Electronic Supplementary Information - Structural relationships for the design of responsive azobenzene-based lyotropic liquid crystals

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Synthesis:

General Notes:

All reagents sourced were of ≥95% purity and were used as received without further purification unless otherwise stated. Ultrapure water was from a Millipore Direct-Q 5, with minimal resistivity 18.4 MΩ·cm. SANS measurements were taken using the BILBY beam-line at ANSTO, Lucas Heights, NSW.[1, 2] SAXS measurements were taken using the SAXS/WAXS beamline using 12 keV X-ray radiation at the Australian Synchrotron, Clayton, VIC, a Bruker NanoSTAR II SAXS (Bruker AXS, Karlsruhe) using Cu-Kα radiation at ANSTO, Lucas Heights, NSW, or a Bruker N8 Horizon SAXS using Cu-Kα radiation at the Monash X–ray Platform, Monash University, Clayton, VIC. IR spectra were obtained using an Agilent Technologies Cary 630 ATR FTIR spectrometer. NMR spectra were taken on a Bruker BACS 400 spectrometer.

Synthesis of Azobenzene-based molecules:

Synthesis of 4-(4(hydroxyphenyl)diazenyl)benzoic acid (4-carboxy-4'-hydroxyazobenzene) [AZO1] (1): 3.59 g of 4-aminobenzoic acid (26.2 mmol, 1 equiv.) was dissolved in 30 mL of ultrapure water with 3 mL of concentrated HCl and cooled to 0℃. 1.82 g of sodium nitrite (26.3 mmol, 1 equiv.) was predissolved in 50 mL ultrapure water, cooled to 0℃ and slowly added to the reaction solution, before stirring at 0℃ for 2 hours until an opaque, bright yellow solution evolved. Separately, 2.74 g (29.1 mmol, 1.1 equiv.) of phenol was predissolved in 30 mL of ultrapure water with 0.68 g NaOH (17.1 mmol) and 2.55 g K_2CO_3 (18.4 mmol), cooled to 0℃ and slowly added to the reaction solution. The reaction solution was then allowed to warm to RT with stirring for 18 hours. The orange/red microcrystalline product was filtered and recrystallized from 1:1 water:ethanol solution. Yield: 6.28 g (99%) IR: v =3550 (OH, s), 3456 (s), 2850 (OH, s, broad) 2821 (CH, m), 2656 (m), 2531 (m), 2105 (m), 1909 (m), 1660 (C=O, s), 1579 (s), 1507 (m) 1464 (m), 1433 (m), 1400 (w), 1363 (w), 1285 (s), 1224 (s), 1150 (s), 1096 (s), 1005 (w), 913 (m), 873 (m), 842

(s), 774 (s), 713 (m), 694 (m), 660 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, CD_3OD): δ = 6.95 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.88 (2H, d, J(H,H)= 8 Hz, Ar- H), 7.91 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.18 (2H, d, J(H,H)= 8 Hz, Ar-H) ppm; ^{13}C NMR (100 MHz, 300 K, DMSO-d6): δ = 115.5, 121.8, 125.0, 130.4, 131.6, 146.2, 155.6, 161.5, 167.9 ppm.

Synthesis of 3-(4-(hydroxyphenyl)diazenyl)benzoic acid (3-carboxy-4'-hydroxyazobenzene) [AZO2] (2): 2.10 g of 3-aminobenzoic acid (15.3 mmol, 1 equiv.) was dissolved in 30 mL of ultrapure water with 3 mL of concentrated HCl and cooled to 0℃. 1.14 g of sodium nitrite (16.5 mmol, 1.08 equiv.) was predissolved in 25 mL ultrapure water, cooled to 0℃ and slowly added to the reaction solution before stirring at 0℃ for 2 hours until a bright orange solution evolved. 1.50 g (15.9 mmol, 1.05 equiv.) of phenol was predissolved in 30 mL of ultrapure water with 0.68 g NaOH (17.1 mmol) and 2.55 g K_2CO_3 (18.4 mmol), cooled to 0℃ and slowly added to the reaction solution. The reaction solution was then allowed to warm to RT with stirring for 18 hours. The red microcrystalline product was filtered and recrystallized from 1:1 water:ethanol solution. Yield 3.60 g (97%) IR: v = 3558 (OH, s), 2811 (CH, m), 2780 (OH, s, broad), 2663 (m), 2109 (m), 1876 (m), 1677 (C=O, s), 1579 (s), 1514 (w), 1477 (w), 1433 (m), 1373 (w), 1309 (s), 1244 (m), 1203 (m), 1163 (m), 1069 (w), 998 (w), 940 (w), 920 (s), 829 (s), 758 (s), 711 (m), 673 (s) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-*d*6): δ = 6.96 (2H, d, J^3(H,H)= 8 Hz), Ar-H), 7.70 (1H, t, J^3(H,H)= 8 Hz, Ar-H), 7.85 (2H, d, J^3(H,H)= 8 Hz, Ar-H), 8.05 (2H, dt, J^3(H,H)= 8 Hz, J^4(H,H)= 2 Hz, Ar-H), 8.31 (1 H, t, J^4(H,H) = 2 Hz, Ar-H), 10.04 (1H, s, Ph-OH), 13.23 (1H, s, COOH) ppm; ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 116.4, 122.3, 125.6, 127.4, 130.3, 131.3, 132.5, 145.6, 152.6, 161.8, 167.3 ppm.

Synthesis of 5-(4-(hydroxyphenyl)diazenyl)isophthalic acid (3,5-dicarboxy-4'-hydroxyazobenzene) [AZO3] (3): 2.70 g of 5-aminoisophthalic acid (14.9 mmol, 1 equiv.) was dissolved in 30 mL of ultrapure water with 3 mL of concentrated HCl and cooled to 0℃. 1.14 g of sodium nitrite (16.5 mmol, 1.11 equiv.) was predissolved in 50 mL ultrapure water, cooled to 0℃ and slowly added to the reaction solution before stirring at 0℃ for 2 hours until an opaque bright yellow solution evolved. 1.50 g (15.9 mmol, 1.07 equiv.) of phenol was predissolved in 30 mL of ultrapure water with 0.68 g NaOH (17.1 mmol) and 2.55 g K_2CO3 (18.4 mmol), cooled to 0℃ and slowly added to the reaction solution. The reaction solution was then allowed to warm to RT with stirring for 18 hours. The yellow microcrystalline product was filtered and recrystallized from 1:1 water:ethanol solution. Yield 4.08 g (96%) IR: v = 3328 (OH, s), 2970 (OH, s, broad), 2815 (CH, m), 2619 (m), 1700 (C=O, s), 1605 (m), 1585 (s), 1505 (s), 1457 (m), 1420 (w), 1268 (s), 1224 (s), 1146 (s), 1099 (m), 974 (w), 913 (m), 839 (s), 751 (s), 666 (s) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-*d*6): δ = 6.98 (2H, d, J^3(H,H)= 8 Hz), Ar-H), 7.89 (2H, d, J^3(H,H)= 8 Hz), Ar-H), 8.50 (2 H, d, J^4(H,H)= 2 Hz, Ar-H), 8.55 (1 H, t, J^4(H,H)= 2 Hz, Ar-H), 10.47 (1 H, s, Ph-OH), 13.47 (1 H, s, -COOH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 116.6, 125.9, 126.7,

131.4, 133.1, 145.6, 152.7, 162.2, 166.6 ppm.

Synthesis of 4-((4-hydroxyphenyl)diazenyl)-*N*-R-benzamide (Figure 16): 0.25 g 4-((4- hydroxyphenyl)diazenyl)benzoic acid **(1)** (1 mmol, 1 equiv.), 0.23 g DCC (1.1 mmol, 1.1 equiv.), catalytic quantities of NHS and stoichiometric excess of *R*-amine (≥1.1 equiv.) were dissolved in 5 mL DMF and stirred at RT for 18 hours. The resultant deep red reaction solution was filtered, washed twice with 20 mL of hexane, extracted into ethylacetate, and washed with 1 × 30 mL dilute acetic acid and 4 × 30 mL ultrapure water before the solvent was removed under vacuum. Where further purification was needed, the product was dissolved in the minimum volume of dichloromethane (DCM) and left for two days. The clear crystalline solids were filtered and discarded before the solvent was removed under vacuum to yield orange products that were recrystallized from a 1:1 water:ethanol mixture.

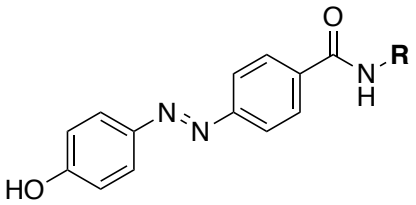

Figure 1. 4-((4-hydroxyphenyl)diazenyl)-*N*-R-benzamide.

4-((4-hydroxyphenyl)diazenyl)-*N*-ethyl-benzamide [AZO1-C2]: Yield 0.26 g (96%); IR: v = 3321 (NH, m), 3200 (OH, s, broad), 2973 (m), 2926 (CH, m), 2851 (CH, m), 1690 (C=O, s), 1636 (s), 1582 (s), 1534 (s), 1494 (m), 1460 (m), 1386 (w), 1352 (w), 1308 (w), 1252 (s), 1224 (s), 1197 (s), 1133 (s), 1099 (s), 1007 (m), 890 (m), 842 (s), 765 (m), 717 (w), 663 (w) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.16 (3 H, t, J(H,H)= 8 Hz, CH_3), 4.03 (2 H, q, J(H,H)= 8 Hz, CH_2), 6.97 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.83 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.86 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.01 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.58 (1 H, s, NH), 10.39 (1 H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 15.3, 34.9, 116.5, 125.4, 125.8, 132.1, 136.4, 146.0, 156.1, 160.7, 165.4 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-propyl-benzamide [AZO-*n*C3]: Yield 0.29 g (99%); IR: v = 3328 (NH, m), 3179 (OH, s, broad), 2926 (CH, s), 2845 (CH, m), 1694 (C=O, s), 1636 (s), 1582 (s), 1528 (s), 1501 (m), 1464 (s), 1430 (m), 1379 (w), 1332 (w), 1278 (s), 1227 (s), 1183 (m), 1140 (s), 1099 (m), 1001 (m), 960 (w), 853 (s), 765 (m), 714 (m), 690 (w), 660 (w) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.91 (3H, t, J(H,H)= 8 Hz, CH_3), 1.74 (2H, m, J(H,H)= 8 Hz, CH_2), 3.25 (2H, t, J(H,H)= 8 Hz, CH_2), 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.84 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.87 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.01 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.59 (1H, s, NH), 10.41 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 11.9, 22.8, 41.6, 116.5, 122.2, 122.5, 125.7, 129.0, 131.0, 136.4, 145.8, 161.8 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-*iso*-propyl-benzamide [AZO1-*i*C3]: Yield 0.29 g (99%); IR: v = 3298 (NH, s), 3163 (OH, s, broad), 2977 (m), 2923 (CH, s), 2838 (CH, s), 1636 (m), 1615 (s), 1585 (s), 1541 (s), 1497 (m), 1450 (m), 1352 (m), 1311 (w), 1268 (m), 1234 (s), 1170 (w), 1133 (s), 1089 (m), 1001 (m), 893 (w), 839 (s), 772 (m), 710 (m), 677 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.19 (6 H, d, J(H,H)= 8 Hz, CH_3), 4.12 (1 H, sept, J(H,H)= 8 Hz, CH), 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.83 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.86 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.01 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.34 (1 H, s, NH), 10.38 (1 H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 23.6, 45.9, 116.5, 124.8, 125.0, 131.6, 133.6, 146.2, 155.6, 161.5, 165.9 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-butyl-benzamide [AZO1-*n*C4]: Yield 0.31 g (99%); IR: v = 3321 (NH, m), 3142 (OH, s, broad), 2929 (CH, s), 2848 (CH, s), 1683 (s), 1629 (C=O, s), 1571 (s), 1535 (s), 1494 (m), 1457 (s), 1430 (m), 1373 (w), 1346 (w), 1305 (m), 1268 (s), 1231 (s), 1180 (m), 1133 (s), 1082 (m), 998 (m), 954 (w), 886 (m), 842 (s), 798 (w), 772 (m), 721 (m), 687 (w) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.87 (3H, t, J(H,H)= 8 Hz, CH_3), 1.27 (2H, sextet, J(H,H)= 8 Hz, CH_2), 1.37 (2H, pentet, J(H,H)= 8 Hz, CH_2), 3.07 (2H, t, J(H,H)= 8 Hz, CH_2), 6.97 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.85 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.89 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.98 (1 H, s, NH), 8.11 (2H, d, J(H,H)= 8 Hz, Ar-H), 10.44 (1 H, s, OH) ppm. ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 13.4, 21.2, 32.2, 40.5, 116.6, 123.8, 125.2, 130.4, 131.6, 145.2, 155.5, 161.5, 166.3 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-*iso*-butyl-benzamide [AZO1-*i*C4]: Yield 0.30 g (99%); IR: v = 3328 (NH, m), 3125 (OH, s, broad), 2926 (CH, s), 2855 (CH, s), 1687 (s), 1626 (s), 1592 (s), 1541 (s), 1504 (m), 1454 (s), 1423 (w), 1386 (w), 1308 (m), 1268 (m), 1227 (s), 1180 (w), 1130 (s), 1092 (w), 1005 (w), 897 (w), 863 (m), 846 (s), 792 (w), 755 (m), 721 (m), 687 (w) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.82 (6H, d, J(H,H)= 8 Hz, CH_3), 2.22 (1H, m, CH), 2.90 (2H, d, J(H,H)= 8 Hz), 6.97 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.88 (4H, m, Ar-H), 8.12 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.36 (1H, s, NH), 10.44 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 20.7, 28.8, 47.3, 116.5, 122.3, 125.5, 128.9, 131.0, 145.8, 145.8, 153.9, 161.9 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-*tert*-butyl-benzamide [AZO1-*t*C4]: Yield 0.31 g (99%); IR: v = 3318 (NH, m), 3129 (OH, s, broad), 2929 (CH, s), 2845 (CH, s), 1632 (s), 1585 (s), 1538 (s), 1498 (m), 1443 (m), 1363 (m), 1315 (w), 1278 (m), 1234 (s), 1133 (s), 1103 (w), 1072 (w), 1005 (w), 957 (w), 883 (m), 842 (s), 774 (m), 724 (w) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.41 (9 H, s, CH_3), 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.83 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.85 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.89 (1 H, s, NH), 7.98 (2H, d, J(H,H)= 8 Hz, Ar-H), 10.38 (1 H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 29.1, 60.6, 116.7, 124.7, 125.2, 131.2, 131.8, 145.1, 154.4, 162.3, 165.6 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-octyl-benzamide [AZO1-*n*C8]: Yield 0.35 g (96%); IR: v = 3331 (NH, m), 3247 (OH, s, broad), 2926 (CH, s), 2848 (CH, s), 1669 (C=O, s), 1633 (s), 1589 (s), 1525 (s), 1501 (s), 1464 (s), 1426 (m), 1369 (s), 1305 (w), 1282 (s), 1227 (s), 1133 (s), 1078 (m), 998 (m), 893 (m), 836 (s), 772 (w), 728 (m), 667 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.85 (3H, t, J(H,H)= 8 Hz, CH_3), 1.18 (12H, m, CH_2), 1.24 (2H, m, CH_2), 3.28 (2H, t, J(H,H)= 8 Hz, CH_2), 6.97 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.83 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.85 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.01 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.56 (1H, s, NH), 10.38 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 14.4, 22.7, 26.5, 30.1, 30.4, 32.1, 42.4, 116.5, 121.8, 125.3, 130.4, 131.9, 146.2, 155.2, 161.5, 166.7 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-*tert*-octyl-benzamide [AZO1-*t*C8]: Yield 0.37 g (100%); IR: v = 3317 (NH, m), 3254 (OH, s, broad), 2926 (CH, s), 2852 (CH, s), 1707 (m), 1670 (C=O, s), 1636 (s), 1629 (s), 1579 (s), 1531 (s), 1494 (m), 1470 (m), 1373 (m), 1302 (w), 1282 (s), 1221 (s), 1133 (s), 1072 (w), 1001 (m), 890 (m), 839 (s), 758 (m), 724 (w), 677 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.99 (9 H, s, CH_3), 1.44 (6 H, s, CH_3), 1.88 (2 H, s, CH_2), 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.76 (1 H, s, NH), 7.82 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.83 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.94 (2H, d, J(H,H)= 8 Hz, Ar-H), 10.38 (1 H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 29.1, 30.5, 32.1, 45.8, 53.2, 116.6, 123.3, 125.2, 131.2, 131.9, 146.4, 155.7, 162.5, 166.3 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-2-ethylhexyl-benzamide [AZO1-EH]: Yield 0.36 g (98%); IR: v = 3328 (NH, m), 3132 (OH, s, broad), 2936 (CH, s), 2859 (CH, s), 1727 (w), 1636 (C=O, s), 1582 (s), 1548 (s), 1498 (m), 1460 (s), 1427 (m), 1366 (m), 1312 (m), 1275 (s), 1227 (s), 1177 (w), 1123 (s), 1082 (m), 1045 (m), 1011 (m), 964 (w), 897 (m), 842 (s), 765 (m), 718 (m), 670 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.88 (3H, t, J(H,H)= 8 Hz, CH_3), 1.06 (3H, t, J(H,H)= 8 Hz, CH_3), 1.29 (8H, m, CH_2), 1.58 (1H, m, J(H,H)= 8 Hz, CH), 3.21 (2H, d, J(H,H)= 8 Hz, CH_2), 6.95 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.83 (4H, m, Ar-H), 8.00 (2H, J(H,H)= 8Hz, Ar-H), 8.50 (1H, s, NH), 10.4 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 11.1, 14.4, 19.0, 23.0, 24.2, 28.8, 30.9, 43.0, 116.5, 122.3, 125.6, 128.8, 136.5, 145.7, 153.9, 162.0, 166.1 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-dodecyl-benzamide [AZO1-*n*C12]: Yield 0.42 g (99%); IR: v = 3327 (s), 3277 (OH, s, broad), 3250 (s), 2920 (CH, s), 2845 (CH, s), 1710 (m), 1673 (m), 1626 (s), 1585 (s), 1528 (s), 1497 (m), 1464 (m), 1430 (w), 1376 (s), 1339 (w), 1309 (m), 1278 (s), 1244 (s), 1211 (s), 1140 (s), 1082 (m), 1032 (m), 960 (w), 930 (w), 893 (m), 836 (s), 768 (w), 718 (m), 666 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.88 (9H, m, alkyl), 1.29 (12H, m, alkyl), 1.59 (2H, m, CH_2), 3.21 (2H, t, J(H,H)= 8 Hz, CH_2), 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.85 (4H, t, J(H,H)= 8 Hz, Ar-H), 8.00 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.50 (1H, s, NH), 10.4 (1H, s, OH, broad) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 13.9, 23.0, 27.2, 30.2,

31.5, 41.2, 116.6, 121.6, 125.2, 130.7, 131.6, 145.7, 155.6, 161.5, 165.4 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-octadec-9-en-1-yl-benzamide [AZO-C18:1]: Yield 0.34 g (67%); IR: v = 3340 (OH, s, broad), 3298 (NH, s), 2960 (s), 2915 (CH, s), 2848 (CH, s), 1673 (m), 1633 (s), 1552 (s), 1454 (s), 1376 (s), 1339 (m), 1258 (s), 1217 (m), 1140 (w), 1092 (s), 1048 (s), 1015 (s), 883 (w), 799 (s), 724 (m), 697 (w), 660 (w) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.83 (3H, t, J(H,H)= 8 Hz, CH_3), 1.23 (24H, m, CH_2), 1.54 (2H, pentet, J(H,H)= 8 Hz, CH_2), 1.97 (4H, m, CH_2), 5.32 (2H, m, =CH), 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.83 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.85 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.98 (1 H, s, NH), 8.06 (2H, d, J(H,H)= 8 Hz, Ar-H), ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 14.4, 22.5, 27.0, 29.0, 29.4, 29.5, 31.8, 32.4, 116.5, 122.3, 125.6, 128.8, 130.1, 130.5, 136.4, 145.7, 153.9, 162.0, 165.8 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-2-hydroxyethyl-benzamide [AZO1-EtOH]: Yield 0.26 g (90%); IR: v = 3325 (NH, m), 3227 (OH, s, broad), 2923 (CH, s), 2952 (CH, s), 1687 (s), 1633 (s), 1589 (s), 1538 (s), 1504 (m), 1464 (m), 1433 (m), 1386 (m), 1342 (m), 1309 (m), 1271 (s), 1234 (s), 1133 (s), 1082 (m), 1008 (m), 967 (w), 886 (m), 859 (m), 839 (s), 768 (m), 714 (m), 664 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 3.13 (2H, t, J(H,H)= 8 Hz, CH_2), 4.68 (2H, t, J(H,H)= 8 Hz, 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.84 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.86 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.01 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.55 (1H, s, NH), 10.40 (1 H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 42.4, 61.3, 116.5, 121.8, 125.2, 130.4, 131.6, 146.1, 155.6, 161.5, 166.2 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-*(R)*-2-cyclohexyl-2-ethyl-benzamide [AZO1-*(R)*CE]: Yield 0.36 g (100%); IR: v = 3264 (NH, s), 3223 (OH, s, broad), 3058 (m), 2926 (s), 2845 (s), 1710 (m), 1677 (s), 1629 (s), 1579 (s), 1542 (s), 1490 (s), 1467 (m), 1673 (s), 1305 (m), 1275 (s), 1211 (s), 1136 (s), 1072 (m), 1001 (m), 886 (m), 836 (s), 765 (m), 721 (m), 670 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.13 (3H, d, J(H,H)= 8 Hz, CH_3), 1.29 (4H, m, CH_2), 1.74 (5H, m, CH_2 and CH), 3.17 (1H, m, CH), 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.64 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.80 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.85 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.25 (1H, s, NH), 10.40 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 18.1, 25.6, 25.7, 31.7 48.0, 54.1, 116.5, 122.0, 125.6, 128.9,139.2, 145.7, 154.2, 161.8, 167.9 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-4-tetrahydropyran-benzamide [AZO1-THP]: Yield 0.33 g (98%); IR: v = 3254 (NH, s), 3190 (OH, s, broad), 3035 (m), 2923 (CH, s), 2848 (CH, s), 1704 (m), 1670 (s), 1619 (s), 1589 (s), 1538 (s), 1494 (s), 1464 (m), 1379 (s), 1278 (s), 1234 (m), 1217 (s), 1133 (s), 1072 (m), 1048 (w), 1001 (m), 890 (m), 839 (s), 765 (m), 728 (m), 666 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.60 (2H, m, CH_2), 1.79 (2H, m, CH_2), 3.40 (2H, m, CH_2), 3.90 (2H, m, CH_2), 6.95 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.84 (4H, m, Ar-H), 8.02 (2H, d, J(H,H)= 8 Hz, Ar-H), Ar-H), 8.44 (1H, s, NH), 10.39 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6):

23.3, 38.3, 44.9, 116.5, 121.8, 125.0, 130.2, 131.4, 145.2, 153.6, 160.7, 165.4 ppm.

4-((4-hydroxyphenyl)diazenyl)-*N*-3,5-bistrifluoromethylbenzyl-benzamide [AZO1-BTFMB]: Yield 0.41 g (85%); IR: v = 3318 (NH, s), 3260 (OH, s, broad), 3054 (m), 2926 (CH, s), 2842 (CH, s), 1704 (w), 1673 (s), 1633 (s), 1606 (s), 1582 (s), 1535 (s), 1501 (s), 1457 (m), 1430 (w), 1379 (s), 1325 (m), 1275 (s), 1231 (w), 1166 (s), 1123 (s), 1011 (m), 971 (w), 886 (m), 836 (s), 768 (w), 724 (w), 714 (m), 680 (s) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6 /MeOD): δ = 3.54 (2 H, s, CH_2), 6.94 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.84 (6H, m, Ar-H), 8.02 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.55 (1 H, s, Ar-H) ppm. ^{19}F NMR (300 K, DMSO-D_6 /MeOD): δ = 61.7 ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 45.2, 115.4, 116.5, 121.8, 125.0, 125.3, 130.4, 131.2, 131.6, 146.2, 155.6, 161.5, 167.9 ppm. ^{19}F NMR (275 MHz, 300 K, DMSO-d6): 61.7 ppm.

