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Supplementary Information for

Photoinduced Reversible Phase Transition of Azobenzene-Containing Polydiacetylene Crystals

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EXPERIMENTAL SECTION

Materials. 4,6-Heptadecadiynoic acid (HDDA) was purchased from GFS Chemicals, Ohio, USA. 4-Aminoazobenzene was purchased from TCI. Heptadecanoic acid, 4-phenylazophenol, oxalyl chloride, propylphosphonic anhydride solution (50 wt. % in ethyl acetate), dichloromethane (DCM), dimethylformamide (DMF), methanol and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Triethylamine (TEA) was purchased from Daejung Chemicals & Metals (South Korea).

Instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VNMRS (600 MHz) spectrometer. XRD spectra were recorded on a HR-XRD, D8 discover, Bruker. Optical microscopic images were obtained with an Olympus BX 51W/DP70 microscope. IR spectra

were recorded on a Thermo Nicolet NEXUS 870 FT-IR equipped with ATR sampling Accessory (ZnSe plate). Raman spectra were collected with excitation at 785 nm laser using a Raman microscope, LabRAM HR Evolution, Horiba.

*(E)-N-(4-(Phenyldiazenyl)phenyl)heptadeca-4,6-diynamide (**HDDA-Azo**).* To a solution of 4,6-heptadecadiynoic acid (1.00 g, 3.81 mmol) in dichloromethane (DCM) (20 mL), a propylphosphonic anhydride solution (50 wt. % in ethyl acetate) (3.64 g, 5.72 mmol) and triethylamine (TEA) (1.16 g, 11.43 mmol) were added at 0 ^{o}C. To this solution, 4-aminoazobenzene (0.83 g, 4.19 mmol) was added and the reaction mixture was stirred overnight at ambient temperature under a N_2 atmosphere. The mixture was diluted with DCM and washed with 10% sodium bicarbonate and brine. The organic layer was dried over sodium sulfate and filtered. The solvent was removed *in vacuo* and the crude residue was subjected to a silica gel column chromatography (hexane/ethyl acetate = 4/1) to yield **HDDA-AZO** (1.01g, 60%) as a yellow solid. mp 162-164 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95-7.87 (m, 4H), 7.71 (d, 2H, J = 8.70 Hz), 7.59 (s, 1H), 7.54-7.42 (m, 3H), 2.71 (t, 2H, J = 7.20 Hz), 2.62 (t, 2H, J = 6.30 Hz), 2.25 (t, 2H, J = 6.90 Hz), 1.56-1.25 (m, 16H), 0.87 (t, 3H, J = 6.60 Hz). ^{13}C NMR (300 MHz, $CDCl_3$): δ 169.21, 152.84, 149.30, 140.30, 130.98, 129.25, 124.20, 122.93, 120.04, 79.20, 75.06, 67.19, 64.96, 36.45, 32.07, 29.75, 29.67, 29.48, 29.27, 29.04, 28.42, 22.86, 19.38, 15.76, 14.30. FT-IR (ZnSe, cm^{-1}): 3259, 3040, 2952, 2918, 2847, 1656, 1602, 1538, 1461, 1406, 1378, 1303, 1246, 1182, 1156, 1108, 1072, 1040, 1019, 976, 918, 848, 762, 720, 685. HR-MS (ESI): calculated for $C_{29}H_{35}N_3ONa$ [M+Na^+] 464.2678, found 464.2680.

