, 27.82, 26.00, 25.07, 24.30, 23.85, 22.86, 22.60, 21.03, 19.35, 18.73, 11.88.

MS (MALDI): *m/z* for $C_{168}H_{266}N_2O_{16}$ 2569.0096; found 2569.0582.

Compound **5h**

FT-IR (cm^{-1}): 2932.0, 2853.3, 1732.5, 1467.3, 1380.1, 1330.8, 1313.6, 1236.8, 1188.9, 1138.8, 1107.8, 1028.2, 997.6, 966.4, 923.6, 840.22, 801.1, 758.7, 739.1, 686.4, 628.5, 593.4.

UV-vis (nm): 236.2, 315.5, 333.0, 348.5, 447.8.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ 8.84 (t, 2H, J = 1.6 Hz), 8.80 (d, 4H, J = 1.6 Hz), 5.38 (d, 4H, J = 4 Hz), 4.62 (m, 4H), 4.42 (t, 8H, J = 8 Hz), 2.29 (m, 16H), 1.99 (m, 8H), 1.85 (m, 20H), 1.46 (m, 104H), 1.07 (m, 56H), 0.90 (m, 36H), 0.68 (s, 12H).

^{13}C NMR (400 MHz, $CDCl_3$, δ in ppm): 173.31, 165.51, 152.31, 139.70, 132.25, 127.76, 122.59, 73.67, 65.96, 56.68, 56.11, 50.01, 42.31, 39.72, 39.52, 38.17, 37.00, 36.60, 36.18, 35.81, 34.72, 31.90, 31.85, 29.56, 29.53, 29.46, 29.31, 29.29, 29.14, 28.71, 28.25, 28.03, 27.81, 26.00, 25.07, 24.29, 23.84, 22.85, 22.59, 21.03, 19.34, 18.72, 11.87.

MS (MALDI): *m/z* for $C_{172}H_{274}N_2O_{16}$ 2625.0722; found 2625.1021.

2. FTIR Spectra

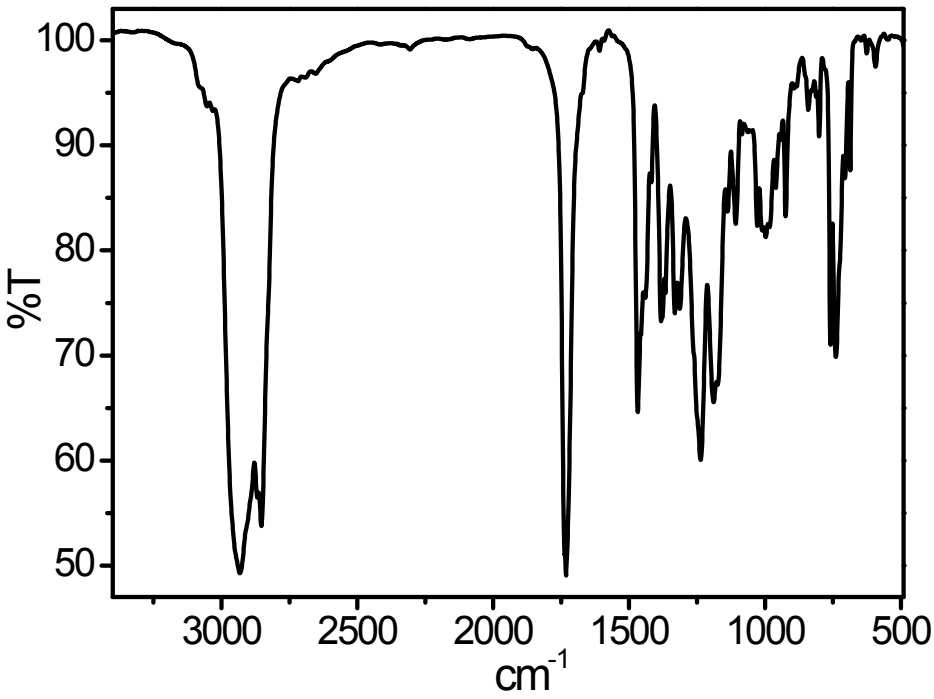

Figure S1 Representative FTIR spectrum of compound **5a**. Other compounds show similar spectra.