S**ynthesis of 3-((4-hydroxyphenyl)diazenyl)-N-R-benzamide (Figure 17):** 0.25 g 3-((4- hydroxyphenyl)diazenyl)benzoic acid **(2)** (1 mmol, 1 equiv.) 0.23 g DCC (1.1 mmol, 1.1 equiv.), catalytic quantities of NHS and stoichiometric excess of amine (≥1.1 equiv.) were dissolved in 5 mL DMF and stirred at RT for 18 hours. The resultant deep red reaction solution was filtered, washed twice with 20 mL of hexane, extracted into ethylacetate, and washed with 1 × 30 mL dilute acetic acid and 4 × 30 mL ultrapure water before the solvent was removed under vacuum. Where further purification was needed the product was dissolved in the minimum volume of dichloromethane (DCM) and left for two days. The clear crystalline solids were filtered and discarded before the solvent was removed under vacuum to yield the orange products which were recrystallized from a 1:1 water:ethanol mixture.

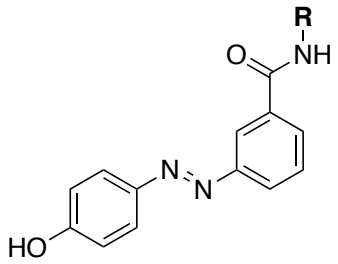

Figure 2. 3-((4-hydroxyphenyl)diazenyl)-*N*-R-benzamide.

3-((4-hydroxyphenyl)diazenyl)-*N*-ethyl-benzamide [AZO2-C2]: Yield 0.19 g (67%); IR: v = 3334 (NH, m), 3213 (OH, s, broad), 3065 (m), 2933 (CH, s), 2848 (CH, s), 1636 (s), 1598 (s), 1538 (s), 1501 (s), 1433 (s), 1376 (w), 1352 (w), 1309 (m), 1268 (s), 1224 (s), 1143 (s), 1092 (m), 1062 (w), 907 (m), 890 (m), 842 (s), 805 (m), 755 (m), 718 (w), 680 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.15 (3H, t, J(H,H)= 8 Hz, CH_3), 2.98 (2H, q, J(H,H)= 8 Hz, CH_2), 6.97 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.63 (1H, m, Ar-H), 7.84 (2H, d, J(H,H)= 8 Hz, 7.95 (2H, m, Ar-H), 8.27 (1H, s, Ar-H), 8.41 (1H, s, NH), 10.35 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 15.3, 34.9, 116.4, 122.3, 125.6, 127.4, 130.1, 131.3, 132.5, 145.4, 152.6,

161.8, 166.2 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-propyl-benzamide [AZO2-*n*C3]: Yield 0.20 g (68%); IR: v = 3260 (NH, s), 2975 (OH, s, broad), 2933 (CH, s), 2852 (CH, s), 1741 (m), 1626 (s), 1585 (s), 1542 (s), 1498 (s), 1433 (s), 1366 (m), 1315 (w), 1271 (s), 1221 (s), 1130 (s), 1069 (m), 886 (m), 836 (m), 802 (w), 751 (m), 717 (w), 680 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.90 (3H, t, J(H,H)= 8 Hz, CH_3), 1.60 (2H, sextet, J(H,H)= 8 Hz, CH_2), 3.26 (2H, t, J(H,H)= 8 Hz, CH_2), 6.97 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.64 (1H, m, Ar-H), 7.83 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.95 (2H, m, Ar-H), 8.27 (1H, s, Ar-H), 8.66 (1H, s, NH), 10.34 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 11.9, 22.7, 49.1, 116.5, 122.3, 125.7, 127.3, 131.4, 132.3, 132.7, 145.6, 152.6, 161.6, 165.2 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-*iso*-propyl-benzamide [AZO2-*i*C3]: Yield 0.21 g (71%); IR: v = 3328 (NH, s), 3068 (OH, s, broad), 2923 (CH, s), 2842 (CH, s), 1630 (s), 1572 (s), 1531 (s), 1498 (s), 1437 (s), 1359 (w), 1312 (m), 1268 (s), 1241 (s), 1214 (s), 1136 (s), 1086 (s), 1042 (m), 897 (s), 832 (s), 795 (w), 778 (w), 748 (m), 718 (w), 670 (s) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.19 (6H, d, J(H,H)= 8 Hz, CH_3), 4.14 (1H, septet, J(H,H)= 8 Hz, CH), 6.95 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.62 (1H, m, Ar-H), 7.83 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.95 (2H, m, Ar-H), 8.27 (1H, s, Ar-H), 8.41 (1H, s, NH), 10.35 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 24.2, 46.5, 116.4, 123.1, 125.2, 127.5, 130.2, 131.4, 133.2, 145.6, 152.6, 161.8, 165.8 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-butyl-benzamide [AZO2-*n*C4]: Yield 0.30 g (99%); IR: v = 3321 (NH, s), 3054 (OH, s, broad), 2926 (CH, s), 2848 (CH, s), 1734 (w), 1679 (m), 1626 (s), 1575 (s), 1538 (s), 1504 (s), 1433 (s), 1369 (m), 1309 (s), 1268 (m), 1207 (s), 1140 (s), 1086 (m), 1035 (w), 964 (w), 893 (m), 836 (m), 755 (m), 711 (w), 674 (s) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.92 (3H, t, J(H,H)= 8 Hz, CH_3), 1.32 (2H, m J(H,H)= 8 Hz, CH_2), 1.52 (2H, m, J(H,H)= 8 Hz, CH_2), 3.27 (2H, m, J(H,H)= 8 Hz, CH_2), 6.97 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.64 (1H, m, Ar-H), 7.84 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.06 (2H, m, Ar-H), 8.29 (1H, s, Ar-H), 8.62 (1H, s, NH), 10.36 (1H, s, OH) ppm. ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 13.4, 21.1, 32.2, 40.2, 116.5, 122.5, 125.8, 127.5, 130.5, 131.5, 132.6, 145.8, 152.8, 160.6, 165.7 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-*iso*-butyl-benzamide [AZO2-*i*C4]: Yield 0.30 g (99%); IR: v = 3300 (NH, s), 3055 (OH, s, broad), 2963 (s), 2933 (CH, s), 2952 (CH, s), 1694 (m), 1609 (s), 1589 (s), 1538 (s), 1501 (s), 1460 (s), 1383 (m), 1318 (w), 1271 (s), 1210 (s), 1140 (s), 1092 (m), 1018 (s), 903 (m), 839 (s), 802 (m), 751 (m), 721 (m), 687 (s) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.91 (6H, d, J(H,H)= 8 Hz, CH_3), 1.90 (1H, m, CH), 3.12 (2H, t, J(H,H)= 8 Hz, CH_2), 6.97 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.64(1H, m, Ar-H), 7.84 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.95 (2H, m, Ar-H), 8.27 (1H, s, Ar-H), 8.65 (1H, s, NH), 10.35 (1H, s, OH) ppm. ^{13}C NMR

(100 MHz, 300 K, DMSO-d6): 20.4, 28.9, 48.0, 116.6, 121.2, 125.4, 127.6, 130.4, 132.5, 133.3, 145.6, 152.6, 161.9, 165.3 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-*tert*-butyl-benzamide [AZO2-*t*C4]: Yield 0.26 g (84%); IR: v = 3409 (NH, m), 3162 (OH, s, broad), 2929 (CH, m), 2845 (CH, m), 1697 (m), 1643 (s), 1575 (s), 1521 (s), 1490 (s), 1460 (s), 1390 (w), 1369 (m), 1302 (w), 1268 (s), 1207 (s), 1140 (s), 1092 (w), 1015 (m), 913 (m), 883 (m), 832 (s), 815 (m), 745 (m), 711 (m), 677 (s) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.44 (9H, s, CH_3), 7.00 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.61 (1H, s, NH), 7.84 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.99 (1H, m, Ar-H), 8.06 (2H, d, J(H,H)= 8 Hz), 8.21 (1H, s, NH), 10.4 (1H, s, broad, Ar-OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 28.9, 51.5, 116.5, 121.4, 124.6, 125.5, 129.6, 137.2, 145.8, 152.2, 161.6, 166.5 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-octyl-benzamide [AZO2-*n*C8]: Yield 0.32 g (89%); IR: v = 3331 (NH, s), 3081 (OH, s, broad), 2923 (CH, s), 2855 (CH, s), 1629 (s), 1582 (s), 1542 (s), 1508 (m), 1464 (s), 1437 (s), 1383 (m), 1319 (w), 1278 (s), 1214 (s), 1140 (s), 1085 (m), 913 (w), 897 (m), 846 (s), 802 (w), 755 (m), 721 (m), 680 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.85 (3H, t, J(H,H)= 8 Hz, CH_3), 1.25 (10H, m, CH_2), 1.61 (2H, m, CH_2), 3.26 (2H, m, CH_2), 6.97 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.64 (1H, t, J(H,H)= 8 Hz, Ar-H), 7.84 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.94 (2H, m, Ar-H), 8.2627 (1H, s, Ar-H), 8.40 (1H, s, NH), 10.41 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 14.4, 22.5, 24.9, 25.7, 27.1, 30.2, 33.8, 116.4, 121.5, 125.5, 128.6, 130.3, 131.8, 132.5, 145.6, 152.6, 161.8, 167.3 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-*tert*-octyl-benzamide [AZO2-*t*C8]: Yield 0.32 g (88%);IR: v = 3260 (NH, s), 3027 (OH, s, broad), 2923 (CH, s), 2852 (CH, s), 1683 (s), 1633 (s), 1589 (s), 1542 (s), 1504 (s), 1437 (s), 1369 (m), 1347 (m), 1278 (s), 1221 (s), 1136 (s), 1072 (m), 998 (w), 910 (w), 893 (m), 839 (s), 802 (m), 748 (m), 721 (w), 680 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.99 (9H, s, CH_3), 1.45 (6H, s, CH_3), 1.88 (2H, s, CH_2), 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.61 (1H, t, J(H,H)= 8 Hz, Ar-H), 7.81 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.91 (1H, m, Ar-H), 8.19 (1H, s, Ar-H), 8.31 (1H, s, NH), 10.37 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 29.1, 30.5, 32.1, 45.8, 53.2, 116.6, 122.3, 125.6, 127.4, 130.3, 131.7, 132.5, 145.6, 152.5, 161.8, 166.8 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-2-ethylhexyl-benzamide [AZO2-EH]: Yield 0.32 g (87%); IR: v = 3264 (NH, s), 2987 (OH, s, broad), 2929 (CH, s), 2952 (CH, s), 1640 (s), 1582 (s), 1542 (s), 1525 (s), 1501 (s), 1453 (s), 1433 (s), 1373 (m), 1275 (s), 1210 (s), 1140 (s), 1092 (m), 998 (w), 897 (m), 842 (s), 805 (m), 748 (m), 718 (m), 684 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.86 (6H, t, J(H,H)= 8 Hz, CH_3), 1.28 (8H, m, CH_2), 1.59 (1H, m, CH), 3.22 (2H, m, CH_2), 6.97 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.64 (1H, t, J(H,H)= 8 Hz, Ar-H), 7.84 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.94 (2H, dd, J^3 (H,H)= 8 Hz, J^4(H,H)= 4 Hz, Ar-H), 8.27 (1H, d, J^4(H,H)= 4 Hz, Ar-H), 8.58 (1H, s, NH), 10.40 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-

d6): 11.4, 14.4, 22.9, 24.1, 22.8, 30.9, 33.8, 43.6, 116.5, 121.4, 124.7, 125.4, 129.5, 129.8, 136.5, 145.7, 152.5, 161.7, 166.2 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-dodecyl-benzamide [AZO2-*n*C12]: Yield 0.38 g (89%); IR: v = 3274 (NH, s), 2994 (OH, s, broad), 2919 (CH, s), 2845 (CH, s), 1633 (s), 1582 (s), 1538 (s), 1501 (s), 1454 (s), 1359 (m), 1305 (w), 1275 (s), 1214 (s), 1143 (s), 1082 (m), 994 (w), 893 (m), 842 (s), 812 (w), 755 (w), 728 (w), 691 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.86 (3H, t, J(H,H)= 8 Hz, CH_3), 1.25 (18H, m, CH_2), 1.74 (2H, m, CH_2), 3.27 (2H, t, J(H,H)= 8 Hz, CH_2), 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.63 (1H, t, J(H,H)= 8 Hz, Ar-H), 7.84 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.94 (1H, m, Ar-H), 8.26 (1H, s, Ar-H), 8.62 (1H, s, NH), 10.34 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 14.4, 22.5, 24.9, 25.1, 25.7, 29.1, 29.4, 31.7, 32.8, 33.8, 116.4, 121.3, 125.4, 129.4, 130.3, 131.8, 132.5, 145.6, 152.6, 161.8, 167.3 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-octadec-9-en-1-yl-benzamide [AZO2-C18:1]: Yield 0.46 g (91%); IR: v = 3287 (NH, s), 3007 (OH, s, broad), 2919 (CH, s), 2848 (CH, s), 1740 (m), 1633 (s), 1585 (s), 1535 (s), 1501 (s), 1454 (s), 1373 (s), 1278 (s), 1227 (s), 1136 (s), 1096 (w), 964 (w), 897 (m), 846 (s), 812 (w), 775 (m), 728 (m), 680 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.86 (3H, t, J(H,H)= 8 Hz, CH_3), 1.24 (20H, m, CH_2), 1.70 (2H, m, CH_2), 1.97 (4H, m, CH_2), 3.28 (2H, t, J(H,H)= 8 Hz, CH_2), 5.32 (2H, m, =CH), 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.63 (1H, t, J(H,H)= 8 Hz, Ar-H), 7.81 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.94 (1H, m, Ar-H), 8.26 (1H, s, Ar-H), 8.63 (1H, s, NH), 9.85 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 14.4, 22.2, 27.3, 29.2, 29.5, 29.7, 31.9, 32.5, 116.5, 122.3, 126.6, 127.5, 130.5, 131.4, 132.7, 145.4, 152.7, 161.6, 166.4 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-2-hydroxyethyl-benzamide [AZO2-EtOH]: Yield 0.27 g (91%); IR: v = 3318 (NH, s), 3048 (OH, s, broad), 2936 (CH, s), 2852 (CH, s), 1680 (s), 1623 (s), 1582 (s), 1498 (s), 1460 (m), 1440 (s), 1373 (m), 1309 (s), 1217 (s), 1136 (s), 1082 (s), 998 (w), 913 (m), 890 (m), 829 (s), 755 (s), 714 (w), 674 (s) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 3.39 (2H, t, J(H,H)= 8 Hz, CH_2), 3.54 (2H, t, J(H,H)= 8 Hz, CH_2), 4.75 (1H, s, OH), 6.97 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.70 (1H, t, J(H,H)= 8 Hz, Ar-H), 7.86 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.06 (2H, m, Ar-H), 8.31 (1H, m, Ar-H), 8.64 (1H, s, NH), 10.39 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 24.9, 33.8, 116.5, 122.3, 125.5, 127.4, 130.3, 131.3, 132.5, 145.6, 152.6, 161.8, 167.3 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-*(R)*-2-cyclohexyl-2-ethyl-benzamide [AZO2-*(R)*CE]: Yield 0.32 g (87%); IR: v = 3300 (NH, s), 2990 (OH, s, broad), 2916 (CH, s), 2852 (CH, s), 1683 (w), 1629 (s), 1595 (s), 1558 (s), 1542 (s), 1501 (s), 1430 (s), 1386 (m), 1356 (m), 1275 (s), 1217 (s), 1133 (s), 1089 (m), 1025 (m), 879 (m), 842 (s), 795 (m), 761 (m), 684 (s) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.29 (3H, d, J(H,H)= 8 Hz, CH_3), 1.34 (5H, m, CH_2 and CH), 1.77 (6H, m, CH_2), 3.17 (1H,

m, CH), 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.62 (1H, t, J(H,H)= 8 Hz, Ar-H), 7.82 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.92 (2H, m, Ar-H), 8.27 (1H, s, NH), 8.31 (1H, m, Ar-H), 10.36 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 18.1, 26.4, 30.8, 31.6, 42.9, 49.9, 54.1, 116.5, 120.9, 125.5, 129.4, 129.6, 129.7, 132.9, 145.6, 152.0, 161.8, 167.7 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-4-tetrahydropyran-benzamide [AZO2-THP]: Yield 0.33 g (98%); IR: v = 3325 (NH, s), 3260 (OH, s, broad), 2926 (CH, s), 2848 (CH, s), 1669 (s), 1623 (s), 1575 (s), 1525 (s), 1498 (s), 1464 (m), 1433 (m), 1376 (s), 1339 (w), 1308 (m), 1265 (s), 1224 (s), 1184 (w), 1136 (s), 1076 (s), 1005 (m), 971 (w), 917 (w), 893 (m), 839 (s), 809 (s), 778 (w), 748 (m), 670 (s) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.62 (2H, m, CH_2), 1.80 (2H, m, CH_2), 3.17 (2H, m, CH_2), 3.40 (2H, m CH_2), 4.04 (1H, m, CH), 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.64 (1H, t, J(H,H)= 8 Hz, Ar-H), 7.85 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.92 (2H, m, Ar-H), 7.97 (1H, m, Ar-H), 8.28 (1H, s, NH), 10.37 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 46.6, 53.9, 66.6, 116.5, 121.7, 125.7, 127.4, 129.6, 136.3, 138.5, 145.5, 152.8, 161.7, 165.5 ppm.

3-((4-hydroxyphenyl)diazenyl)-*N*-3,5-bistrifluoromethylbenzyl-benzamide [AZO2-BTFMB]: Yield 0.31 g (63%); IR: v = 3281 (NH, s), 3196 (OH, s, broad), 3065 (m), 2933 (CH, s), 2855 (CH, s), 1670 (m), 1639 (s), 1589 (s), 1545 (s), 1497 (m), 1464 (w), 1437 (w), 1376 (s), 1346 (m), 1278 (s), 1170 (s), 1126 (s), 1025 (w), 1005 (w), 893 (s), 836 (s), 805 (w), 734 (w), 701 (m), 677 (s) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 4.70 (2H, s, CH_2), 6.96 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.58 (2H, m, Ar-H), 7.68 (1H, t, J(H,H)= 8 Hz, Ar-H), 7.81 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.85 (1H, s, Ar-H), 7.92 (2H, m, Ar-H), 8.01 (1H, m, Ar-H), 8.33 (1H, s, NH), 10.37 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 42.9, 116.5, 121.3, 124.4, 125.4, 130.0, 135.5, 138.7, 143.6, 145.6, 152.0, 152.6, 154.1, 161.7, 167.7 ppm. ^{19}F NMR (275 MHz, 300 K, DMSO-d6): -61.3 ppm.

Synthesis of 5-((4-hydroxyphenyl)diazenyl)-N^{1},N^{3}-di-R-isophthalamide (Figure 18): 0.25 g 5-((4-hydroxyphenyl)diazenyl)isophthalic acid **(3)** (0.9 mmol, 1 equiv.) 0.39 g DCC (1.9 mmol, 1.1 equiv.), catalytic quantities of NHS and stoichiometric excess of *R*-amine (≥1.1 equiv.) were dissolved in 5 mL DMF and stirred at RT for 18 hours. The resultant deep red reaction solution was filtered, washed twice with 20 mL of hexane, extracted into ethylacetate, and washed with 1 × 30 mL dilute acetic acid and 4 × 30 mL ultrapure water before the solvent was removed under vacuum. Where further purification was needed the product was dissolved in the minimum volume of dichloromethane (DCM) and left for two days. The clear crystalline solids were filtered and discarded before the solvent was removed under vacuum to yield the orange products which were recrystallized from a 1:1 water:ethanol mixture.