*(E)-4-(Phenyldiazenyl)phenyl heptadeca-4,6-diynoate (**HDDA-Azo-Ester**).* To a solution of 4,6-heptadecadiynoic acid (1.00 g, 3.81 mmol) in dichloromethane (DCM) (20 mL), oxalyl chloride (0.73 g, 5.72 mmol) was added dropwise at ambienttemperature under a N_2

atmosphere. The reaction mixture was stirred for 5 min. To this solution, a catalytic amount (one drop) of dimethylformamide (DMF) was added and the mixture was stirred for 4 h. After concentrating *in vacuo*, the residue was redissolved in 10 mL of DCM. The resulting solution was added dropwise to a DCM solution (15 mL) containing 4-phenylazophenol (0.83 g, 4.19 mmol) and triethylamine (TEA) (1.16 g, 11.43 mmol). The resulting mixture was allowed to stir for overnight at ambient temperature. The solvent was removed *in vacuo* and the residue was subjected to a silica gel column chromatography (hexane/ethyl acetate = 9/1) to give ***HDDA-Azo-Ester*** (0.85g, 50%) as a pale orange solid. mp 75-77 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97-7.87 (m, 4H), 7.53-7.43 (m, 3H), 7.28-7.23 (m, 2H), 2.82 (t, 2H, J = 7.50 Hz), 2.70 (t, 2H, J = 7.80 Hz), 2.25 (t, 2H, J = 7.20 Hz), 1.56-1.25 (m, 16H), 0.86 (t, 3H, J = 6.6 Hz); ^{13}C NMR (300 MHz, $CDCl_3$): δ 169.79, 152.49, 152.45, 150.28, 131.07, 129.08, 124.06, 122.84, 122.15, 78.72, 77.43, 77.00, 76.59, 74.24, 66.60, 64.88, 33.28, 31.88, 29.54, 29.47, 29.29, 29.07, 28.83, 28.23, 22.67, 19.18, 15.23, 14.12; FT-IR (ZnSe, cm^{-1}): 3067, 2954, 2918, 2849, 1742, 1592, 1495, 1469, 1415, 1373, 1291, 1223, 1201, 1146, 1011, 924, 861, 763, 719, 686; HR-MS (ESI): calculated for $C_{29}H_{34}N_2O_2Na$ [M+Na$^+$] 465.2518, found 465.2519.

(E)-N-(4-(Phenyldiazenyl)phenyl)heptadecanamide ***(HDA-Azo)***. To a solution of heptadecanoic acid (1.00 g, 3.70 mmol) in dichloromethane (DCM) (20 mL), oxalyl chloride (0.70 g, 5.55 mmol) was added dropwise at ambient temperature under a N_2 atmosphere. The reaction mixture was stirred for 5 min. To this solution, a catalytic amount (one drop) of dimethylformamide (DMF) was added and stirred for 4 h. After concentrating *in vacuo*, the residue was redissolved in 10 mL of DCM. The resulting solution was added dropwise to a solution of 4-aminoazobenzene (0.88 g, 4.44 mmol) and triethylamine (TEA) (1.12 g, 11.09 mmol) in 15 mL of DCM. The resulting mixture was allowed to stir for overnight at ambient

temperature. The solvent was removed *in vacuo* and the crude product was purified by silica gel column chromatography using hexane/ethyl acetate (v/v = 4/1) as an eluent to yield ***HAD-Azo*** (0.95g, 57%) as a pale orange solid. mp 127-129 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (m, 4H), 7.71 (d, 2H, J = 8.70 Hz), 7.54-7.42 (m, 4H), 2.39 (t, 2H, J = 7.80 Hz), 1.74 (quint, 2H, J = 7.20 Hz), 1.46-1.14 (m, 26H), 0.88 (t, 3H, J = 6.60 Hz); ^{13}C NMR (300 MHz, $CDCl_3$): δ 171.47, 152.67, 148.92, 140.49, 130.73, 129.06, 128.90, 124.03, 122.71, 122.33, 120.12, 119.59, 77.21, 37.97, 31.92, 29.69, 29.62, 29.48, 29.37, 29.27, 25.52, 22.70, 14.13; FT-IR (ZnSe, cm^{-1}): 3300, 3055, 2966, 2917, 2848, 1656, 1602, 1541, 1473, 1440, 1410, 1385, 1301, 1259, 1248, 1199, 1183, 1156, 1105, 1071, 1020, 964, 927, 851, 764, 730, 688, 657; HR-MS (ESI): calculated for $C_{29}H_{43}N_3ONa$ [M+Na$^+$] 472.3304, found 472.3301.