3. NMR spectra

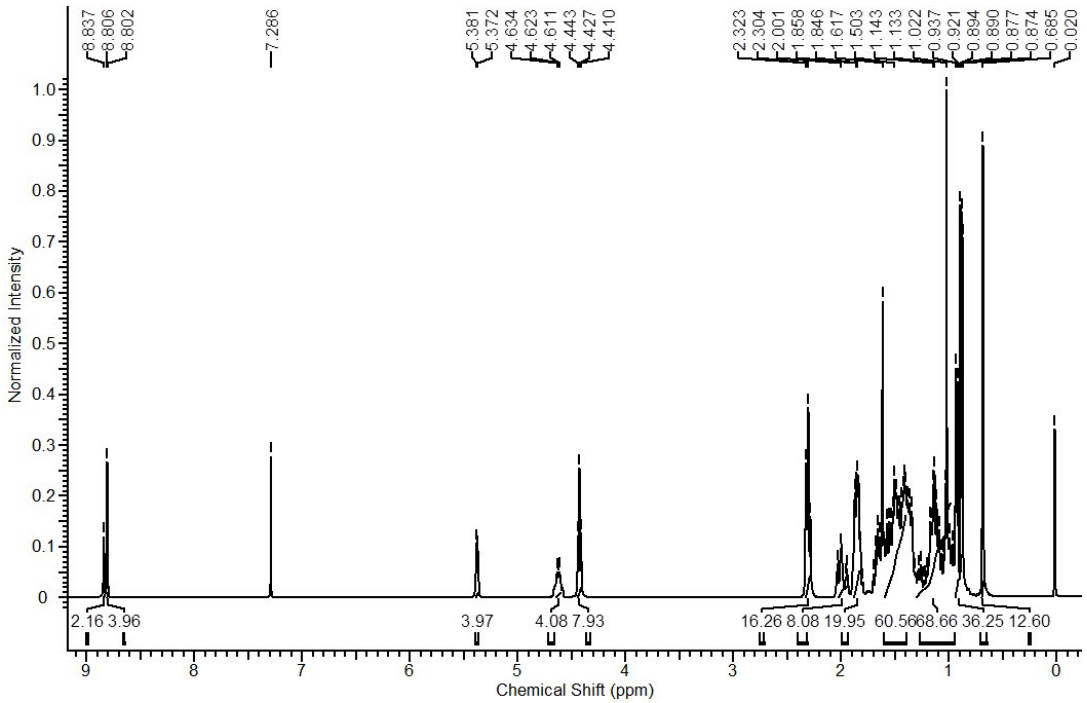

Figure S2 Representative ^{1}H NMR spectrum of compound **5d**. Other compounds show similar spectra.