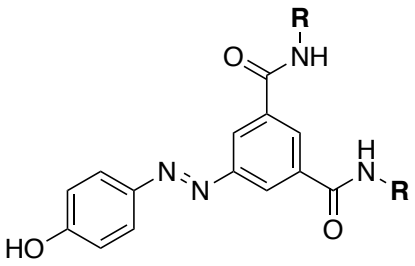

Figure 3. 5-((4-hydroxyphenyl)diazenyl)-N^1,N^3-di-R-isophthalamide.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-ethyl- isophthalamide [AZO3-C2]: Yield 0.17 g (57%); IR: v = 3321 (NH, s), 3237 (OH, s, broad), 3081 (m), 2926 (CH, s), 2848 (CH, s), 1697 (m), 1619 (s), 1582 (s), 1544 (s), 1501 (s), 1471 (m), 1423 (s), 1376 (w), 1332 (w), 1309 (w), 1285 (s), 1214 (s), 1143 (s), 1076 (s), 1021 (s), 937 (w), 913 (m), 893 (s), 842 (s), 799 (w), 755 (w), 674 (s) cm^{-1}; ^1H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.18 (6H, t, J(H,H)= 8 Hz, CH_3), 3.36 (4H, q, J(H,H)= 8 Hz, CH_2), 6.91 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.79 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.97 (2H, s, Ar-H), 8.24 (1H, s, Ar-H), 8.34 (2H, s, NH), 10.05 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 25.4, 33.8, 116.2, 125.2, 125.3, 131.4, 133.1, 145.6, 152.7, 162.2, 166.8 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-propyl- isophthalamide [AZO3-*n*C3]: Yield 0.18 g (58%); IR: v = 3311 (NH, s), 3300 (OH, s, broad), 2929 (CH, s), 2824 (CH, s), 1697 (s), 1619 (s), 1579 (s), 1545 (s), 1498 (m), 1433 (s), 1275 (s), 1241 (m), 1210 (m), 1143 (s), 1086 (w), 1025 (s), 886 (w), 842 (s), 761 (w), 690 (w), 677 (w) cm^{-1}; ^1H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.90 (6H, t, J(H,H)= 8 Hz, CH_3), 1.58 (4H, sextet, J(H,H)= 8 Hz, CH_2), 3.27 (4H, t, J(H,H)= 8 Hz, CH_2), 6.98 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.88 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.41 (1H, s, Ar-H), 8.51 (2H, s, Ar-H), 8.82 (2H, s, NH), 10.5 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 11.9, 22.7, 49.1, 116.5, 124.4, 125.7, 129.7, 136.7, 145.6, 152.6, 162.1, 166.9 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-*iso*-propyl- isophthalamide [AZO3-*i*C3]: Yield 0.26 g (82%); IR: v = 3318 (NH, s), 3226 (OH, s, broad), 3081 (m), 2929 (CH, s), 2851 (CH, s), 1697 (s), 1619 (s), 1579 (s), 1538 (s), 1501 (s), 1444 (s), 1373 (w), 1298 (w), 1271 (s), 1207 (s), 1143 (s), 1082 (m), 1032 (m), 913 (m), 897 (m), 829 (s), 805 (w), 748 (w), 731 (w), 677 (m) cm^{-1}; ^1H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.26 (12H, d, J(H,H)= 8 Hz, CH_3), 4.21 (2H, sept, J(H,H)= 8 Hz, CH), 7.04 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.94 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.43 (1H, s, Ar-H), 8.58 (2H, s, Ar-H), 8.71 (2H, s, NH), 10.5 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 23.7, 47.9, 116.6, 125.6, 125.7, 129.9, 136.8, 145.7, 152.2, 162.1, 166.9 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-butyl- isophthalamide [AZO3-*n*C4]: Yield 0.23 g (66%); IR: v = 3321 (NH, s), 3094 (OH, s, broad), 2929 (CH, s), 2841 (CH, s), 1629 (s), 1572 (s), 1501 (s), 1433 (s), 1332 (m), 1315 (m), 1278 (s), 1227 (s), 1136 (s), 1082 (s), 1038 (w), 907 (w), 897 (m), 839 (s), 795 (w), 711 (w), 687 (w) cm^{-1}; ^1H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.92 (6H, t, J(H,H)= 8 Hz, CH_3), 1.33 (4H, m, J(H,H)= 8 Hz, CH_2), 1.53 (4H, m, CH_2), 3.31 (4H, m, J(H,H)= 8 Hz, CH_2), 6.98 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.87 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.36 (1H, s, Ar-H), 8.53 (2H, s, Ar-H), 8.74 (2H, s, NH), 10.4 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 14.2, 20.1, 31.6, 48.0, 116.5, 125.6, 125.7, 129.9, 136.8, 145.7, 152.2, 157.9, 165.0 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-*iso*-butyl- isophthalamide [AZO3-*i*C4]: Yield 0.23 g (66%); IR: v = 3321 (NH, s), 3223 (OH, s, broad), 2926 (CH, s), 2848 (CH, s), 1626 (s), 1565 (s), 1467 (m), 1436 (m), 1376 (w), 1319 (s), 1268 (m), 1238 (s), 1136 (m), 1079 (s), 1035 (w), 964 (w), 897 (s), 836 (w), 805 (w), 666 (s) cm^{-1}; ^1H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.93 (6H, t, J(H,H)= 8 Hz, CH_3), 1.89 (2H, m, CH), 3.14 (4H, d, J(H,H)= 8 Hz, CH_2), 6.98 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.36 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.39 (1H, s, Ar-H), 8.55 (2H, s, Ar-H), 8.78 (2H, s, NH), 10.44 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 20.7, 25.7, 47.1, 116.6, 125.6, 125.7, 129.9, 136.8, 145.7, 152.2, 157.9, 165.0 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-*tert*-butyl- isophthalamide [AZO3-*t*C4]: Yield 0.28 g (82%); IR: v = 3264 (NH, s), 3084 (OH, s, broad), 2932 (CH, s), 2848 (CH, s), 1633 (s), 1589 (s), 1528 (s), 1477 (s), 1443 (s), 1392 (m), 1363 (m), 1288 (s), 1217 (s), 1133 (s), 1092 (w), 988 (w), 920 (w), 897 (m), 842 (s), 802 (w), 751 (s), 704 (w), 674 (s) cm^{-1}; ^1H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.42 (9H, s, CH_3), 6.98 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.87 (2H, d, Ar-H), 8.12 (1H, s, Ar-H), 8.27 (2H, s, Ar-H), 8.45 (2H, s, NH), 10.44 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 29.2, 59.0, 116.6, 125.6, 125.7, 129.9, 136.8, 145.7, 152.2, 157.9, 165.0 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-octyl- isophthalamide [AZO3-*n*C8]: Yield 0.33 g (74%); IR: v = 3321 (NH, s), 3237 (OH, s, broad), 2926 (CH, s), 2845 (CH, s), 1619 (s), 1558 (s), 1447 (s), 1366 (m), 1319 (m), 1282 (s), 1227 (s), 1136 (s), 1086 (s), 1021 (s), 900 (s), 836 (s), 795 (w), 734 (w) cm^{-1}; ^1H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.85 (6H, t, J(H,H)= 8 Hz, CH_3), 1.24 (24H, m, CH_2), 3.45 (4H, t, J(H,H)= 8 Hz, CH_2), 6.98 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.85 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.98 (1H, s, Ar-H), 8.34 (2H, s, Ar-H), 8.42 (2H, s, NH), 10.56 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 14.4, 22.5, 24.9, 25.8, 29.0, 29.5, 32.8, 33.8, 116.6, 124.6, 125.7, 129.9, 136.8, 145.7, 152.2, 157.9, 165.0 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-*tert*-octyl- isophthalamide [AZO3-*t*C8]: Yield 0.33 g (74%); IR: v = 3311 (NH, s), 30543 (OH, s, broad), 2929 (CH, s), 2848

(CH, s), 1639 (s), 1582 (s), 1538 (s), 1474 (m), 1457 (m), 1349 (s), 1278 (s), 1217 (s), 1143 (s), 1076 (m), 1008 (w), 886 (m), 839 (s), 805 (w), 758 (m), 714 (w), 677 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.99 (18H, s, CH_3), 1.45 (12H, s, CH_3), 2.06 (4H, s, CH_2), 6.98 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.85 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.98 (1H, s, Ar-H), 8.30 (2H, s, Ar-H), 8.41 (2H, s, NH), 10.45 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 29.9, 30.8, 31.6, 48.0, 54.4, 116.6, 125.6, 125.7, 129.6, 138.2 145.6, 153.9, 157.0, 165.9 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-2-ethylhexyl- isophthalamide [AZO3-EH]: Yield 0.28 g (62%); IR: v = 3311 (NH, s), 3084 (OH, s, broad), 2933 (CH, s), 2848 (CH, s), 1700 (m), 1633 (s), 1645 (s), 1554 (s), 1443 (s), 1369 (m), 1336 (w), 1275 (s), 1221 (s), 1133 (s), 1092 (m), 913 (w), 883 (m), 846 (s), 758 (m), 721 (w), 684 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.85 (12H, m, CH_3), 1.24 (16H, m, CH_2), 1.73 (2H, m, CH), 3.16 (4H, m, CH_2), 6.98 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.73 (1H, s, Ar-H), 7.88 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.10 (2H, s, Ar-H), 8.36 (2H, s, NH), 10.46 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 12.1, 14.4, 24.9, 25.3, 26.7, 30.8, 33.8, 45.6, 54.5, 116.5, 125.6, 125.7, 129.6, 137.2 145.6, 153.9, 157.0, 165.9 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-dodecyl- isophthalamide [AZO3-*n*C12]: Yield 0.40 g (74%); IR: v = 3328 (NH, s), 3236 (OH, s, broad), 2916 (CH, s), 2845 (CH, s), 1633 (s), 1569 (s), 1437 (s), 1339 (m), 1312 (s), 1265 (s), 1244 (s), 1140 (m), 1089 (s), 1028 (s), 964 (w), 883 (s), 842 (m), 795 (w), 741 (s) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.85 (6H, t, J(H,H)= 8 Hz, CH_3), 1.23 (36H, m, CH_2), 1.73 (4H, m, CH_2), 3.30 (4H, t, J(H,H)= 8 Hz, CH_2), 7.00 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.50 (1H, s, Ar-H), 7.86 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.35 (2H, s, Ar-H), 8.81 (2H, s, NH), 10.70 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 14.3, 22.5, 24.9, 25.1, 29.2, 29.5, 31.8, 32.8, 33.8, 41.4, 49.1, 50.9, 116.6, 125.3, 125.6, 129.8, 136.5, 146.6, 153.2, 158.7, 162.3 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-octadec-9-en-1-yl- isophthalamide [AZO3-C18:1]: Yield 0.34 g (49%); IR: v = 3206 (NH, s), 3078 (OH, s, broad), 2915 (CH, s), 2852 (CH, s), 1615 (s), 1555 (m), 1508 (m), 1450 (s), 1363 (s), 1285 (m), 1210 (s), 1143 (s), 1096 (m), 967 (m), 893 (s), 846 (s), 768 (w), 724 (m), 674 (m) cm^{-1}; ^{1}H NMR (400 MHz, 300 K, DMSO-D_6): δ = 0.86 (6H, t, J(H,H)= 8 Hz, CH_3), 1.23 (44H, m, CH_2), 1.72 (4H, m, CH_2), 1.97 (4H, m, CH_2), 3.21 (4H, m, CH_2), 4.36 (4H, m, =CH), 7.03 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.50 (1H, s, Ar-H), 7.88 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.44 (2H, s, Ar-H), 8.55 (2H, s, NH), 10.57 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 14.4, 22.5, 24.9, 25.1, 25.3, 25.8, 26.4, 27.0, 28.8, 29.1, 29.3, 29.5, 31.7, 32.7, 33.8, 41.4, 48.0, 50.9, 116.5, 125.3, 125.6, 130.0, 136.5, 146.6, 153.1, 158.7, 162.3 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-2-hydroxyethyl- isophthalamide [AZO3-EtOH]: Yield 0.18 g (56%); IR: v = 3294 (NH, s), 3061 (OH, s, broad), 2929 (CH, s), 2855 (CH, s), 1710 (m), 1639 (s), 1595 (s), 1538 (s), 1497 (s), 1444 (s), 1359 (m), 1275 (s), 1221 (s), 1143 (s), 1079 (m), 974 (w), 900 (m), 842 (s), 758 (s), 680 (s) cm^{-1}; ^1H NMR (400 MHz, 300 K, DMSO-D_6): δ = 3.37 (4H, t, J(H,H)= 8 Hz, CH_2), 3.56 (4H, t, J(H,H)= 8 Hz, CH_2), 3.81 (2H, s, OH), 6.97 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.87 (2H, d, J(H,H)= 8 Hz, CH_2), 8.37 (1H, s, Ar-H), 8.41 (2H, s, Ar-H), 8.50 (2H, s, NH) 10.46 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 48.0, 60.55, 116.6, 125.6, 125.7, 129.9, 136.8, 145.7, 152.2, 157.9, 165.0 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-(*R)*-2-cyclohexyl-2-ethyl- isophthalamide [AZO3-*(R)*CE]: Yield 0.28 g (62%); IR: v = 3287 (NH, s), 3084 (OH, s, broad), 2926 (CH, s), 2852 (CH, s), 1639 (s), 1579 (s), 1538 (s), 1444 (s), 1383 (m), 1332 (m), 1275 (s), 1221 (s), 1133 (s), 1075 (w), 917 (w), 890 (m), 836 (s), 788 (w), 748 (w), 717 (w), 684 (w) cm^{-1}; ^1H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.13 (6H, d, J(H,H)= 8 Hz, CH_3), 1.32 (8H, m, CH_2), 1.69 (10H, m, CH_2 and CH), 3.16 (2H, m, CH), 6.98 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.87 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.00 (1H, s, åMHz, 300 K, DMSO-d6): 18.2, 24.9, 29.0, 29.7, 33.8, 42.8, 62.7, 116.5, 125.6, 125.8, 128.8, 137.0, 146.8, 151.0, 156.1, 165.1 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-4-tetrahydropyran- isophthalamide [AZO3-THP]: Yield 0.19 g (49%); IR: v = 3304 (NH, s), 3081 (OH, s, broad), 2929 (CH, s), 2848 (CH, s), 1673 (m), 1623 (s), 1579 (s), 1535 (s), 1501 (s), 1437 (s), 1339 (m), 1288 (s), 1227 (s), 1136 (s), 1082 (s), 1001 (m), 900 (m), 842 (s), 755 (w), 718 (w), 701 (w) cm^{-1}; ^1H NMR (400 MHz, 300 K, DMSO-D_6): δ = 1.66 (4H, m, CH_2), 1.77 (4H, m, CH_2), 3.40 (9H, m, CH_2 and CH), 6.97 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.86 (2H, d, J(H,H)= 8 Hz, CH_2), 8.36 (1H, s, Ar-H), 8.38(2H, s, Ar-H), 8.54(2H, s, NH), 10.46 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 32.8, 49.1, 66.6, 116.6, 123.4, 125.6, 125,7. 136.8, 145.7, 152.3, 162.0, 165.0 ppm.

5-((4-hydroxyphenyl)diazenyl)- N^1,N^3-di-3,5-bistrifluoromethylbenzyl- isophthalamide [AZO3-BTFMB]: Yield 0.59 g (92%); IR: v = 3294 (NH, s), 3067 (OH, s, broad), 2933 (CH, s), 2845 (CH, s), 1650 (s), 1582 (m), 1525 (s), 1447 (m), 1373 (s), 1271 (s), 1217 (m), 1163 (s), 1126 (s), 1014 (w), 900 (s), 846 (s), 704 (s), 680 (s) cm^{-1}; ^1H NMR (400 MHz, 300 K, DMSO-D_6): δ = 4.68 (4H, s, CH_2), 6.98 (2H, d, J(H,H)= 8 Hz, Ar-H), 7.85 (4H, s, Ar-H), 8.04 (2H, d, J(H,H)= 8 Hz, Ar-H), 8.07 (2H, s, Ar-H), 8.48 (2H, s, Ar-H), 8.52 (1H, s, Ar-H), 9.52 (2H, s, NH), 10.45 (1H, s, OH) ppm. ^{13}C NMR (100 MHz, 300 K, DMSO-d6): 48.1, 116.6, 124.7, 125.2, 125.6, 128.8, 130.5, 130.8, 135.8, 143.5, 145.3, 153.9, 168.0 ppm.

Molecular lengths as estimated using ChemDraw Professional:

Molecular lengths of the various azobenzene molecules were estimated by calculating the distance from the oxygen atom in the phenolic functional group of the azobenzene to the last carbon atom in the R-group. The tables and figures below report the molecular length.

Table 1. AZO1-R compounds and their estimated molecular lengths as obtained from ChemDraw Professional.

Molecule	length min (Å)	length max (Å)	Molecule	length min (Å)	length max (Å)	Molecule	length min (Å)	length max (Å)
A1-C2	15.9	16.9	A1-iC3	15.9	16.9	A1-tC4	16.4	17.4
A1-C3	17.4	18.4	A1-iC4	17.4	18.4			
A1-C4	18.4	19.4	A1-tC8	18.8	19.8			
A1-EH	21.0	22.0						
A1-C8	23.6	24.6						
A1-C12	28.8	29.8						
A1-C18:1	36.9	37.9						

Table 2. AZO2-R compounds and their estimated molecular lengths as obtained from ChemDraw Professional.

				Trans				
Molecule	length min (Å)	length max (Å)	Molecule	length min (Å)	length max (Å)	Molecule	length min (Å)	length max (Å)
A2-C2	15.5	16.5	A2-iC3	15.5	16.5	A2-tC4	15.5	16.5
A2-C3	16.7	17.7	A2-iC4	16.7	17.7			
A2-C4	18.1	19.1	A2-tC8	18.1	19.1			
A2-EH	20.7	21.7						
A2-C8	23.3	24.3						
A2-C12	28.6	29.6						
A2-C18:1	36.6	37.6						

Table 3. AZO3-R compounds and their estimated molecular lengths as obtained from ChemDraw Professional.

				Trans				
Molecule	length min (Å)	length max (Å)	Molecule	length min (Å)	length max (Å)	Molecule	length min (Å)	length max (Å)
A3-C2	15.5	16.5	A3-iC3	15.5	16.5	A3-tC4	15.5	16.5
A3-C3	16.7	17.7	A3-iC4	16.7	17.7			
A3-C4	18.1	19.1	A3-tC8	18.1	19.1			
A3-EH	20.7	21.7						
A3-C8	23.3	24.3						
A3-C12	28.6	29.6						
A3-C18:1	36.6	37.6						

Experimental Set-up for UV-isomerization

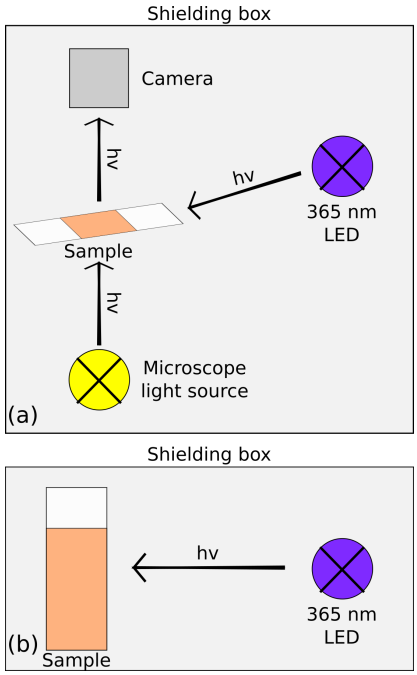

Figure 4. (a) Set-up for *in situ* isomerization of PLM samples. (b) Set-up for off-line isomerization of SAS samples.

SAXS experiments at the Australian Synchrotron:

Samples for experiments at the Australian Synchrotron were prepared using thin-walled special glass capillaries (Length = 80 mm, OD = 1.5 mm, wall thickness = 0.01 mm, Charles Supper Company). Samples of azobenzene molecules were loaded into the bottom of capillaries either as a solid and melted to create a solid plug at the bottom of the capillary, or by dissolving the azobenzene molecule in a small volume of a volatile solvent (chloroform) followed by slow evaporation of the solvent in a fan forced oven at 45ºC for 6 hours, 55ºC for 6 hours, and 60ºC for 12 hours. Approximately 200 µL of the appropriate solvent was then added to the top of the solid and the concentration gradient developed for at least 8 hours before measurement of the sample. Tops of capillaries were sealed with epoxy resin to prevent absorption of water or evaporation of solvent.

Capillaries were scanned at a resolution of approximately every 300 µm from the solid at the bottom of the capillary until solvent was reached, in order to index concentration-dependent phases. Scattering patterns were analysed using standard methods for liquid crystal identification (peak intensity and position ratios) using Scatterbrain for reduction of data to a 1D pattern. SAXS profiles shown in the following graphs are displayed from high concentration at the bottom to low concentration at the top of each plot. The scattering patterns may exhibit a peak at $q = 0.4$ Å^{-1} arising from the Kapton windows of the sample holder. A marked-out scale is indicated in Figure 5 and while the subsequent figures have fewer markings the scale remains the same.

Raw SAS 1D scattering patterns:

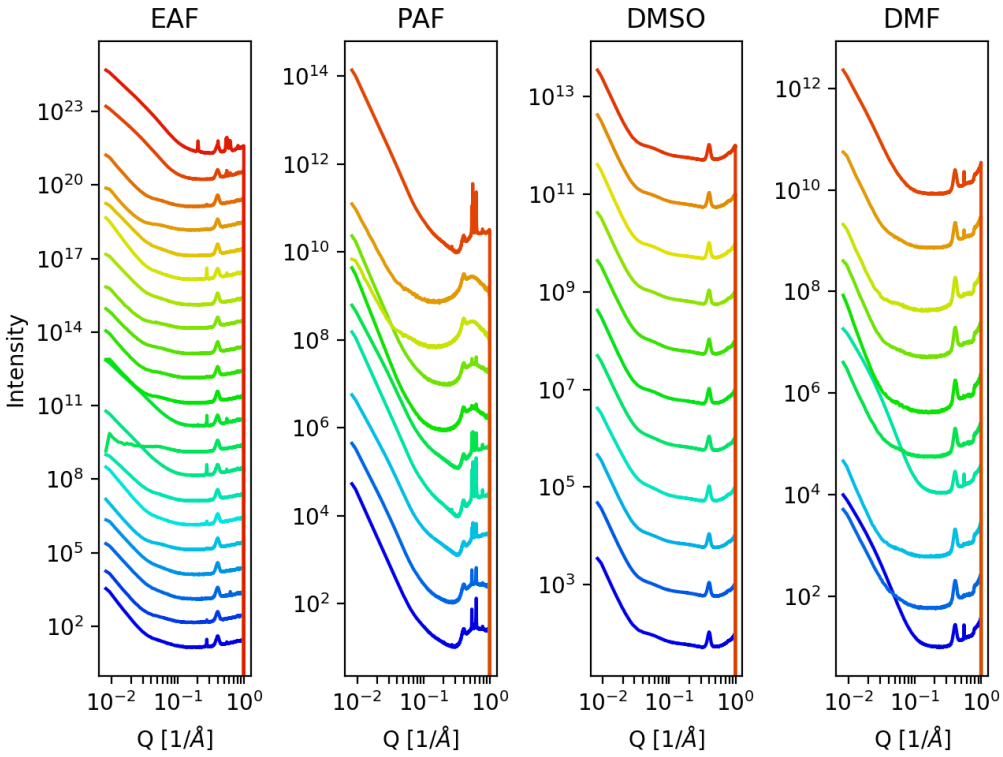

Figure 5. SAXS scattering patterns from AZO1-C2 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO1-C2 concentration increases from top to bottom.

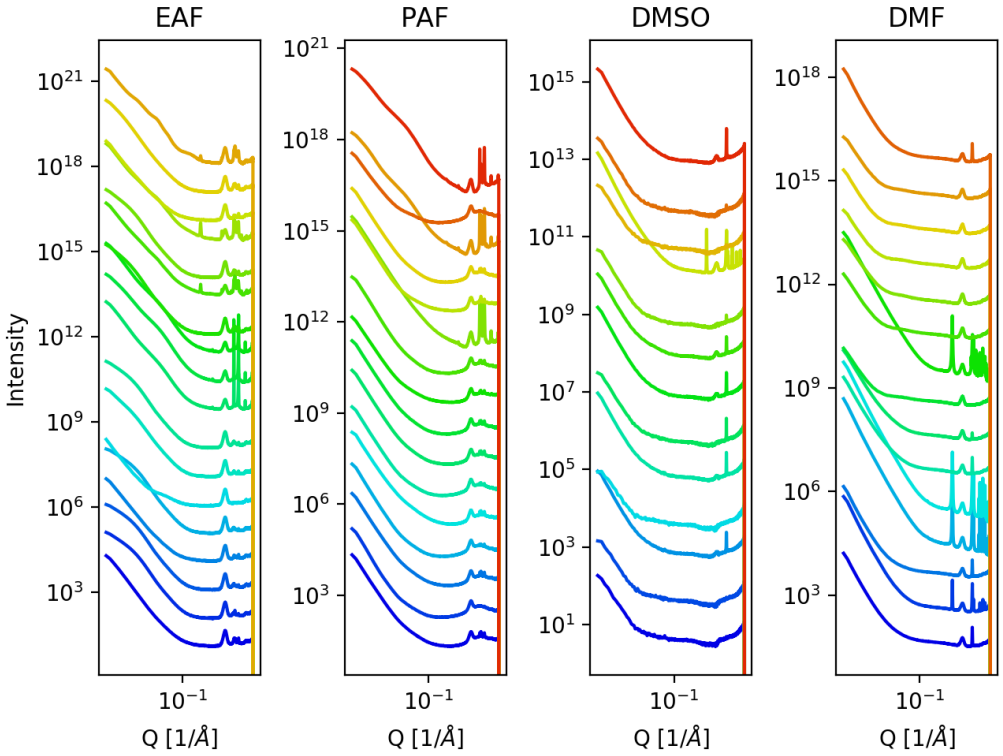

Figure 6. SAXS scattering patterns from AZO1-*n*C3 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO1-*n*C3 concentration increases from top to bottom.

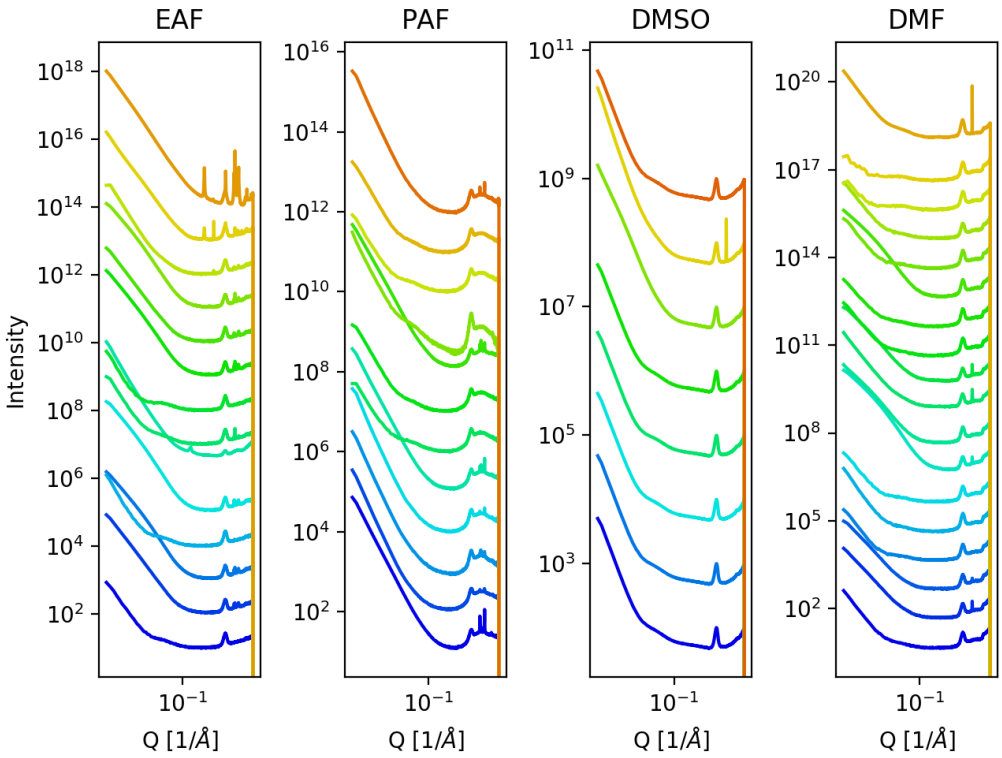

Figure 7. SAXS scattering patterns from AZO1-*n*C3 in EAF, PAF, DMSO and DMF solvents after 20 minutes of UV exposure. The curves are ordered such that AZO1-*n*C3 concentration increases from top to bottom.