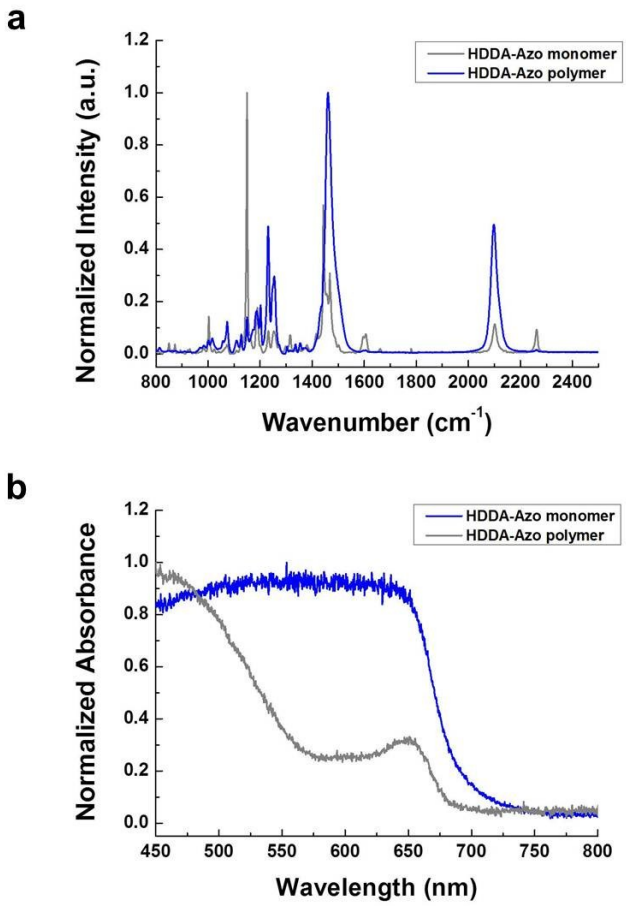

Figure S1. (a) Raman spectra of HDDA-Azo crystal before (gray line) and after (blue line) UV irradiation. The peak at 2263 cm^{-1} represents monomeric HDDA-Azo and the peaks around 1461 cm^{-1} and 2098 cm^{-1} represent conjugated ene-yne structures in the polymer. (b) UV-vis absorption spectra of HDDA-Azo crystal before (gray line) and after (blue line) polymerization.

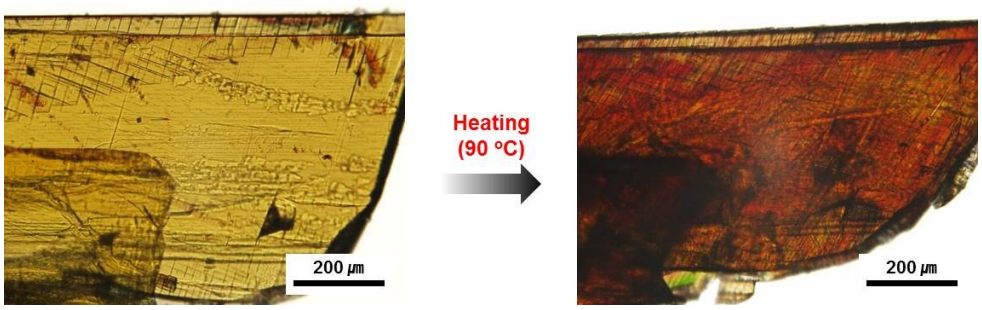

Figure S2. Optical microscopic images of a polymerized crystal derived from HDDA-Azo before (left) and after (right) heating to 90 °C.