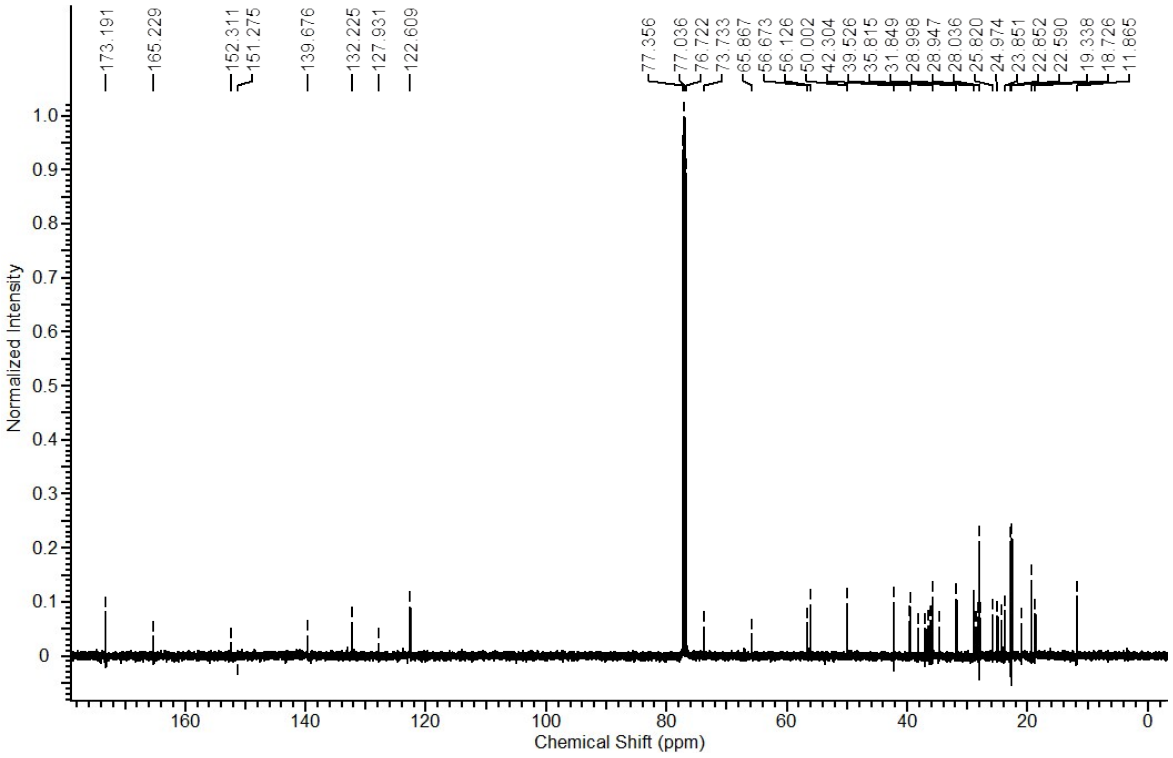

Figure S3 Representative ^{13}C NMR spectrum of compound **5d**. Other compounds show similar spectra.

4. Differential Scanning Calorimetry

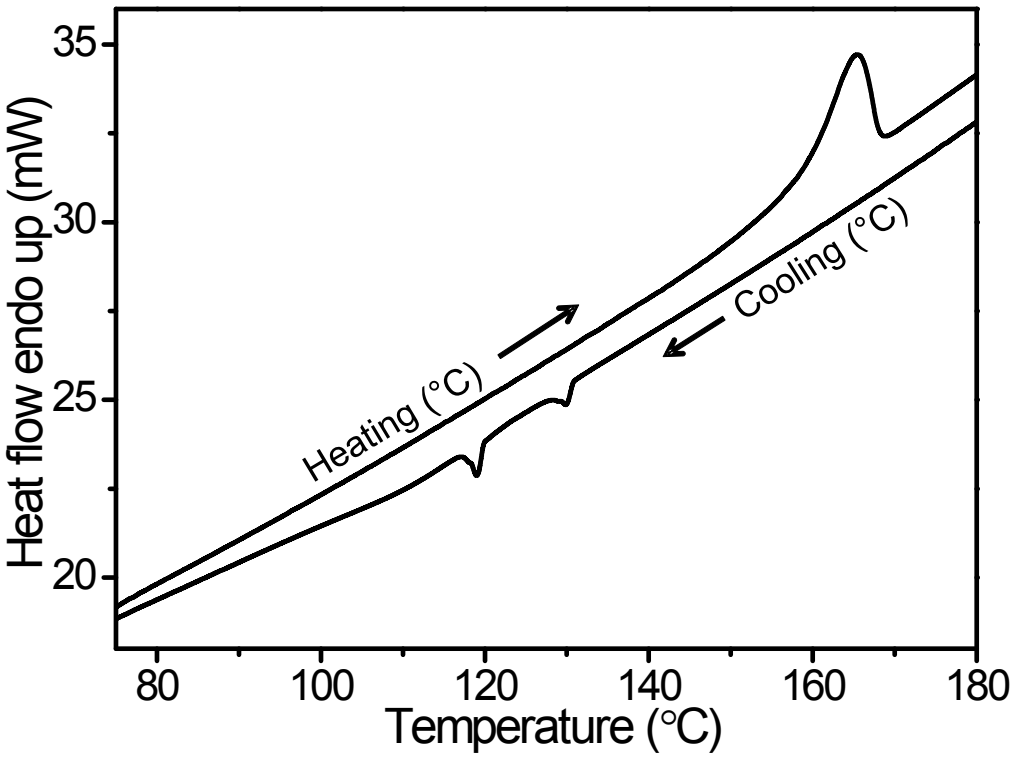

Figure S4 The DSC trace of compound **5d** on heating and cooling (scan rate 5 °C/min).