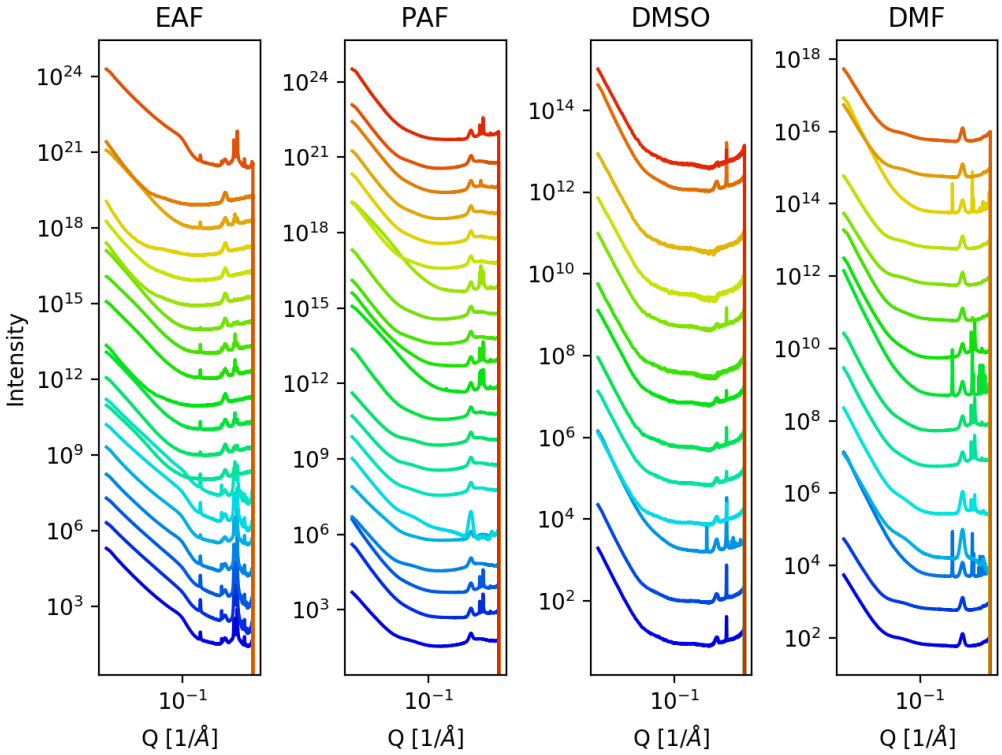

Figure 8. SAXS scattering patterns from AZO1-*n*C4 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO1-*n*C4 concentration increases from top to bottom.

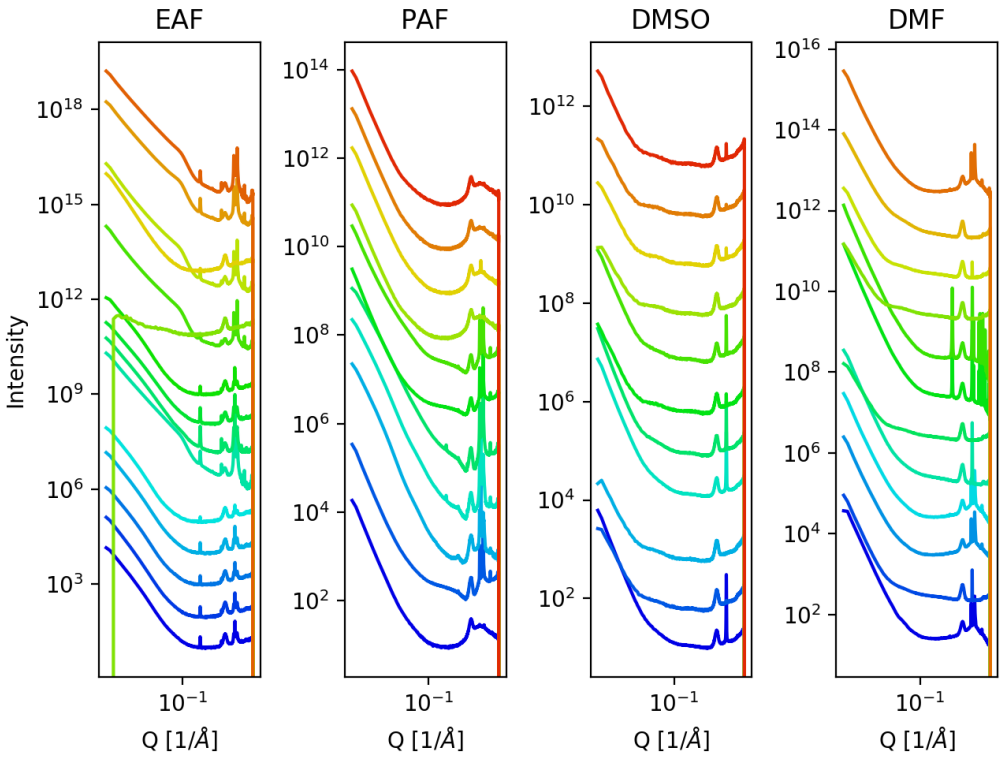

Figure 9. SAXS scattering patterns from AZO1-*n*C4 in EAF, PAF, DMSO and DMF solvents after 20 minutes of UV exposure. The curves are ordered such that AZO1-*n*C4 concentration increases from top to bottom.

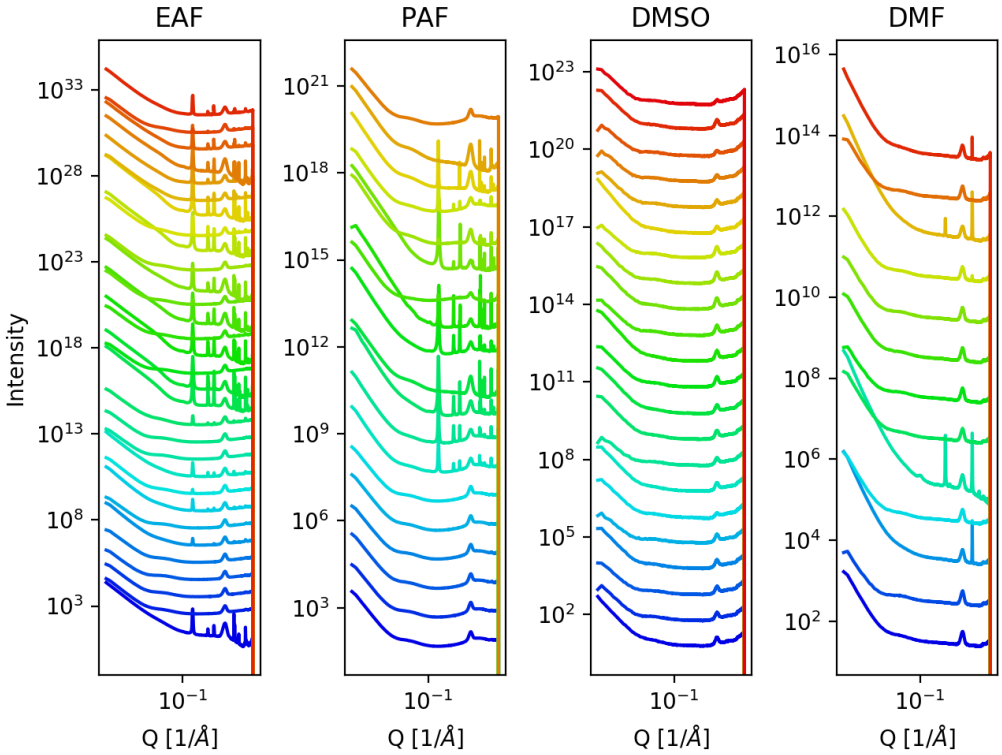

Figure 10. SAXS scattering patterns from AZO1-*n*C8 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO1-*n*C8 concentration increases from top to bottom.

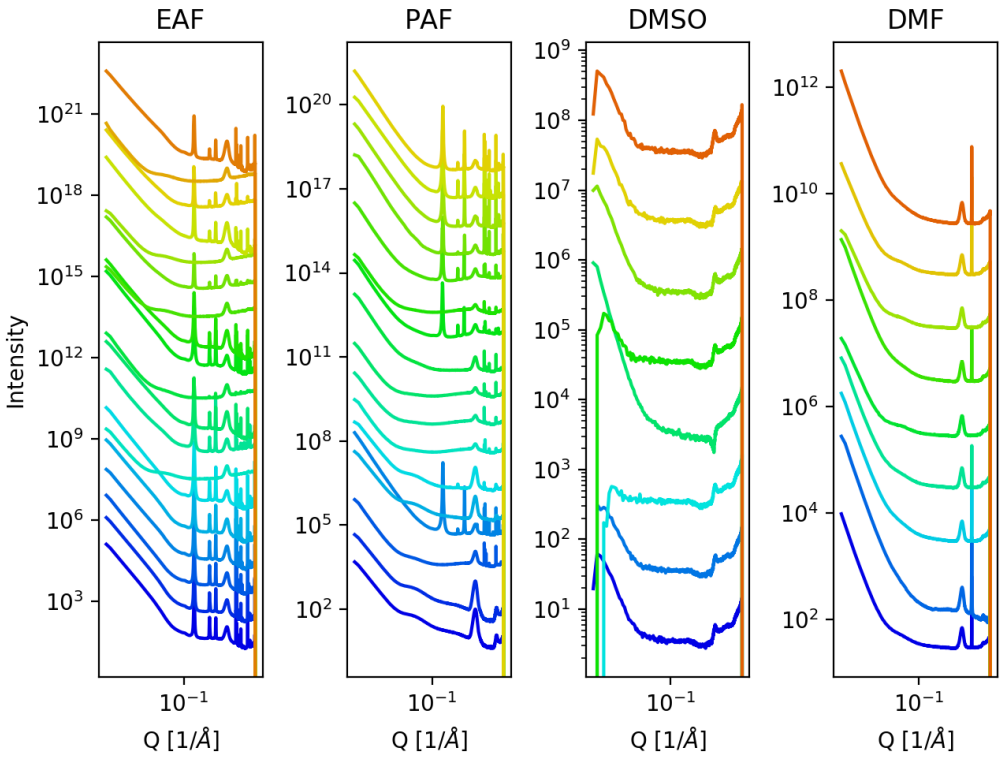

Figure 11. SAXS scattering patterns from AZO1-*n*C8 in EAF, PAF, DMSO and DMF solvents after 20 minutes of UV exposure. The curves are ordered such that AZO1-*n*C8 concentration increases from top to bottom.

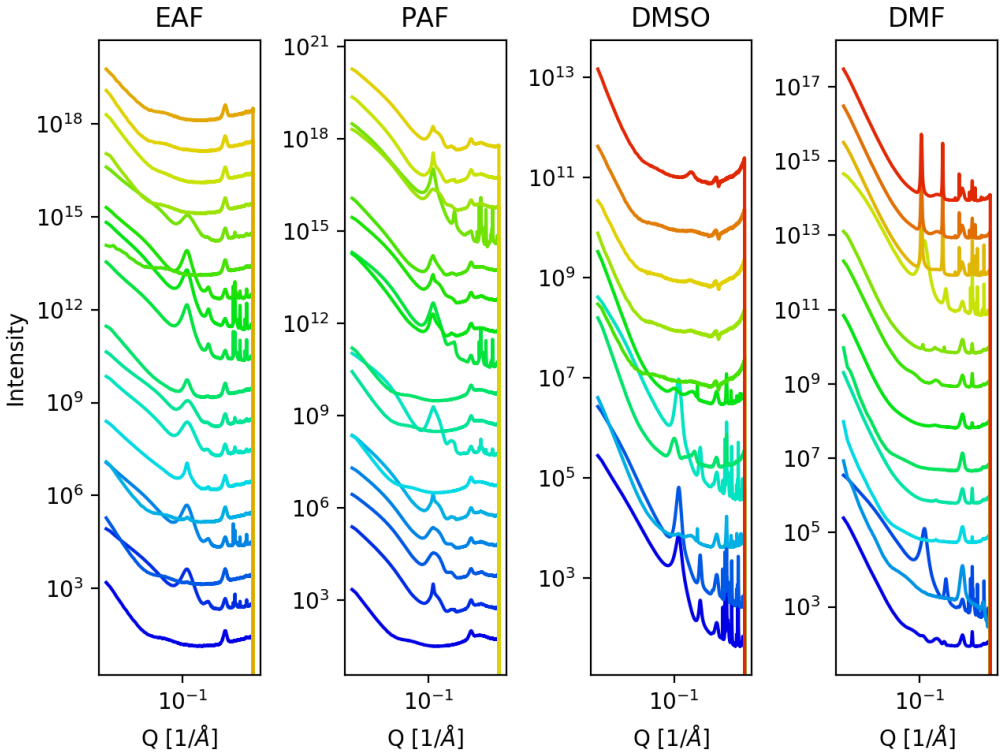

Figure 12. SAXS scattering patterns from AZO1-*n*C12 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO1-*n*C12 concentration increases from top to bottom.

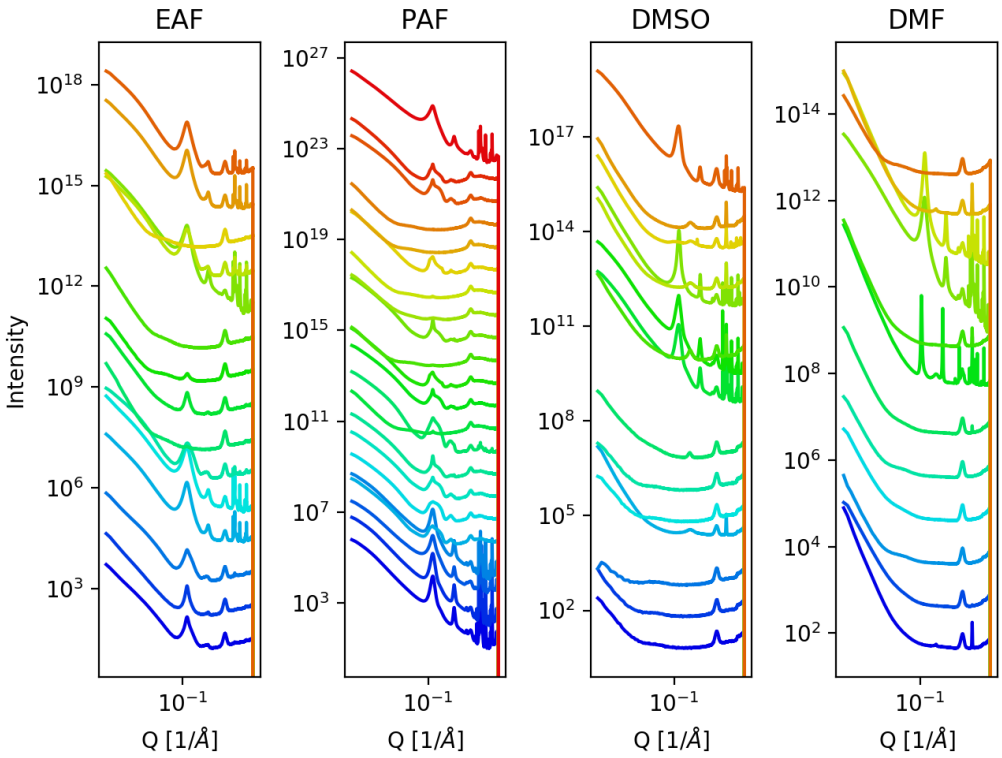

Figure 13. SAXS scattering patterns from AZO1-*n*C12 in EAF, PAF, DMSO and DMF solvents after 20 minutes of UV exposure. The curves are ordered such that AZO1-*n*C12 concentration increases from top to bottom.

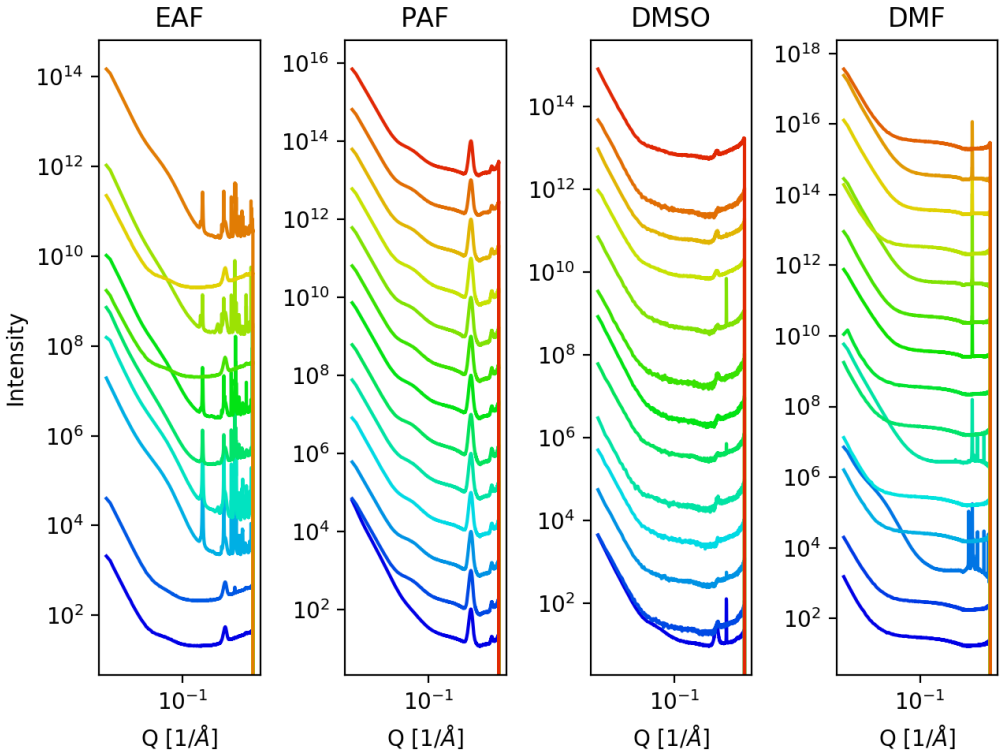

Figure 14. SAXS scattering patterns from AZO1-*i*C3 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO1-*i*C3 concentration increases from top to bottom.

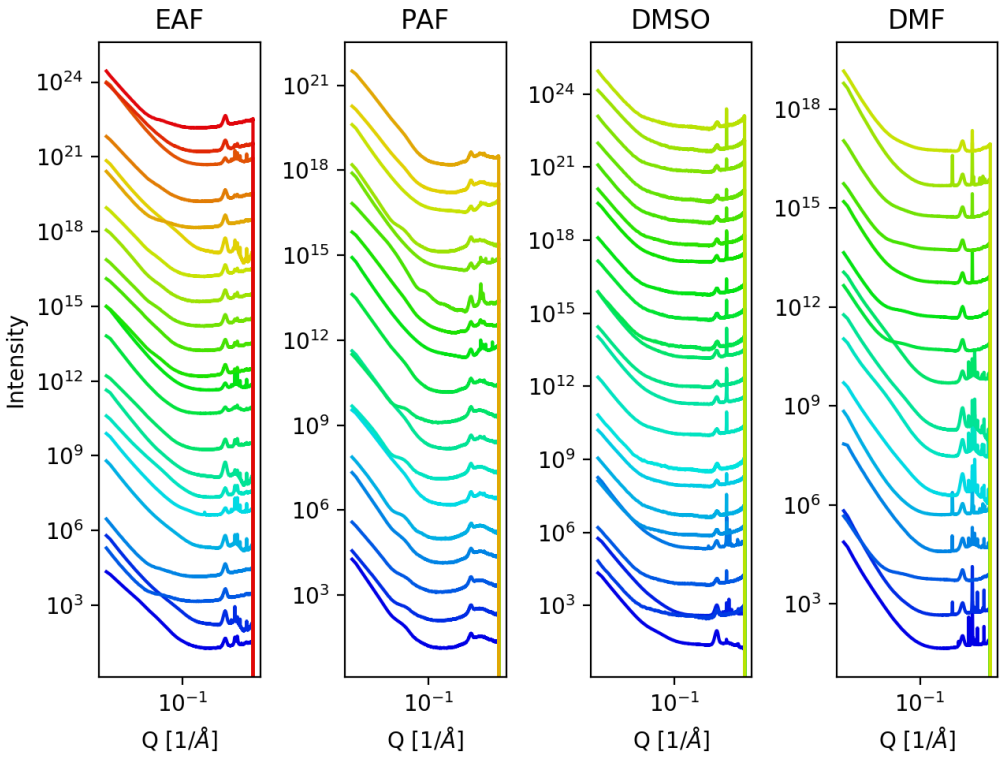

Figure 15. SAXS scattering patterns from AZO1-*i*C4 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO1-*i*C4 concentration increases from top to bottom.

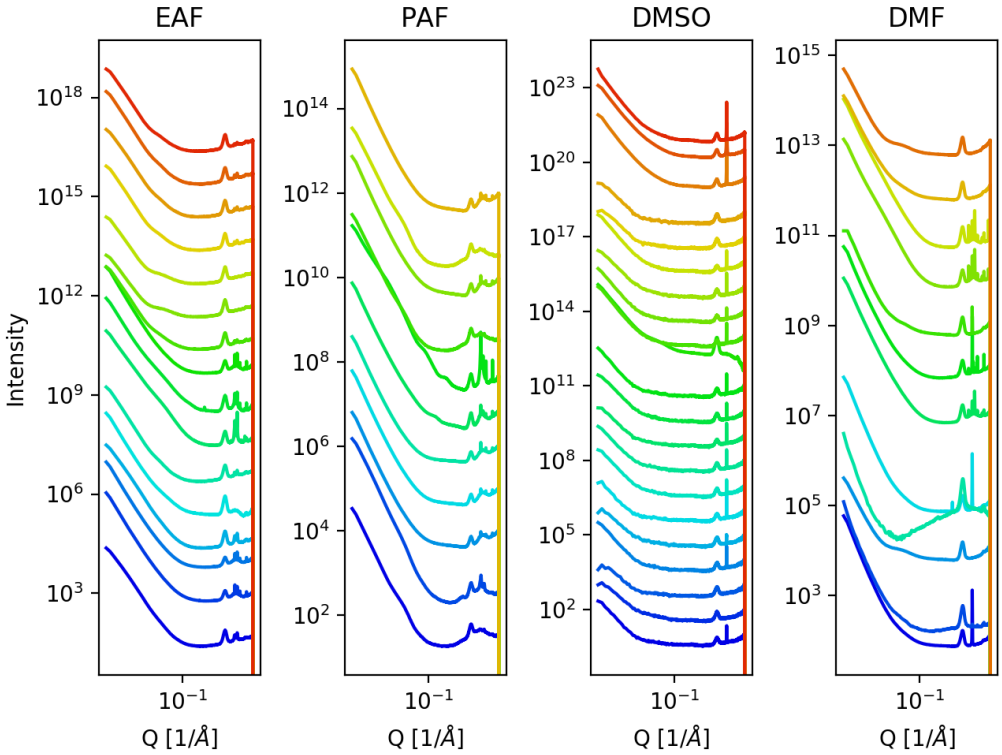

Figure 16. SAXS scattering patterns from AZO1-*i*C4 in EAF, PAF, DMSO and DMF solvents after 20 minutes exposure to UV. The curves are ordered such that AZO1-*i*C4 concentration increases from top to bottom.