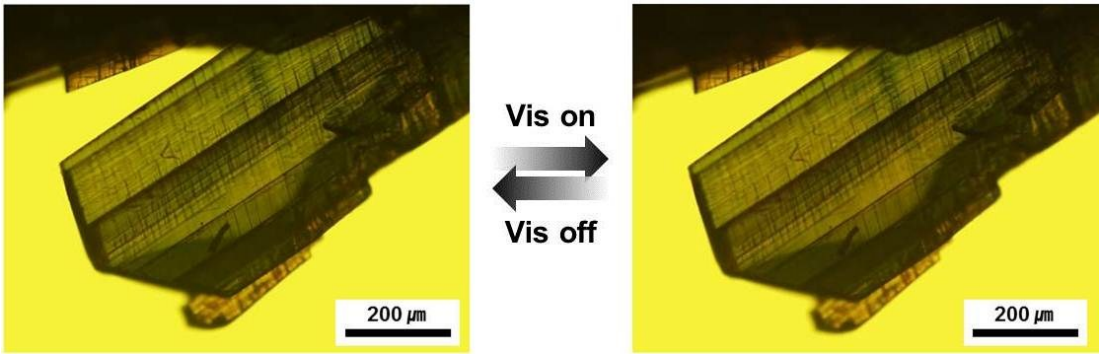

Figure S3. Optical microscopic images of a polymerized crystals derived from HDDA-Azo before (left) and after (right) visible light (460-490 nm) irradiation for 1 min.

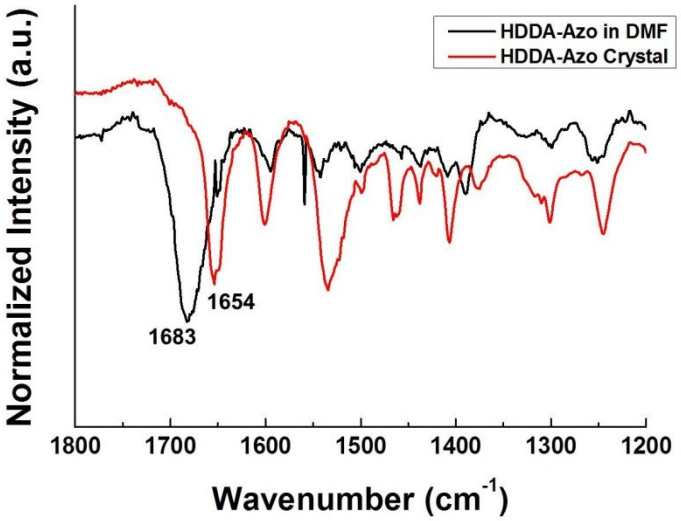

Figure S4. FT-IR spectra of HDDA-Azo in DMF (black line) and polymerized HDDA-Azo crystal (red line).

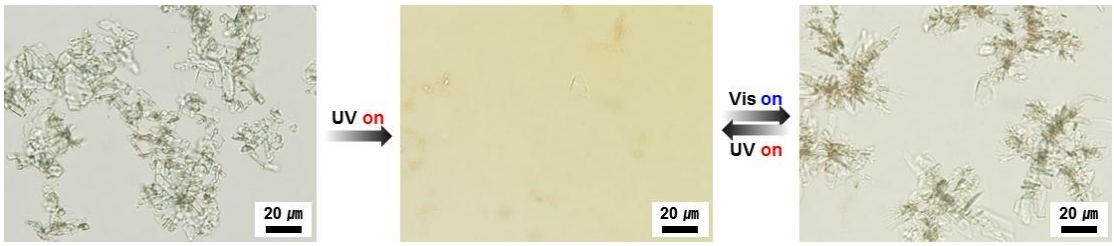

Figure S5. Photoinduced reversible solid-liquid phase transition of HDDA-Azo crystals in aqueous DMSO. (UV source: 365 nm, 10 mW/cm^2, visible light: 460-490 nm)