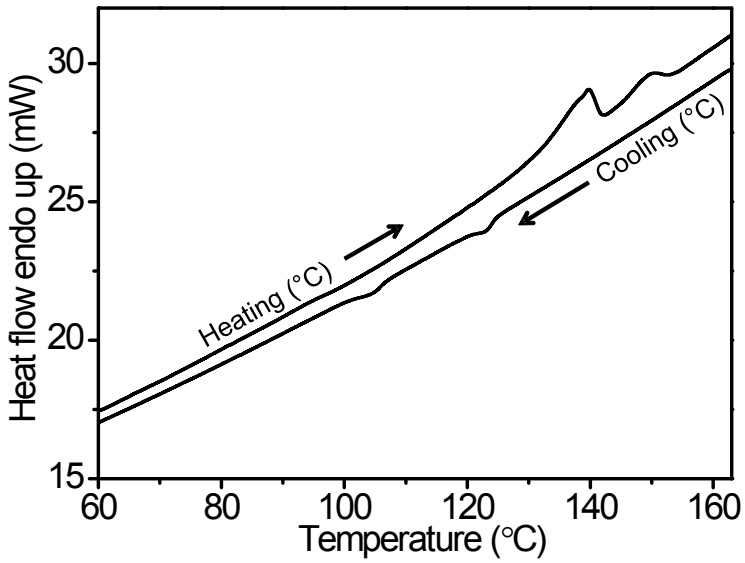

Figure S5 The DSC trace of compound **5e** on heating and cooling (scan rate 5 °C/min).

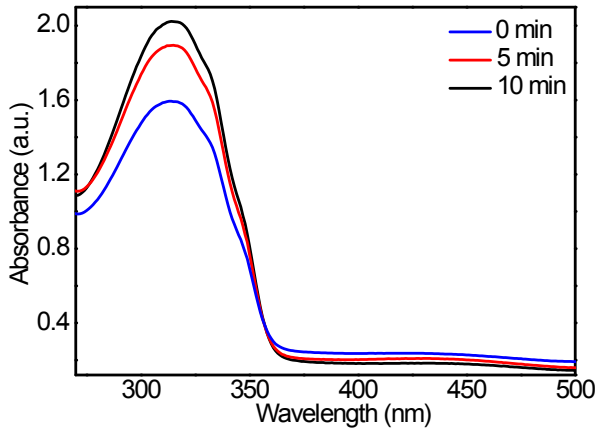

Figure S6 The UV-vis absorption spectra of compound **5a** obtained with respect to time on exposure to visible light.

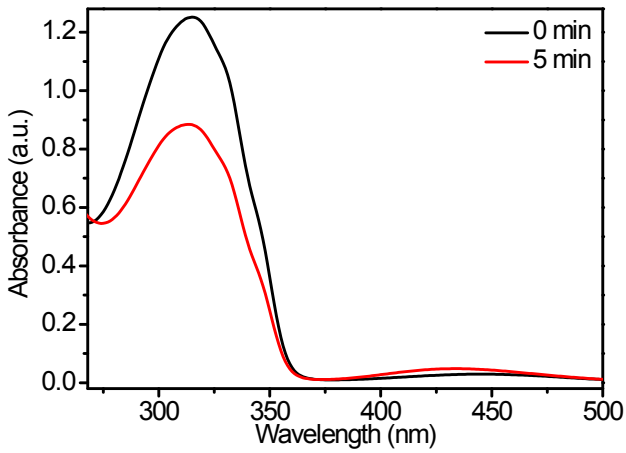

Figure S7 UV-vis absorption spectra of azobenzenetetracarboxylic acid obtained with respect to time on irradiation at 365 nm wavelength.