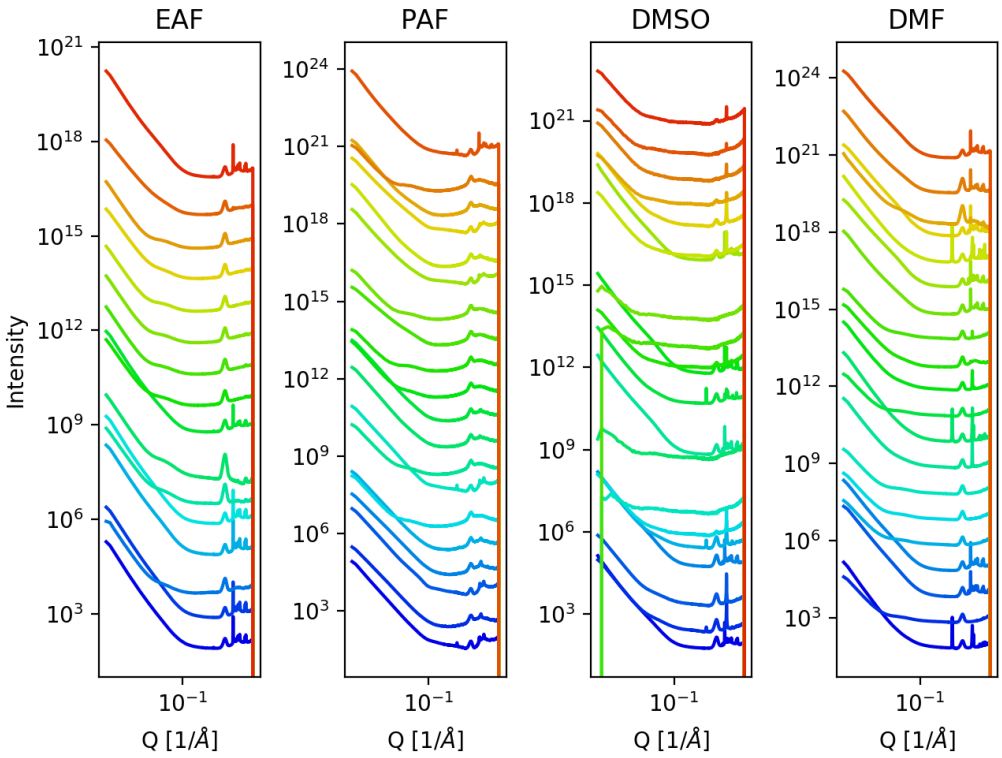

Figure 17. SAXS scattering patterns from AZO1-*t*C4 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO1-*t*C4 concentration increases from top to bottom.

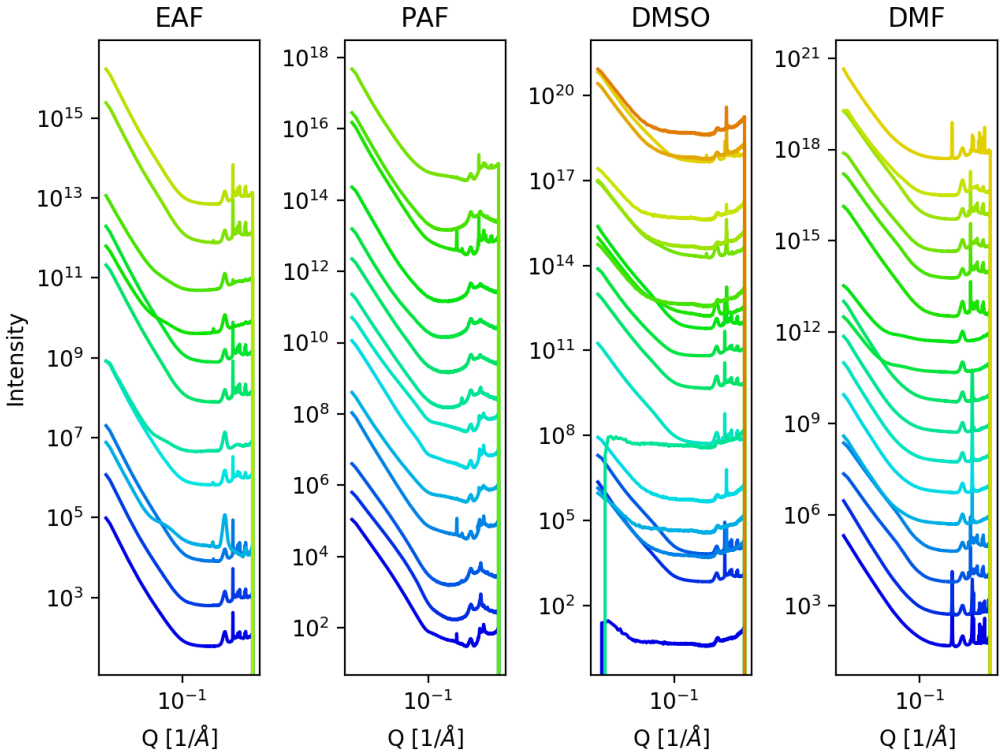

Figure 18. SAXS scattering patterns from AZO1-*t*C4 in EAF, PAF, DMSO and DMF solvents after 20 minutes exposure to UV. The curves are ordered such that AZO1-*t*C4 concentration increases from top to bottom.

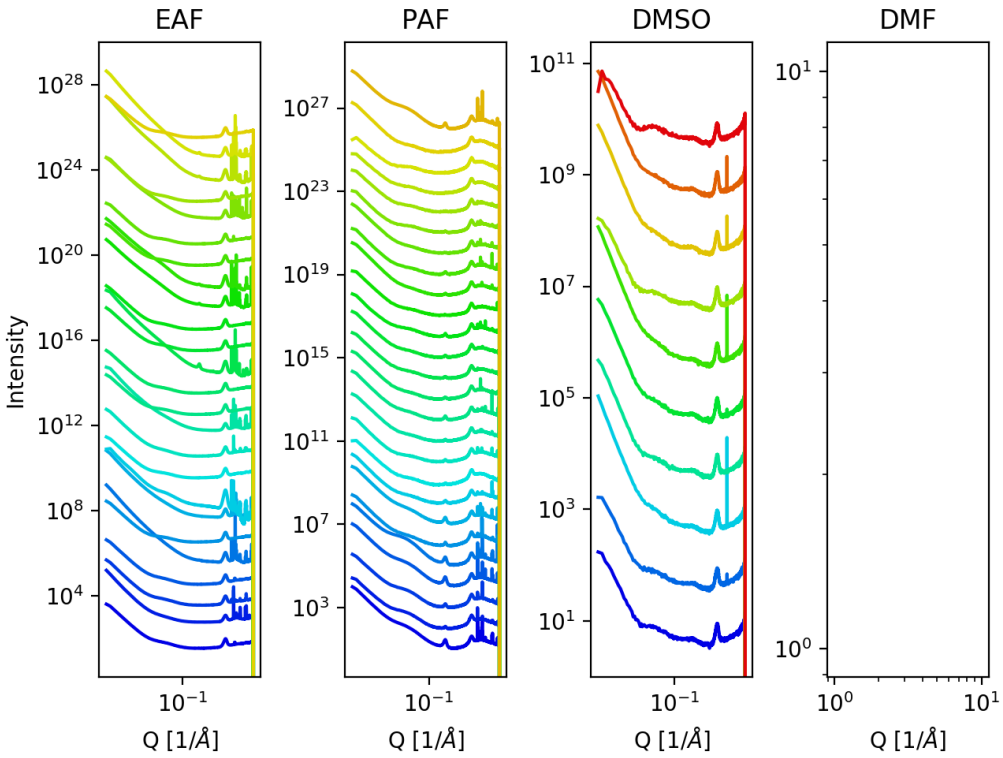

Figure 19. SAXS scattering patterns from AZO1-*t*C8 in EAF, PAF and DMSO solvents. DMF patterns were not taken due to capillary rupture. The curves are ordered such that AZO1-*t*C8 concentration increases from top to bottom.

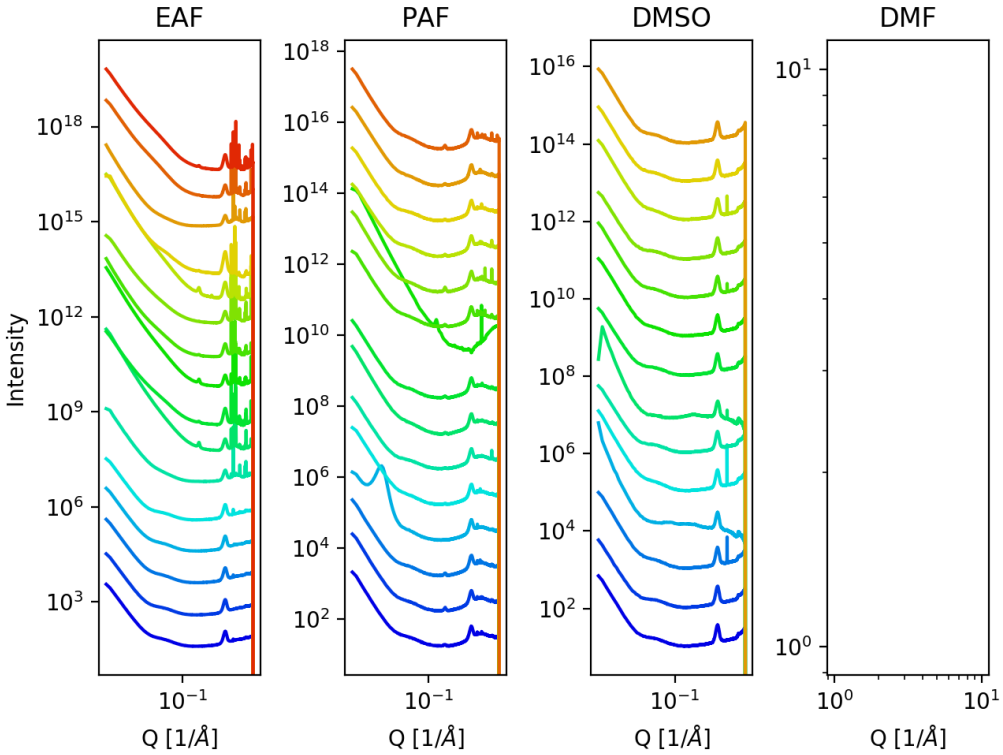

Figure 20. SAXS scattering patterns from AZO1-*t*C8 in EAF, PAF and DMSO solvents after 20 minutes of UV exposure. DMF patterns were not taken due to capillary rupture. The curves are ordered such that AZO1-*t*C8 concentration increases from top to bottom.

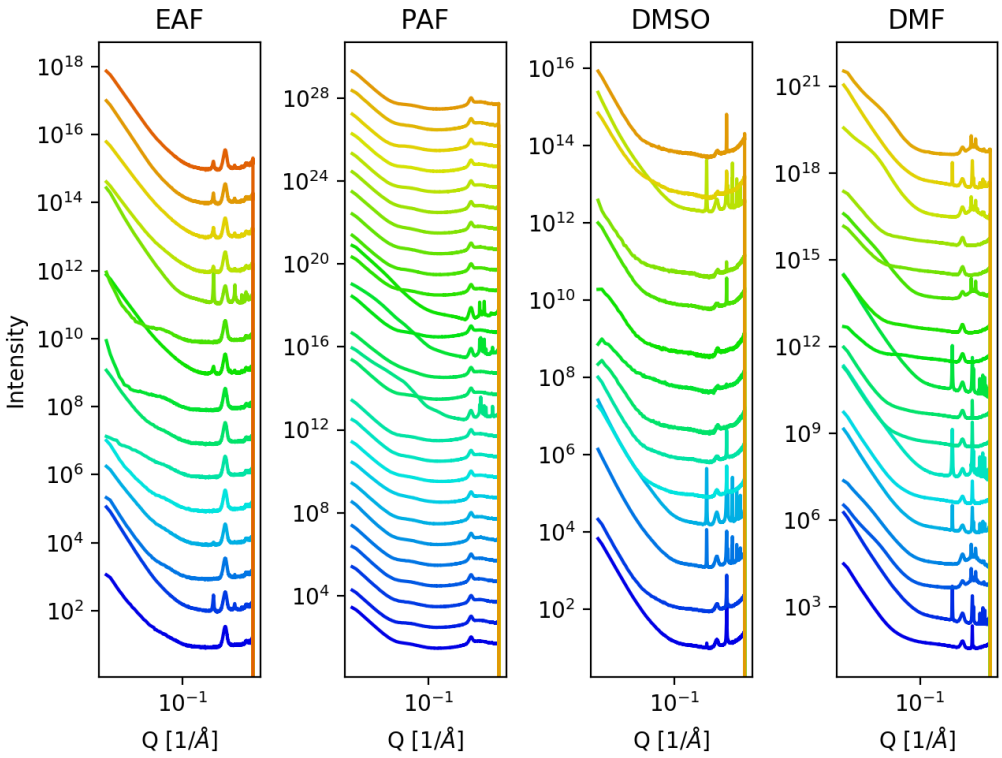

Figure 21. SAXS scattering patterns from AZO1-EtOH in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO1-EtOH concentration increases from top to bottom.

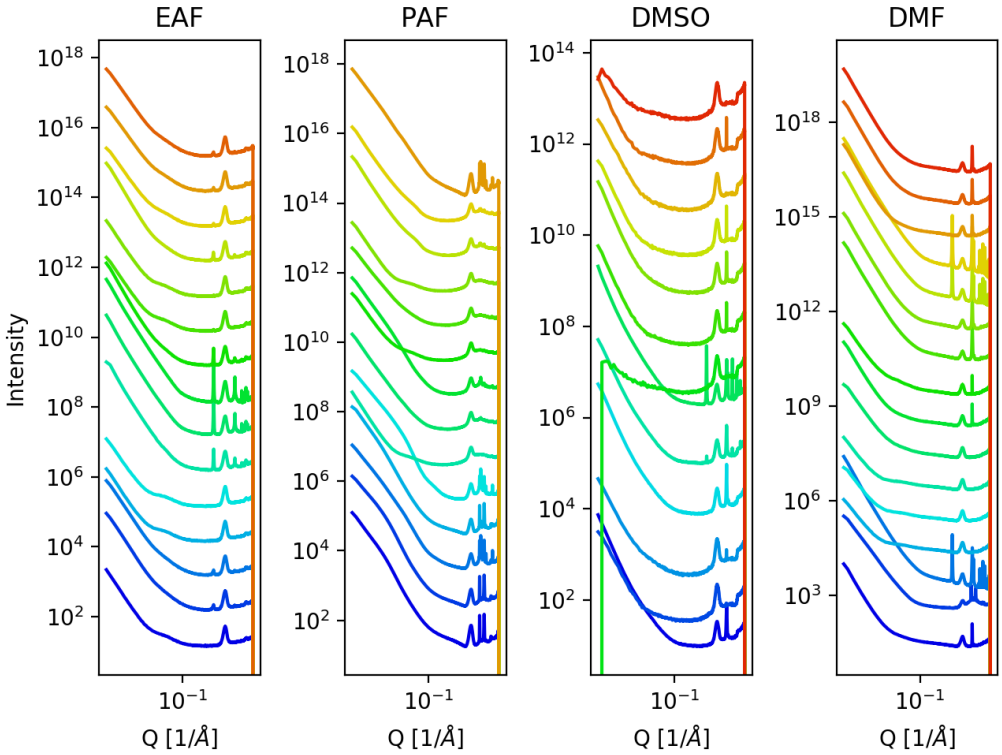

Figure 22. SAXS scattering patterns from AZO1-EtOH in EAF, PAF, DMSO and DMF solvents after 20 minutes of UV exposure. The curves are ordered such that AZO1-EtOH concentration increases from top to bottom.

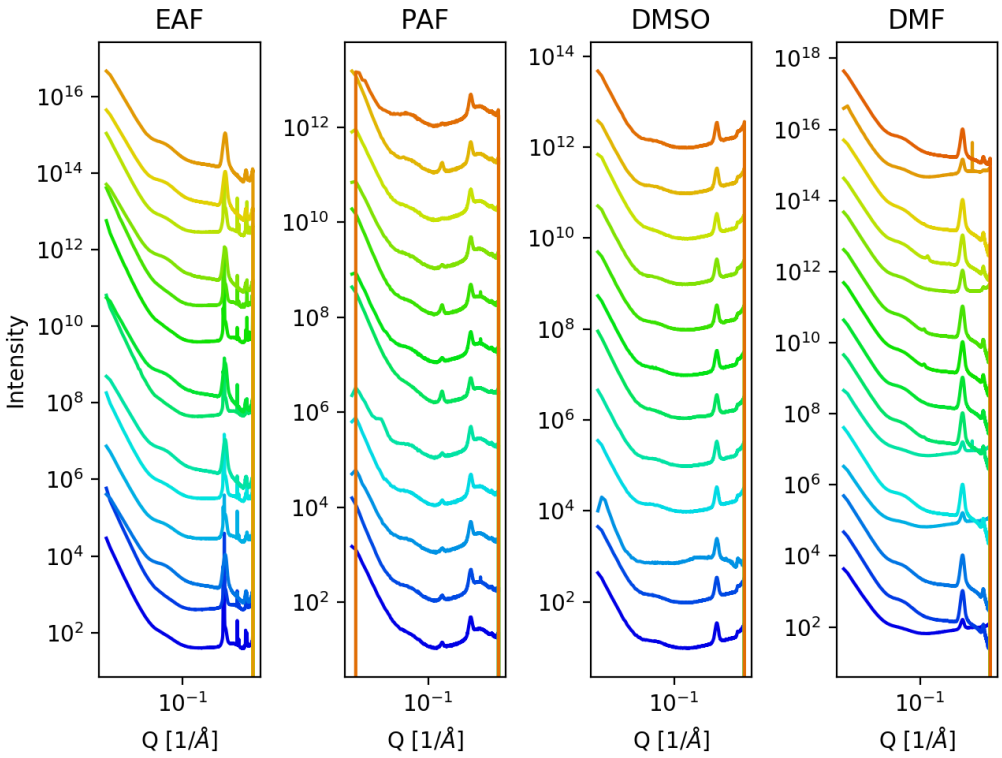

Figure 23. SAXS scattering patterns from AZO1-EH in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO1-EH concentration increases from top to bottom.

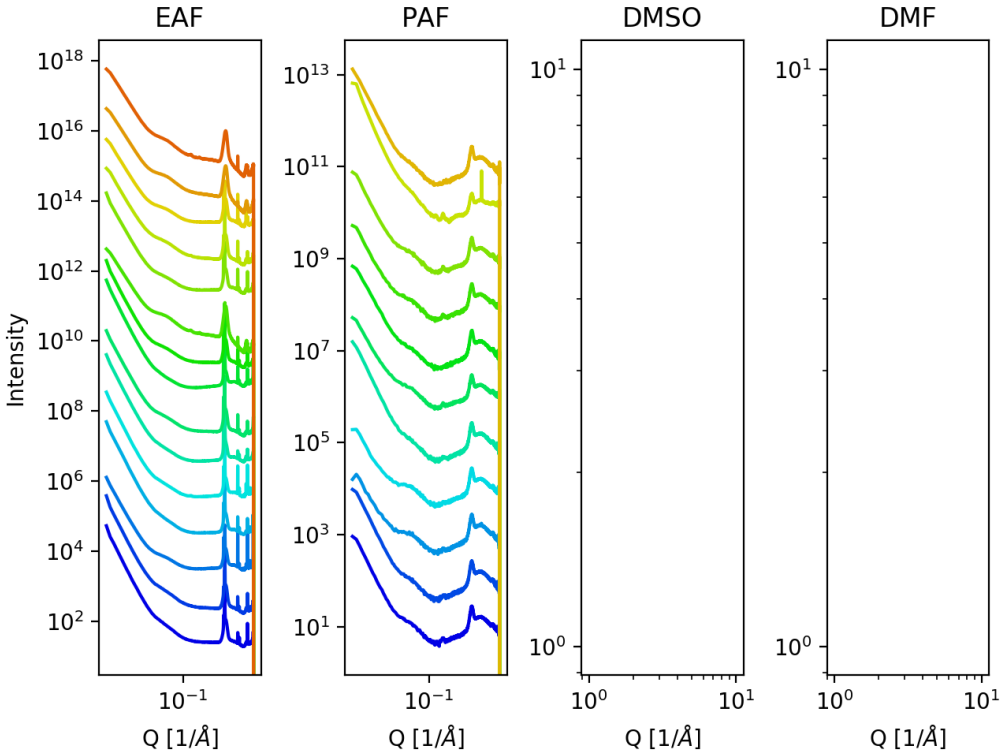

Figure 24. SAXS scattering patterns from AZO1-EH in EAF, PAF, DMSO and DMF solvents after 20 minutes of UV exposure. Omitted solvents were not analysed after UV exposure. The curves are ordered such that AZO1-EH concentration increases from top to bottom.

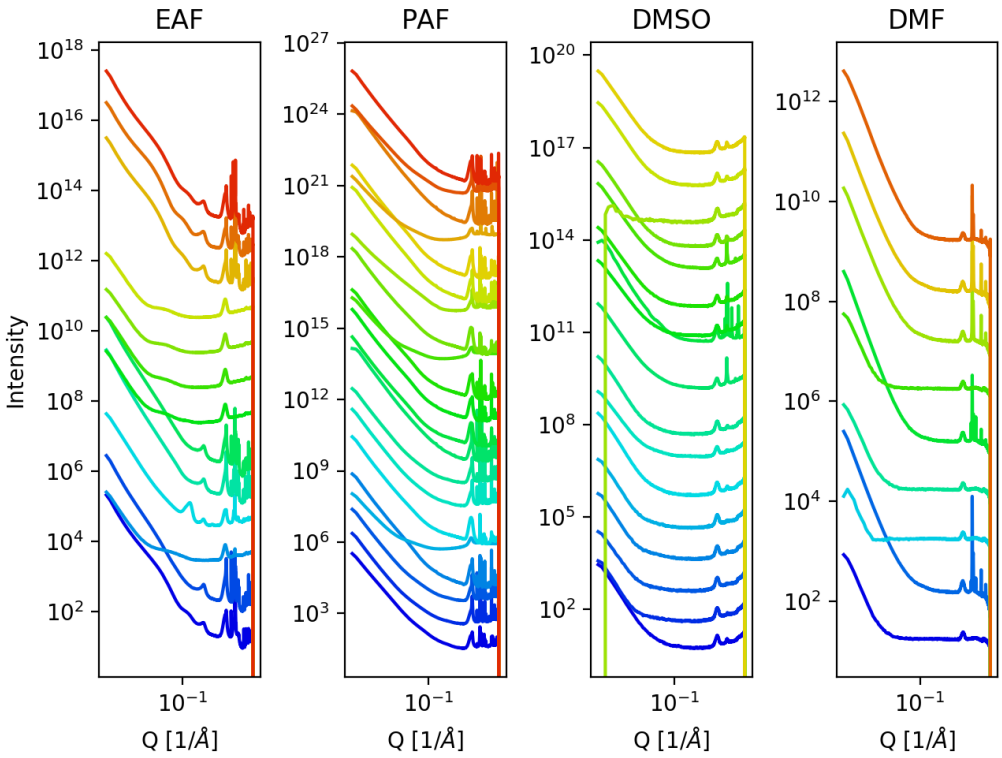

Figure 25. SAXS scattering patterns from AZO1-CE in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO1-CE concentration increases from top to bottom.