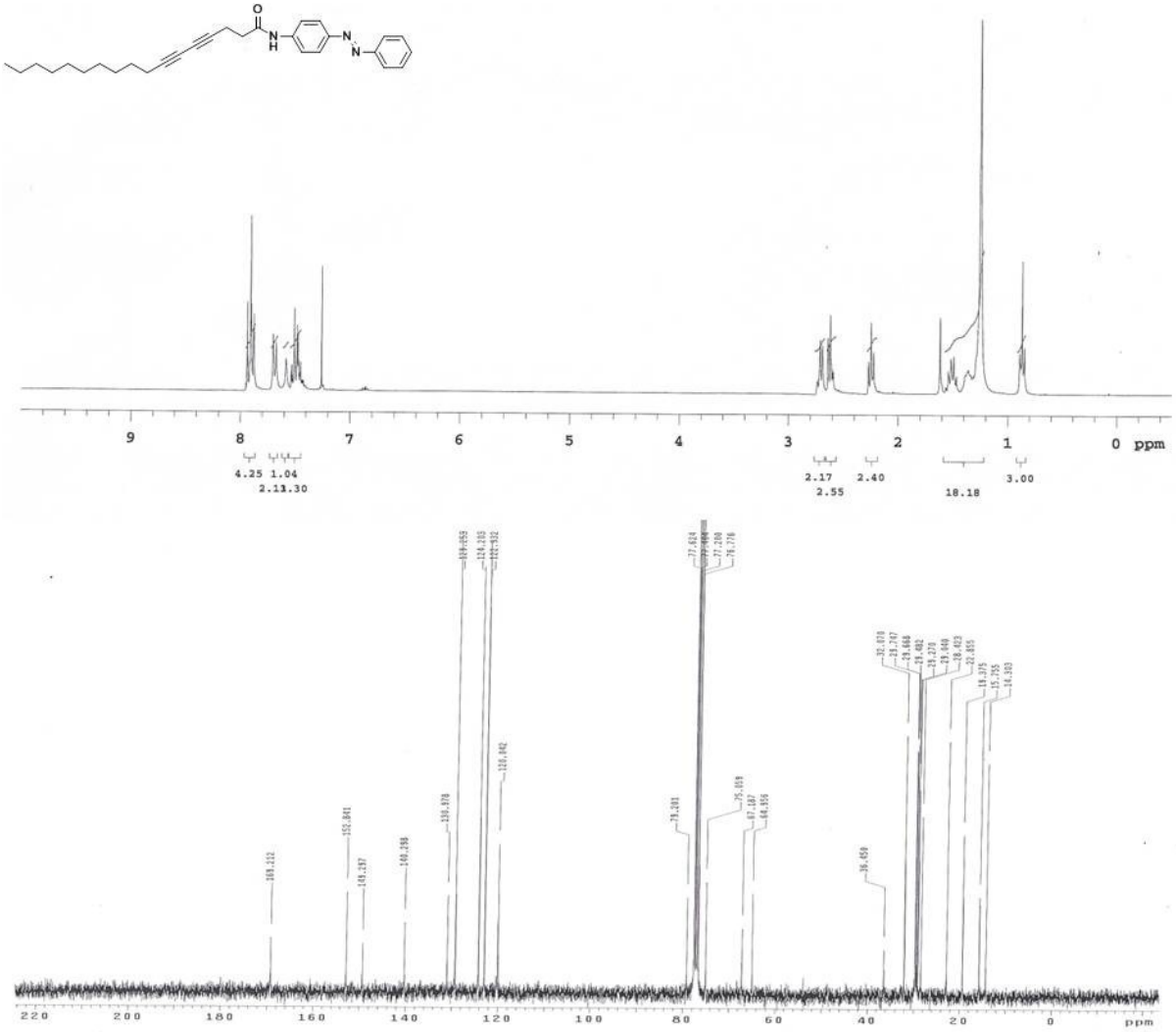

Figure S6. ^{1}H NMR and ^{13}C NMR spectra of HDDA-Azo in $CDCl_3$.