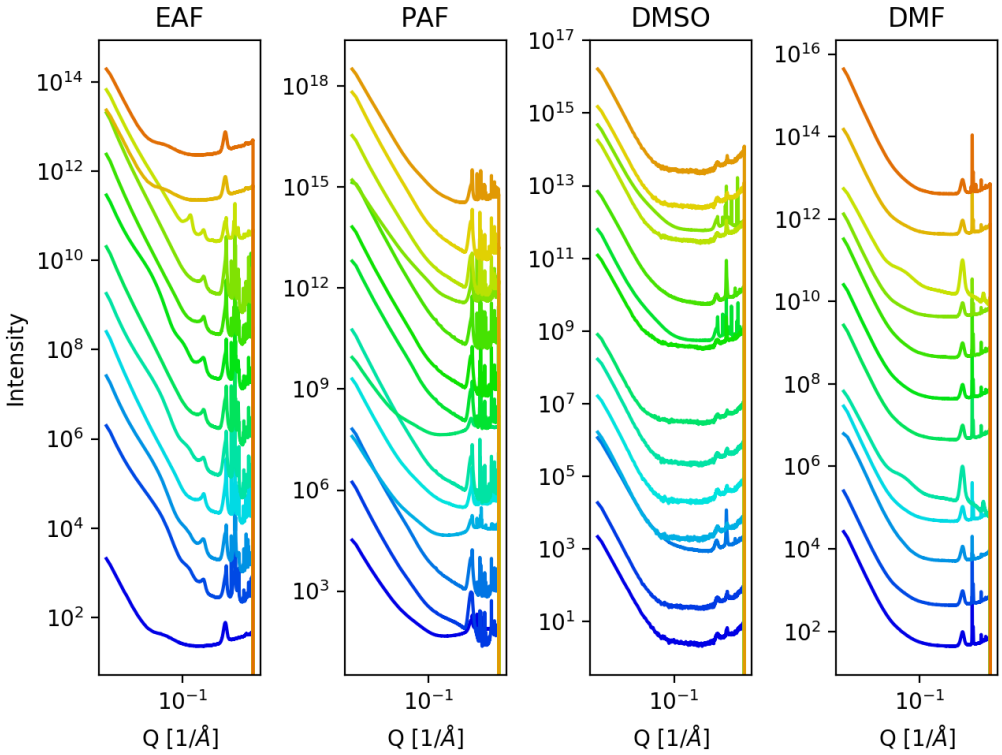

Figure 26. SAXS scattering patterns from AZO1-CE in EAF, PAF, DMSO and DMF solvents after 20 minutes of UV-exposure. The curves are ordered such that AZO1-CE concentration increases from top to bottom.

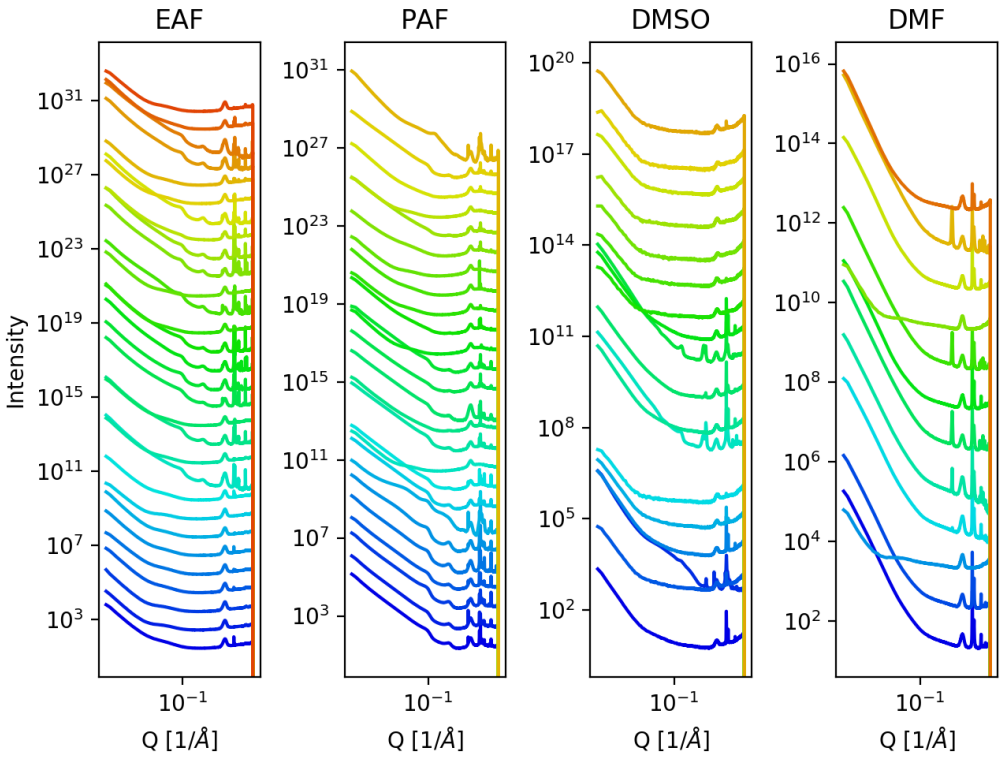

Figure 27. SAXS scattering patterns from AZO1-THP in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO1-THP concentration increases from top to bottom.

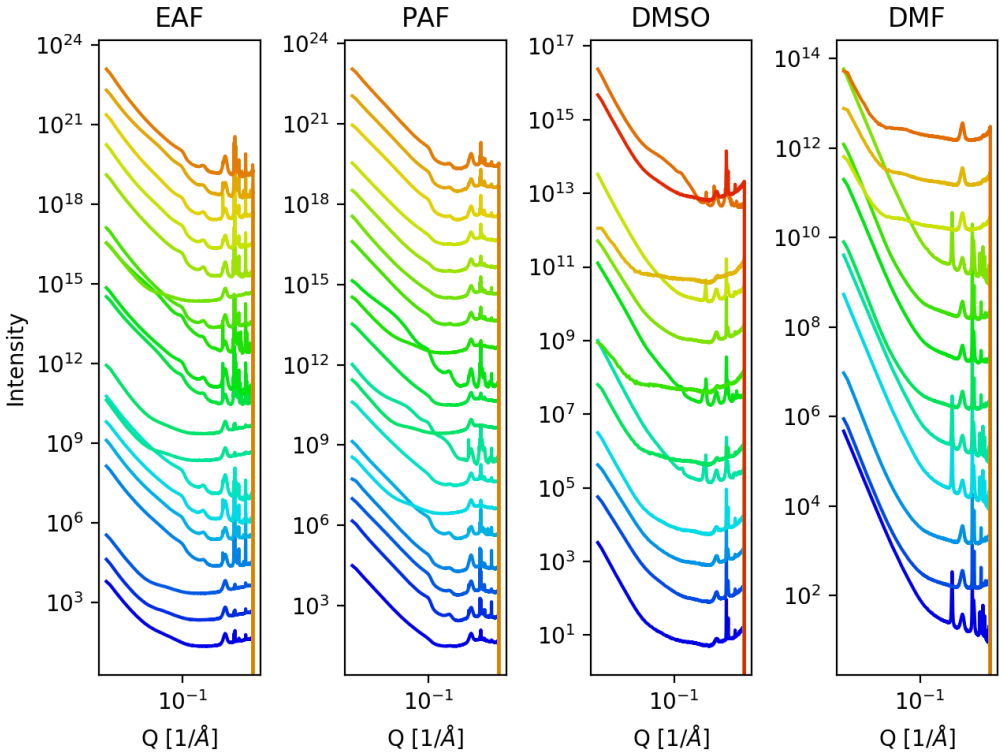

Figure 28. SAXS scattering patterns from AZO1-THP in EAF, PAF, DMSO and DMF solvents after 20 minutes of UV exposure. The curves are ordered such that AZO1-THP concentration increases from top to bottom.

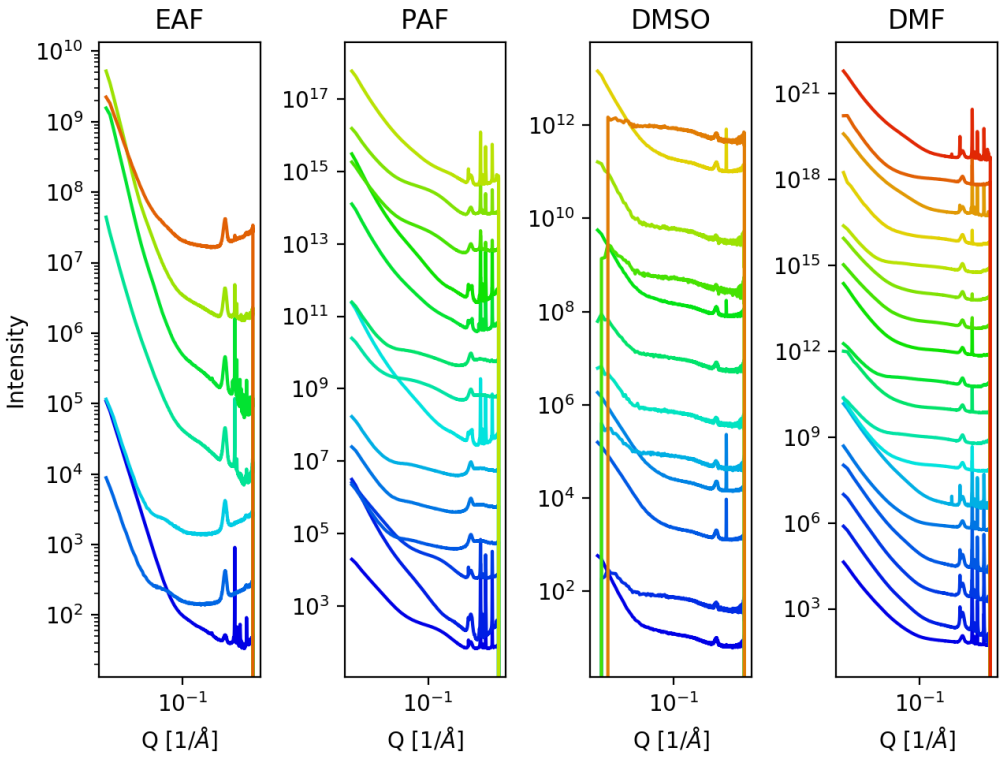

Figure 29. SAXS scattering patterns from AZO1-BTFMB in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO1- BTFMB concentration increases from top to bottom.

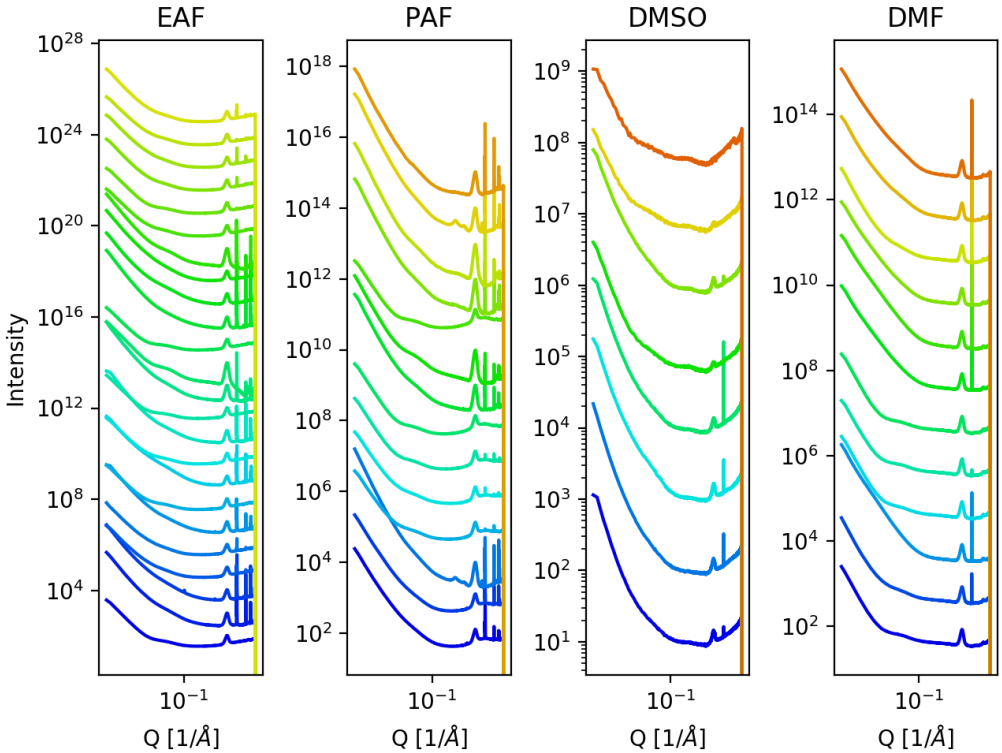

Figure 30. SAXS scattering patterns from AZO2-C2 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-C2 concentration increases from top to bottom.

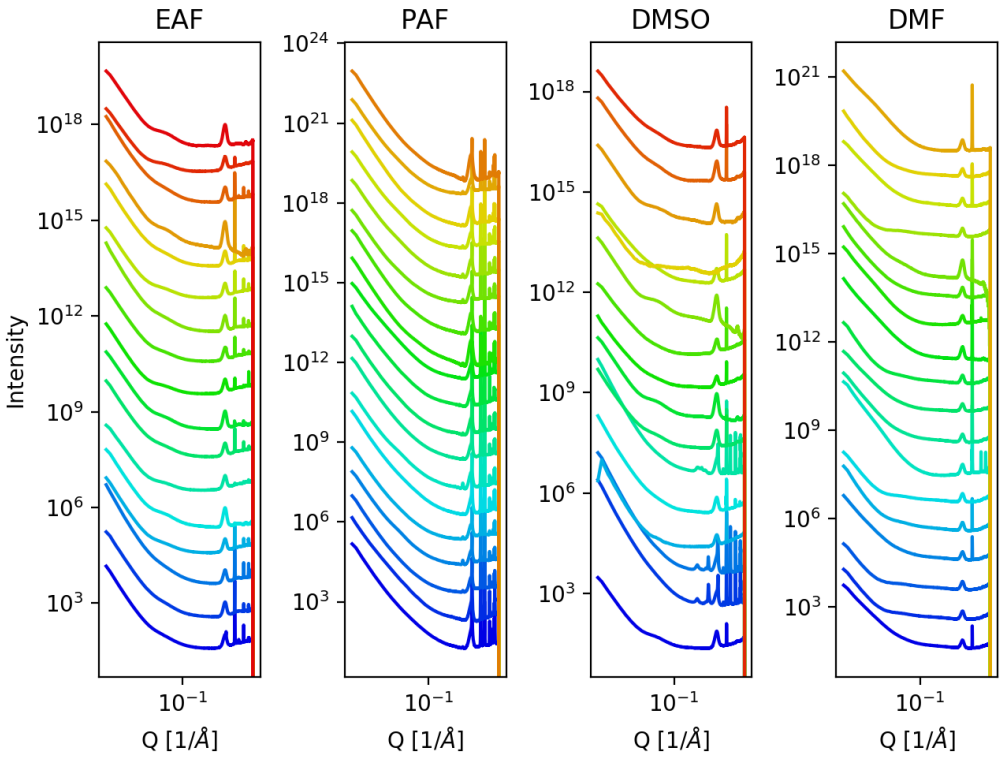

Figure 31. SAXS scattering patterns from AZO2-*n*C3 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-*n*C3 concentration increases from top to bottom.

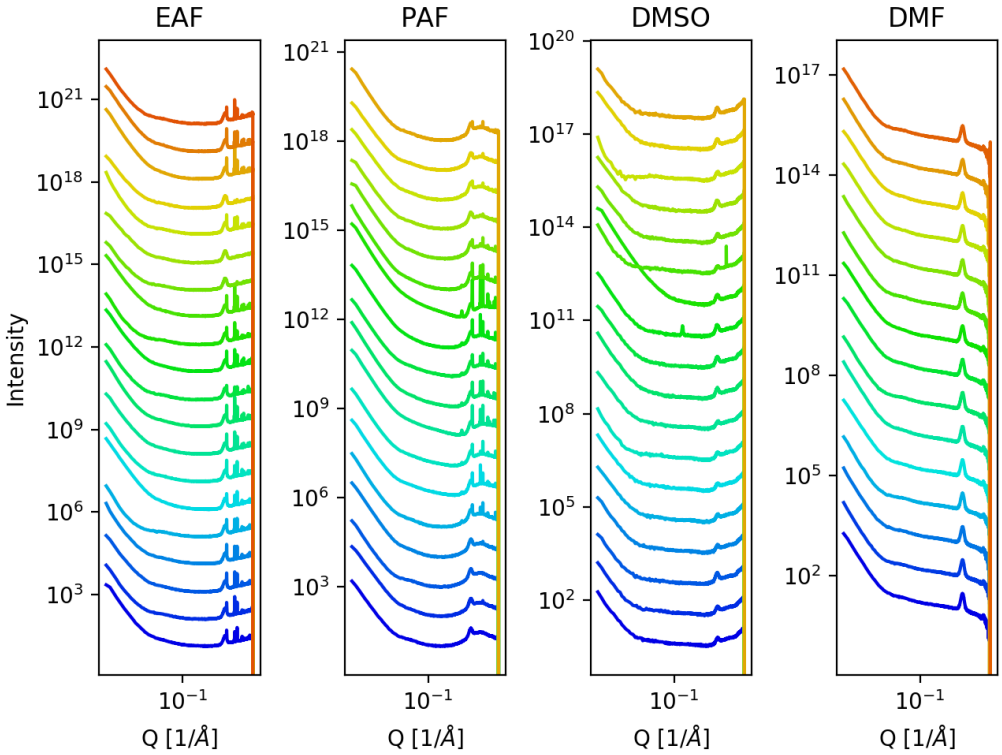

Figure 32. SAXS scattering patterns from AZO2-*n*C4 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-*n*C4 concentration increases from top to bottom.

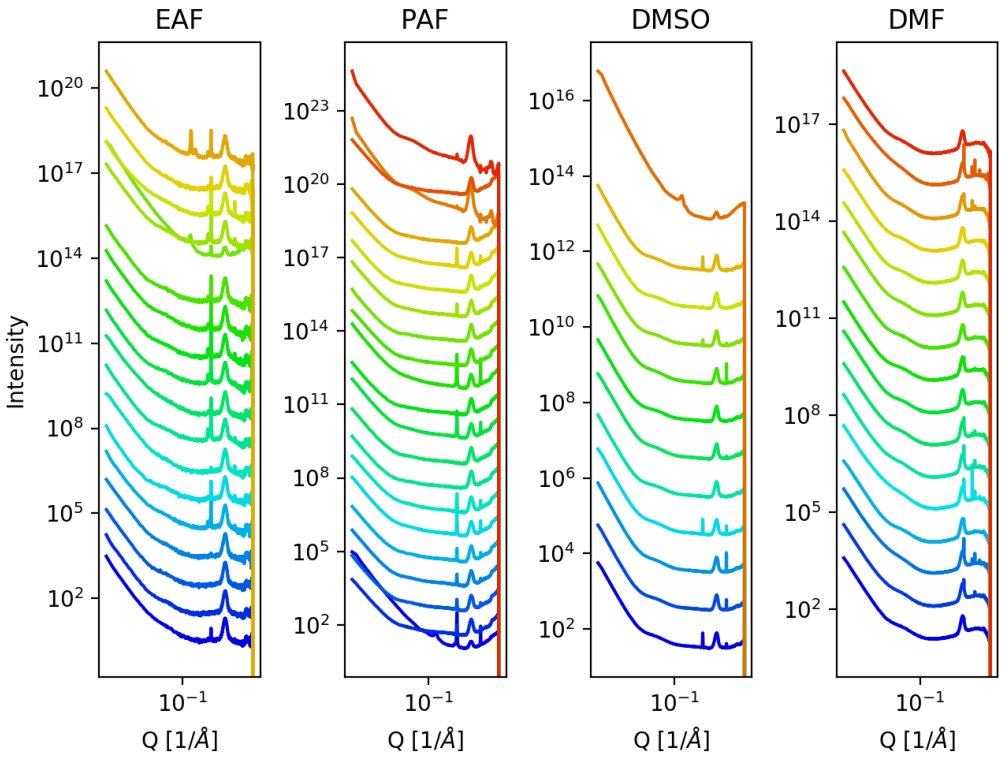

Figure 33. SAXS scattering patterns from AZO2-*n*C8 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-*n*C8 concentration increases from top to bottom.

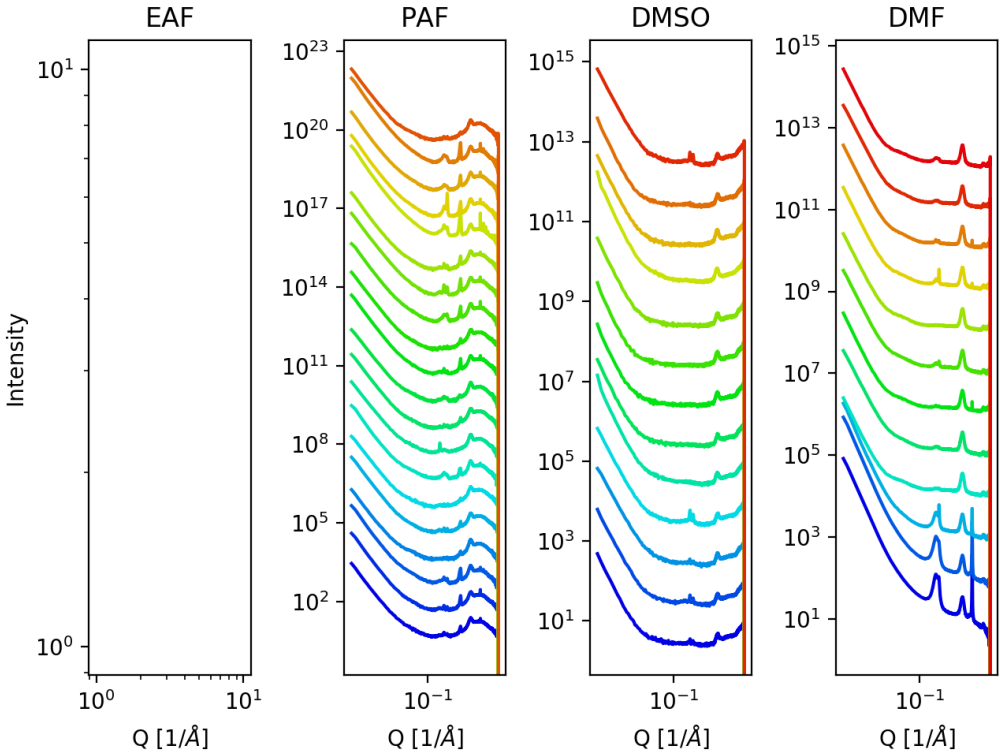

Figure 34. SAXS scattering patterns from AZO2-*n*C12 in PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-*n*C12 concentration increases from top to bottom.

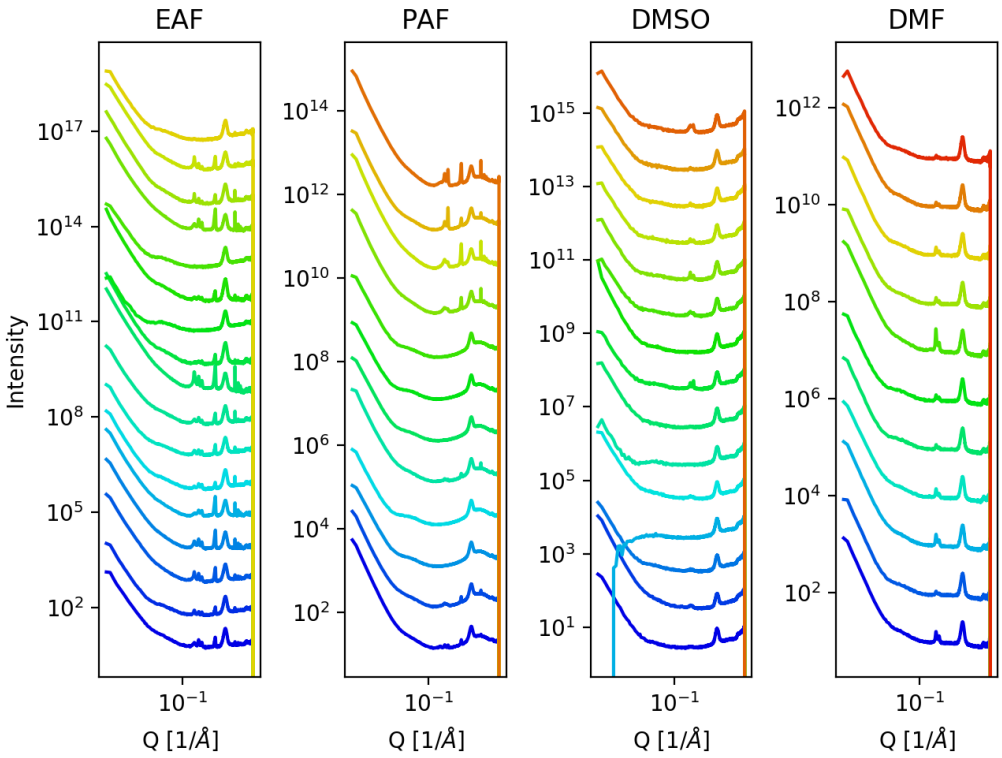

Figure 35. SAXS scattering patterns from AZO2-*n*C12 in EAF, PAF, DMSO and DMF solvents after 20 minutes of UV exposure. The curves are ordered such that AZO2-*n*C12 concentration increases from top to bottom.

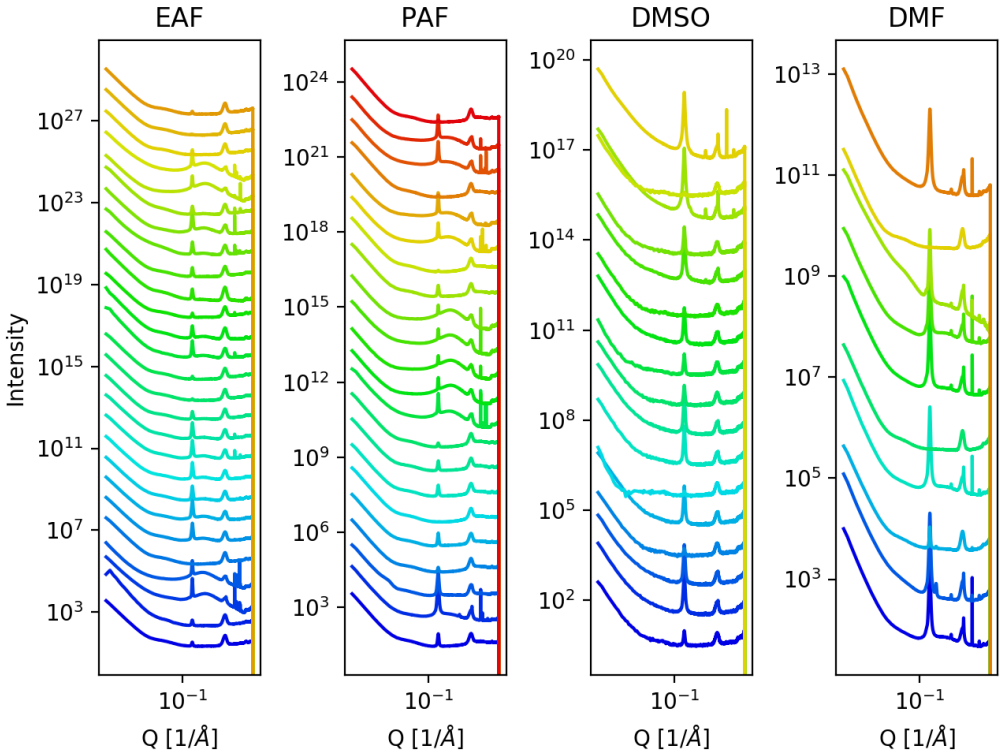

Figure 36. SAXS scattering patterns from AZO2-C18:1 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-C18:1 concentration increases from top to bottom.

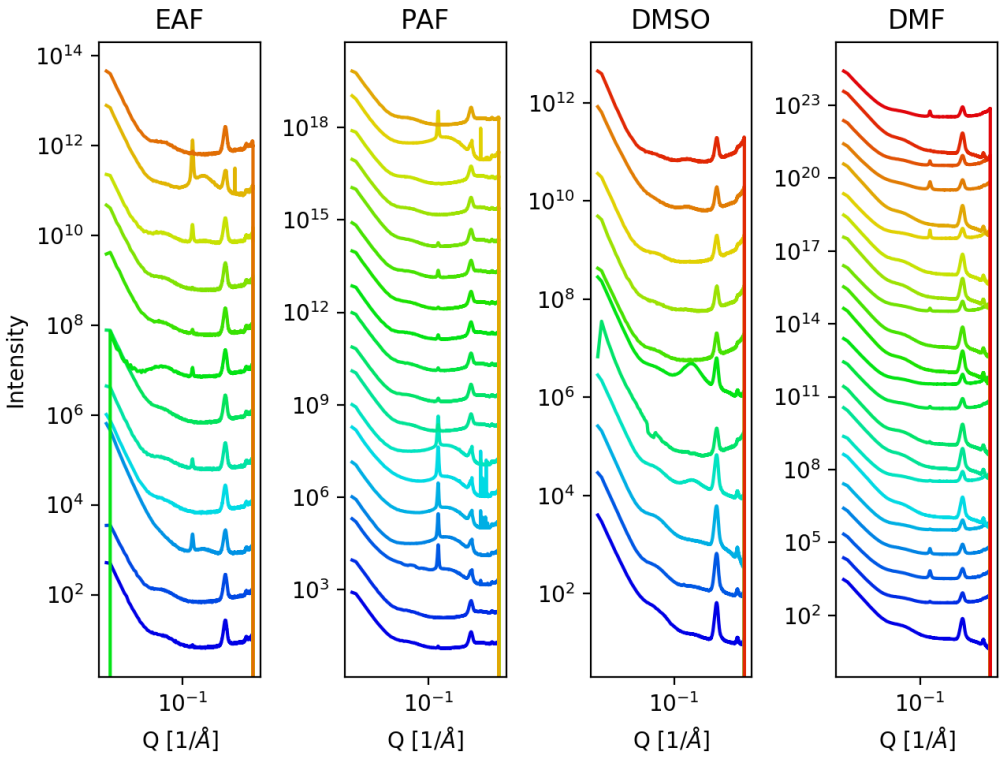

Figure 37. SAXS scattering patterns from AZO2-C18:1 in EAF, PAF, DMSO and DMF solvents after 20 minutes of UV exposure. The curves are ordered such that AZO2-C18:1 concentration increases from top to bottom.

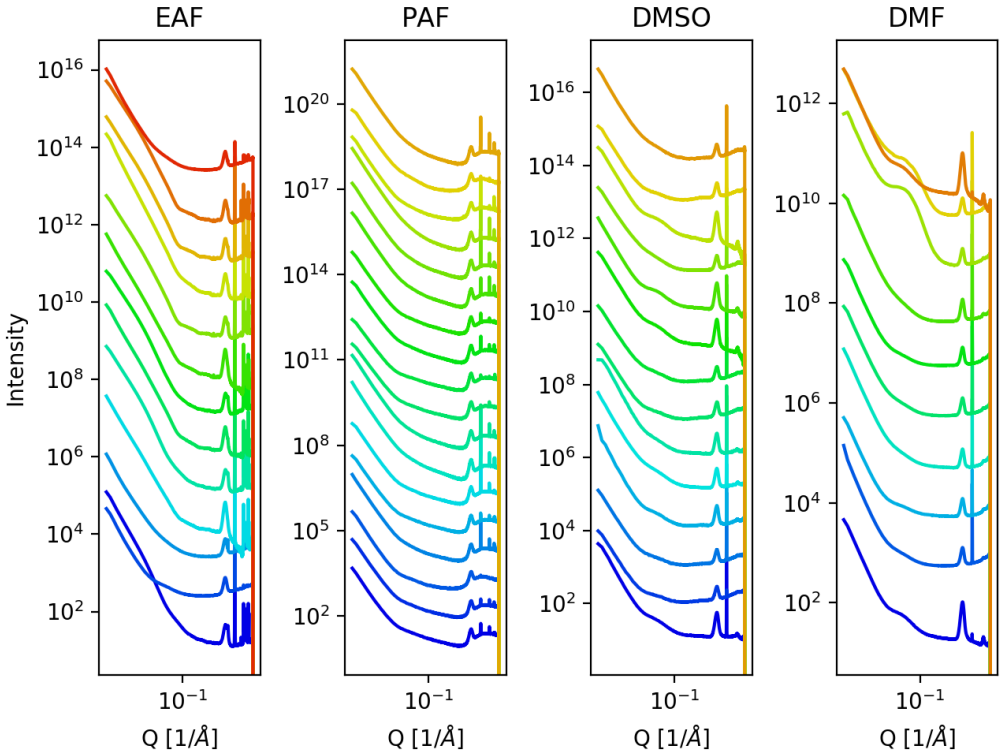

Figure 38. SAXS scattering patterns from AZO2-*i*C3 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-*i*C3 concentration increases from top to bottom.

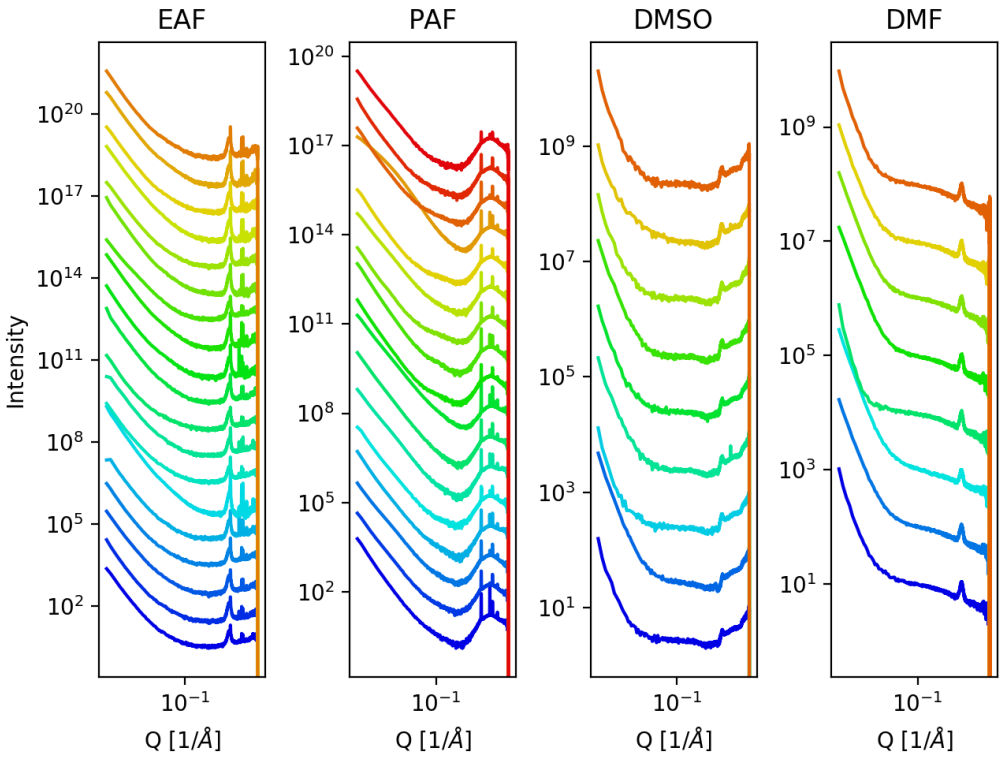

Figure 39. SAXS scattering patterns from AZO2-*i*C4 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-*i*C4 concentration increases from top to bottom.

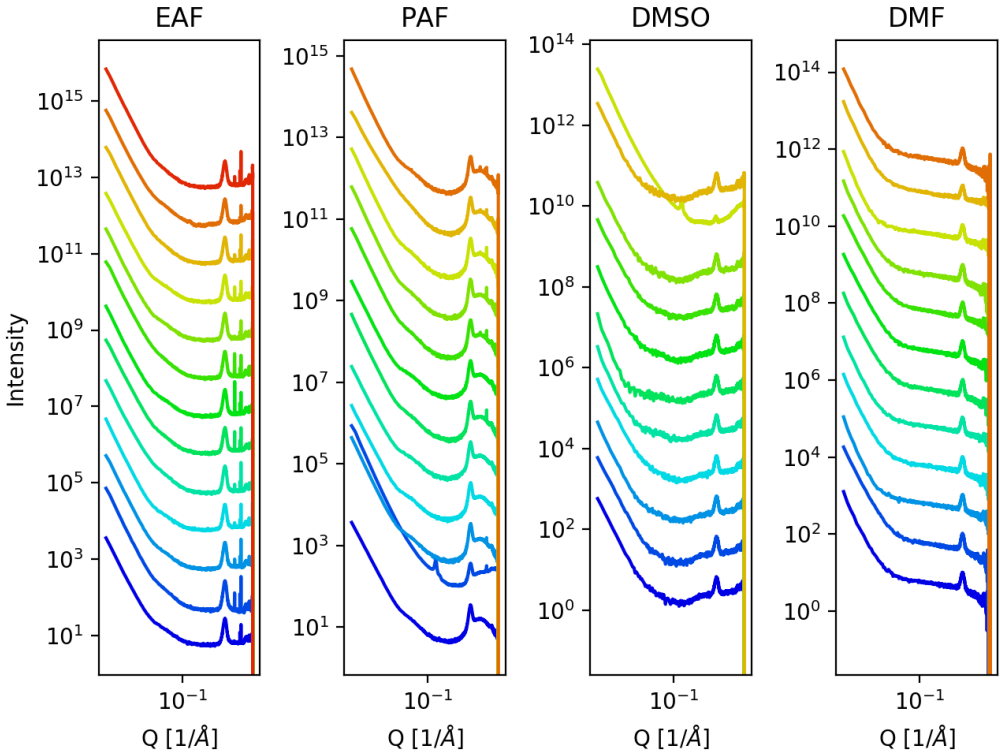

Figure 40. SAXS scattering patterns from AZO2-*t*C4 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-*t*C4 concentration increases from top to bottom.

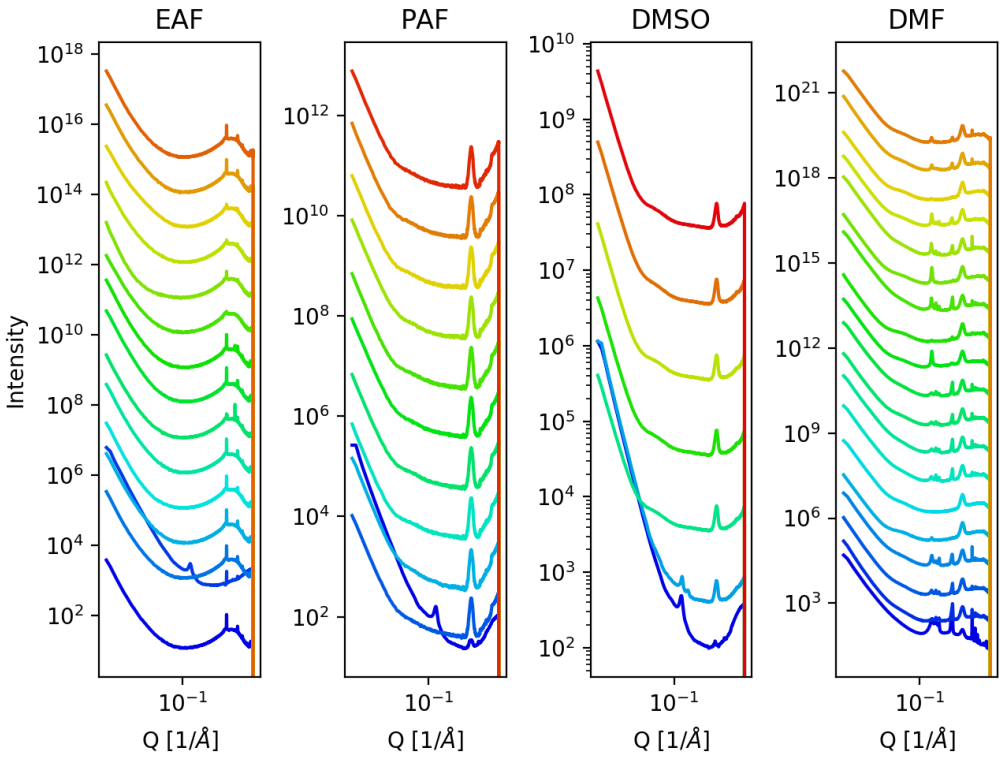

Figure 41. SAXS scattering patterns from AZO2-*t*C8 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-*t*C8 concentration increases from top to bottom.

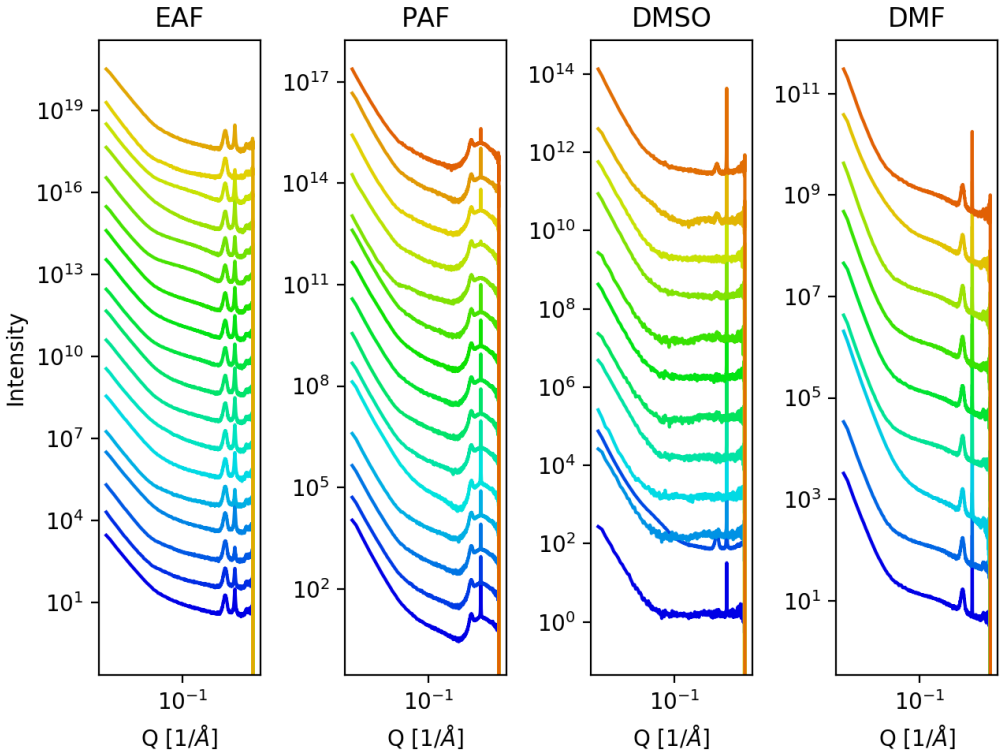

Figure 42. SAXS scattering patterns from AZO2-EtOH in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-EtOH concentration increases from top to bottom.

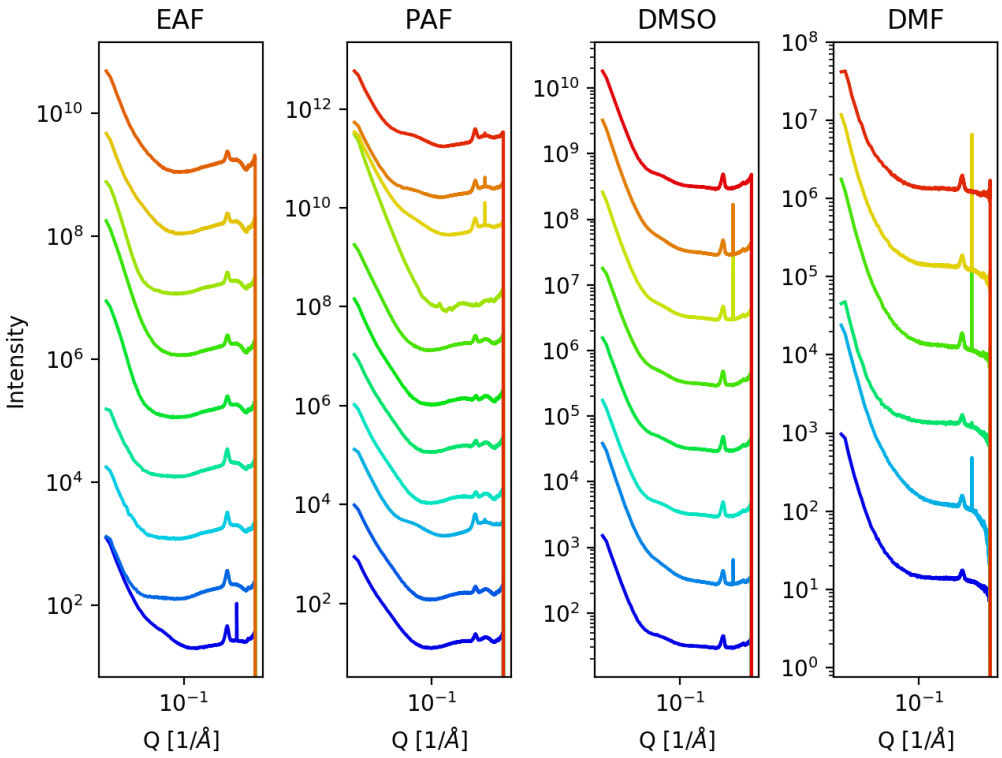

Figure 43. SAXS scattering patterns from AZO2-EH in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-EH concentration increases from top to bottom.

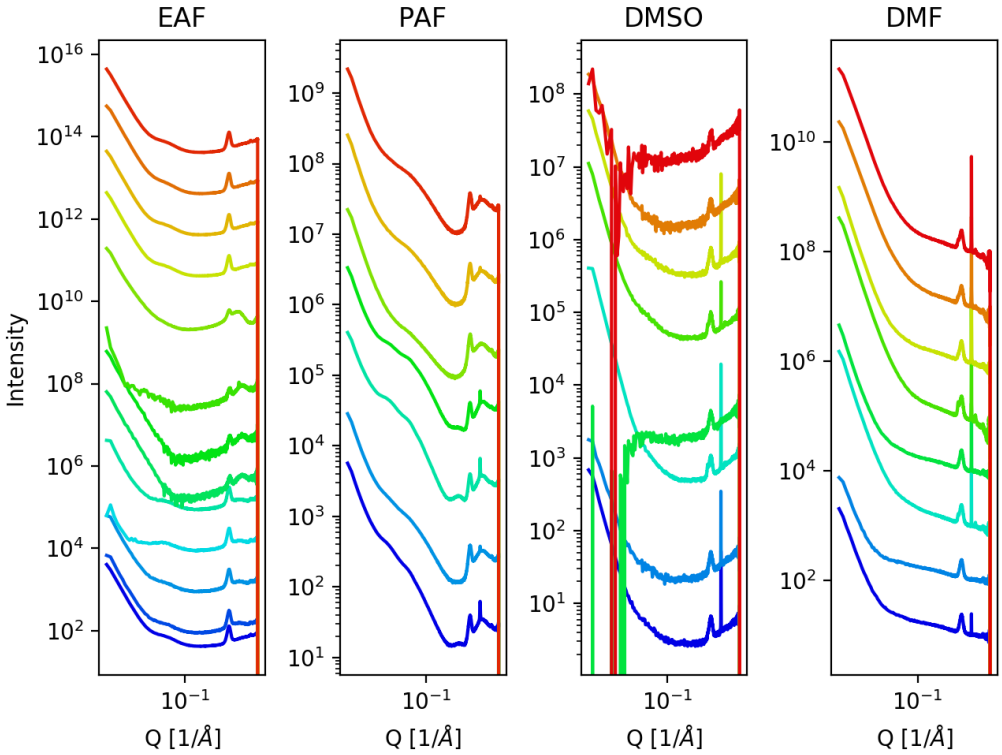

Figure 44. SAXS scattering patterns from AZO2-CE in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-CE concentration increases from top to bottom.