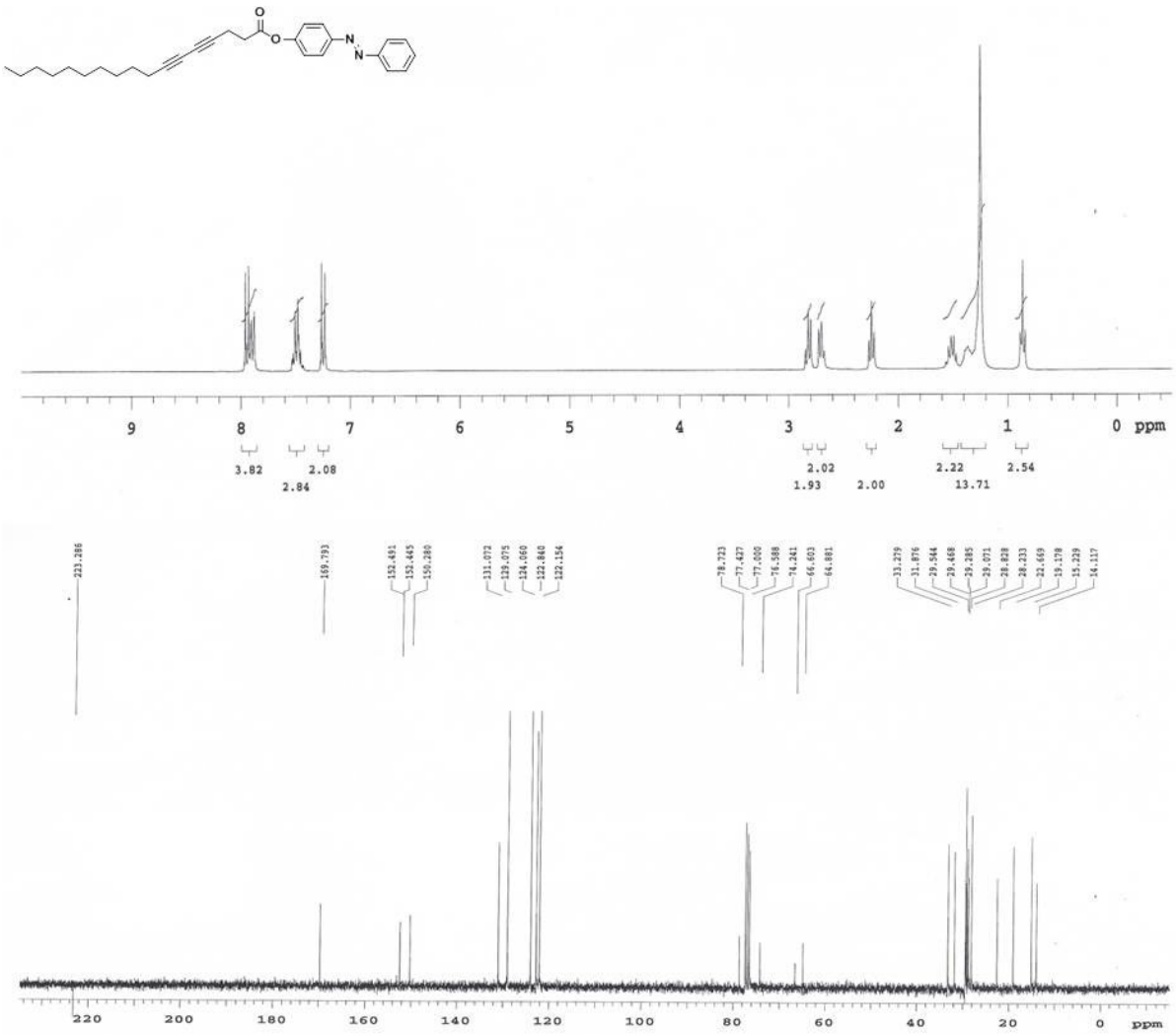

Figure S7. ^{1}H NMR and ^{13}C NMR spectra of HDDA-Azo-ester in $CDCl_3$.

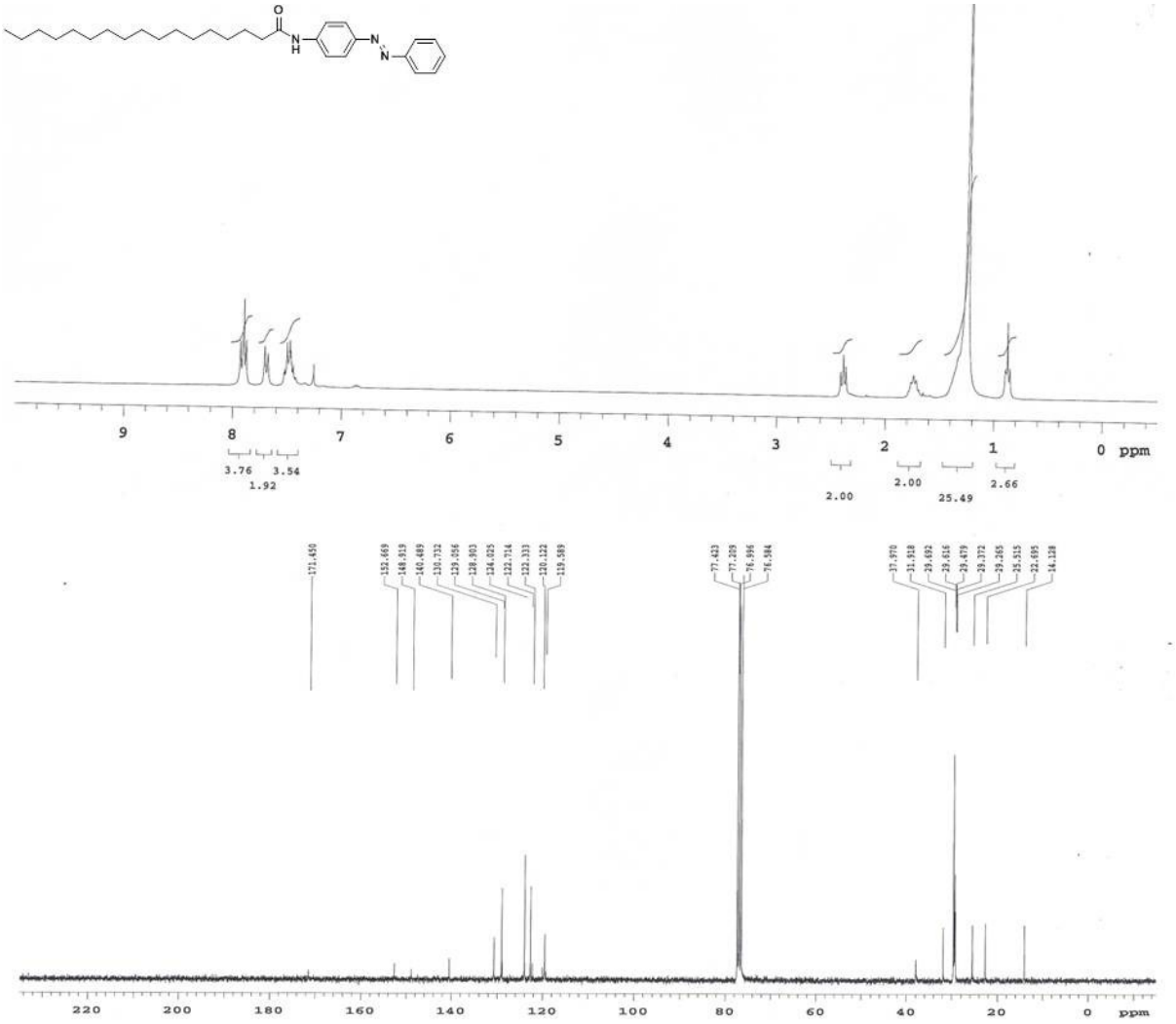

Figure S8. ^{1}H NMR and ^{13}C NMR spectra of HDA-Azo in $CDCl_3$.