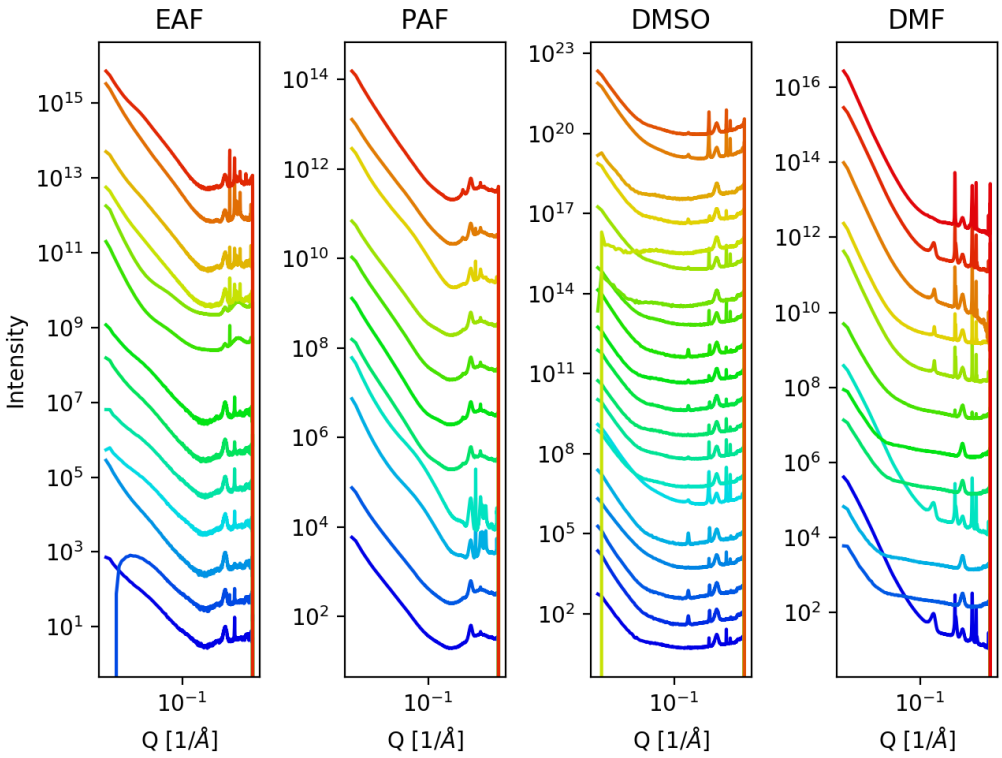

Figure 45. SAXS scattering patterns from AZO2-THP in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-THP concentration increases from top to bottom.

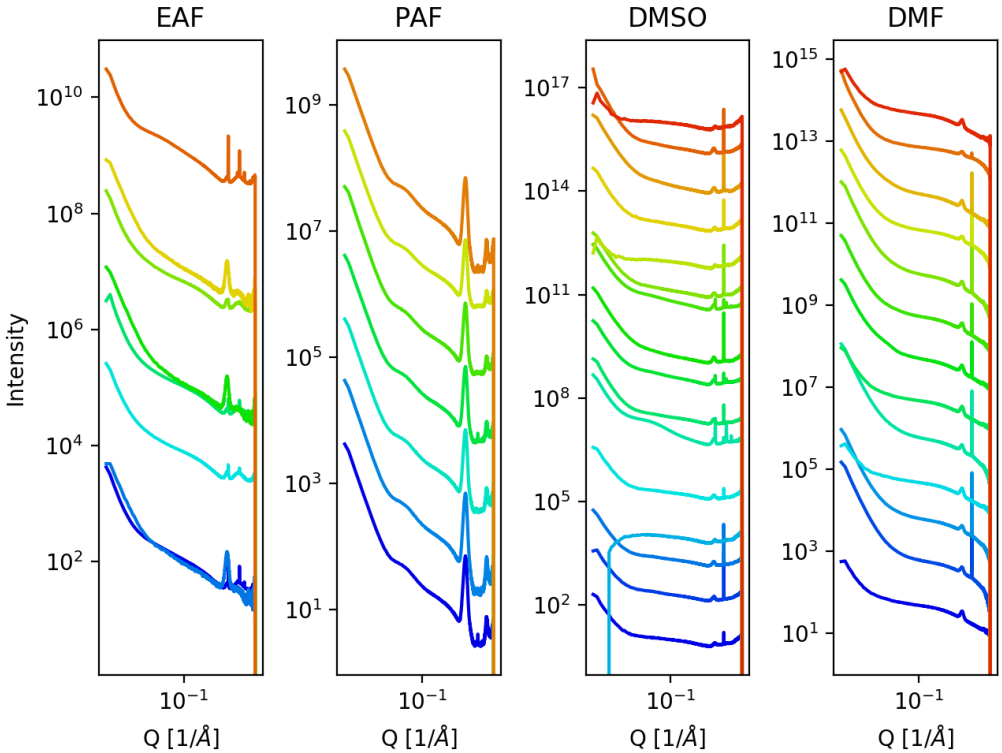

Figure 46. SAXS scattering patterns from AZO2-BTFMB in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO2-BTFMB concentration increases from top to bottom.

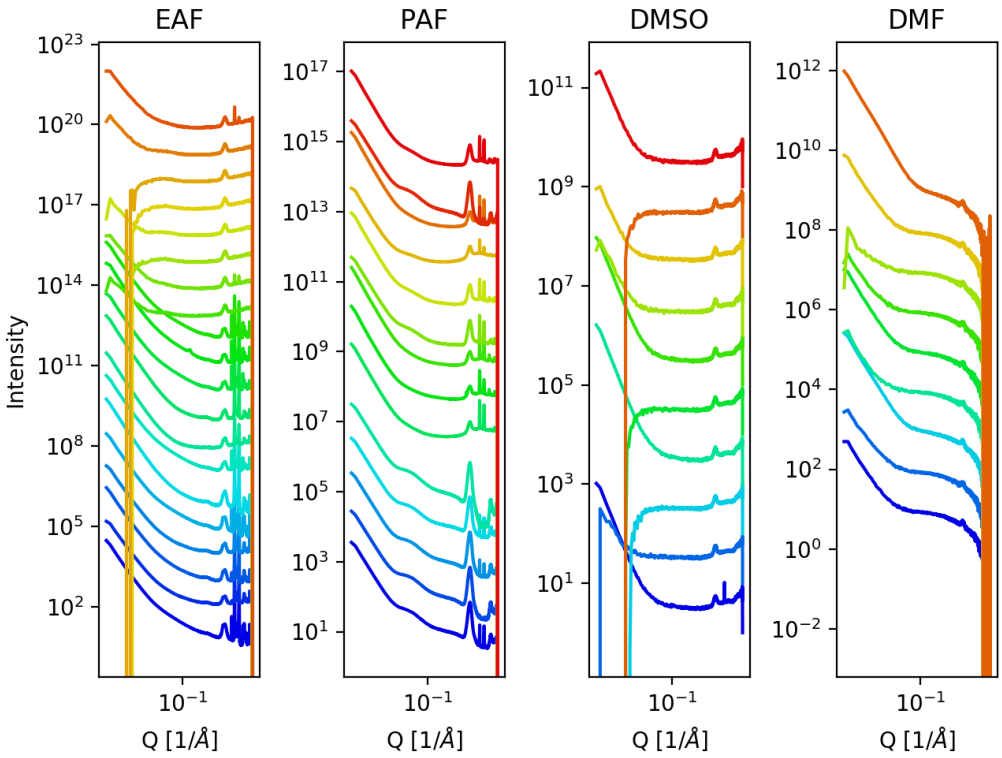

Figure 47. SAXS scattering patterns from AZO3-C2 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-C2 concentration increases from top to bottom.

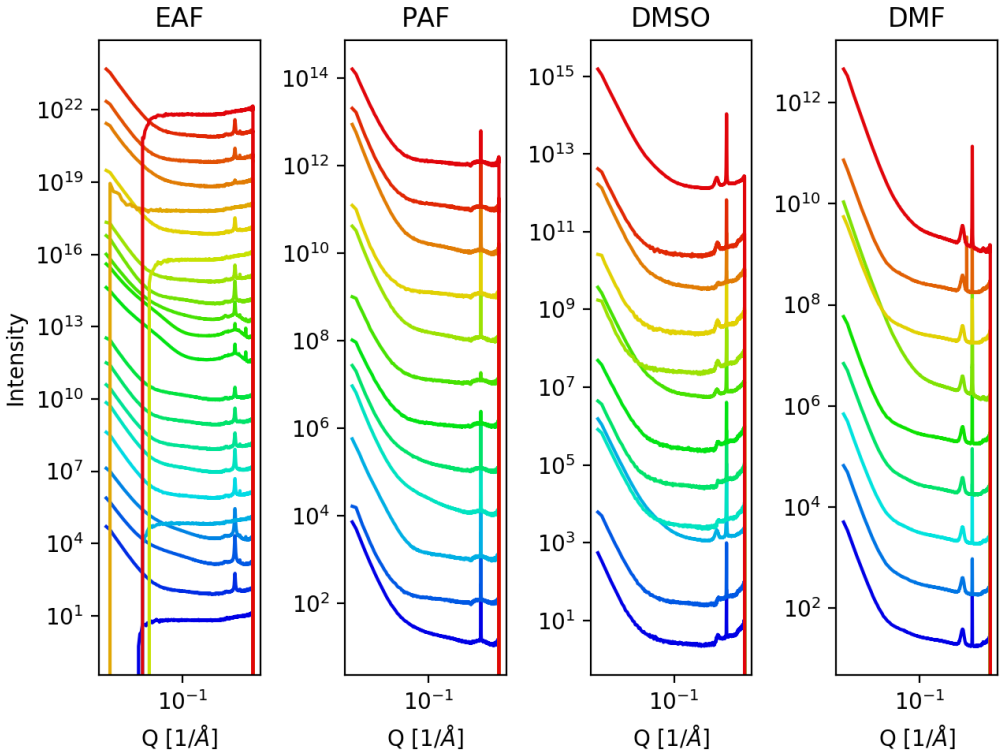

Figure 48. SAXS scattering patterns from AZO3-*n*C2 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-*n*C2 concentration increases from top to bottom.

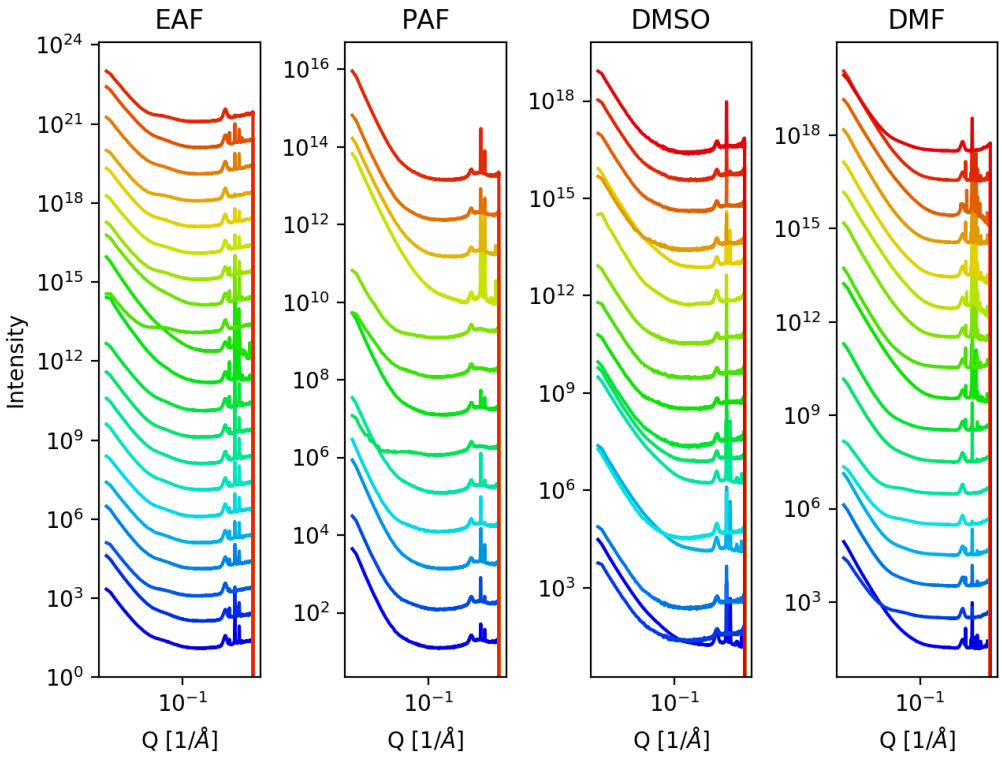

Figure 49. SAXS scattering patterns from AZO3-*n*C4 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-*n*C2 concentration increases from top to bottom.

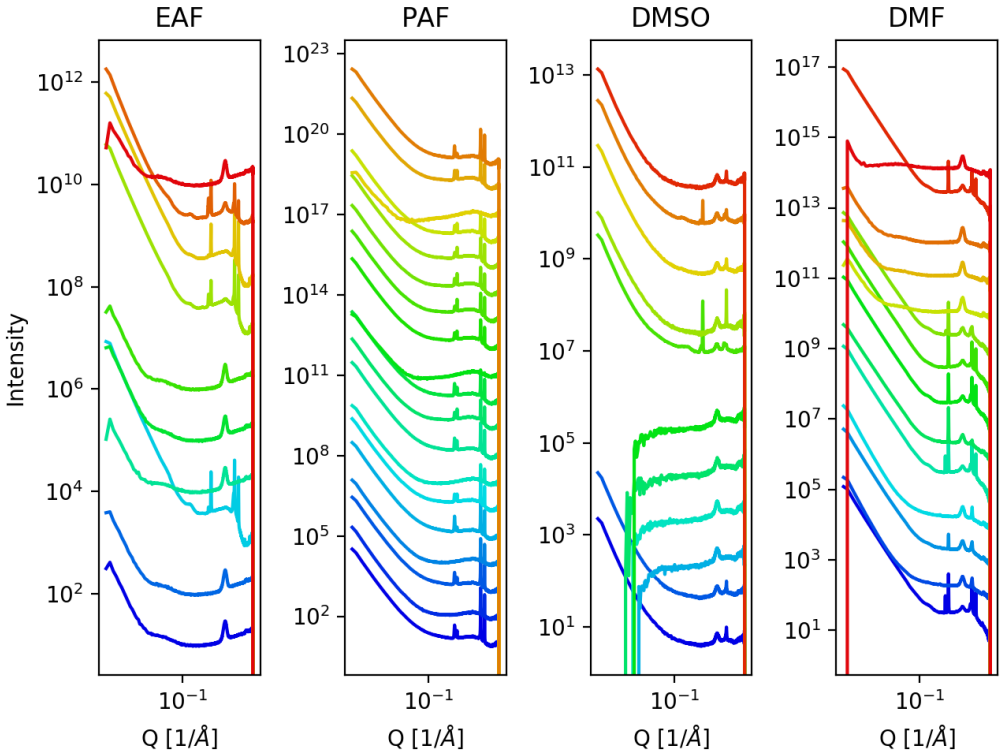

Figure 50. SAXS scattering patterns from AZO3-*n*C8 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-*n*C8 concentration increases from top to bottom.

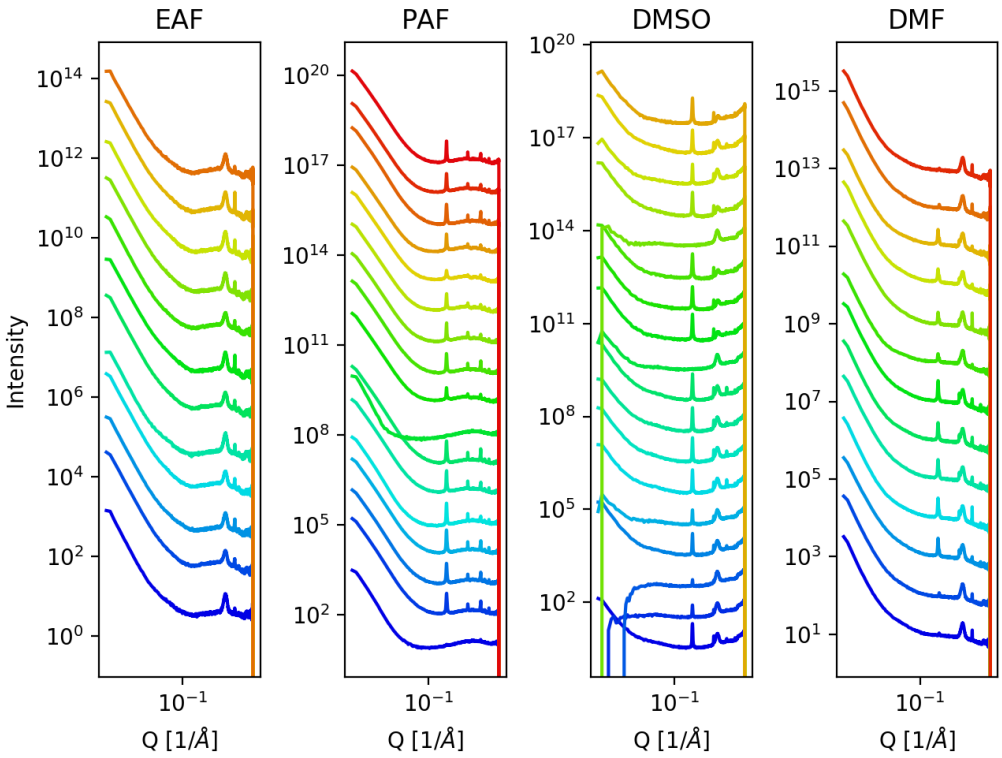

Figure 51. SAXS scattering patterns from AZO3-*n*C12 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-*n*C12 concentration increases from top to bottom.

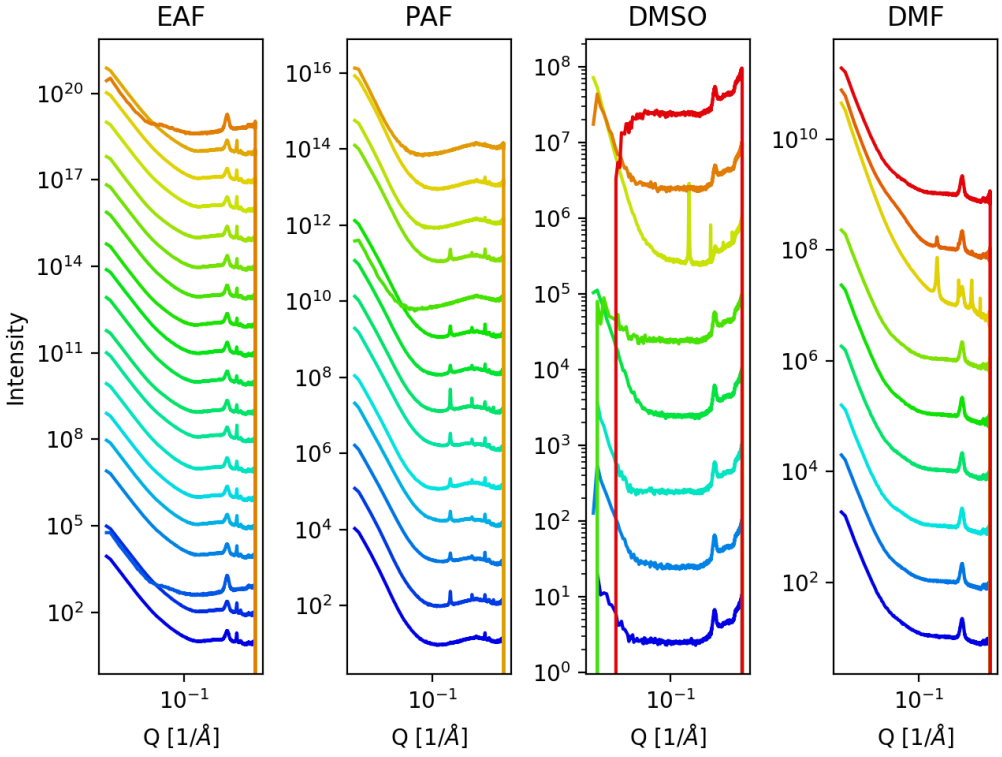

Figure 52. SAXS scattering patterns from AZO3-*n*C12 in EAF, PAF, DMSO and DMF solvents after 20 minutes of UV exposure. The curves are ordered such that AZO3-*n*C12 concentration increases from top to bottom.

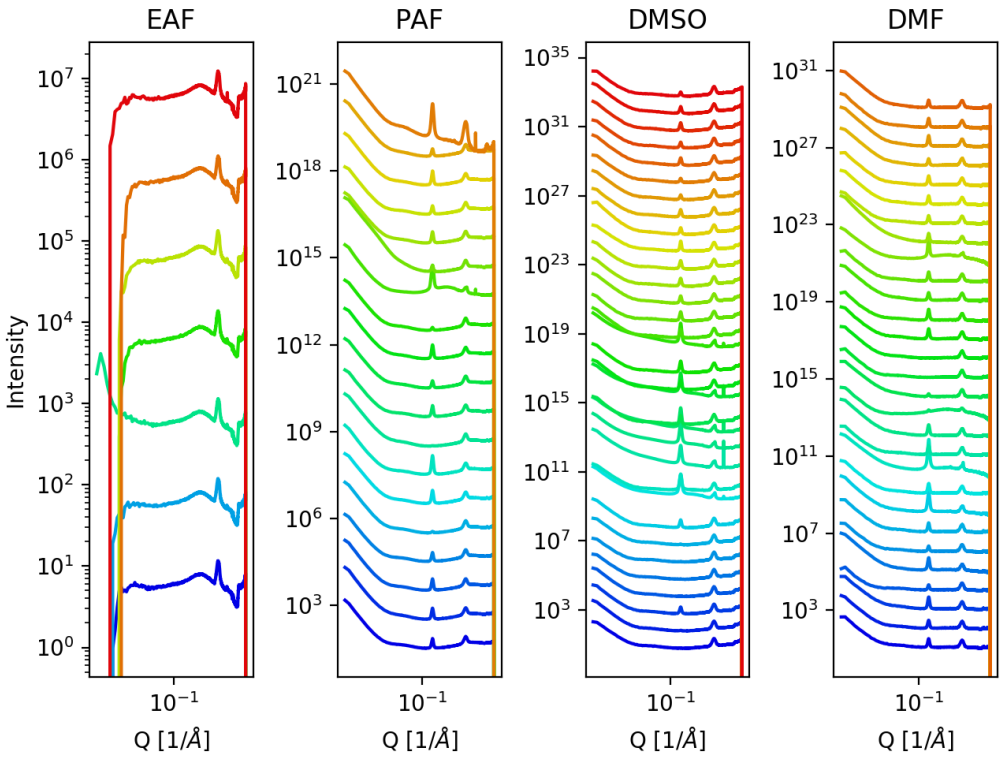

Figure 53. SAXS scattering patterns from AZO3-C18:1 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-C18:1 concentration increases from top to bottom.

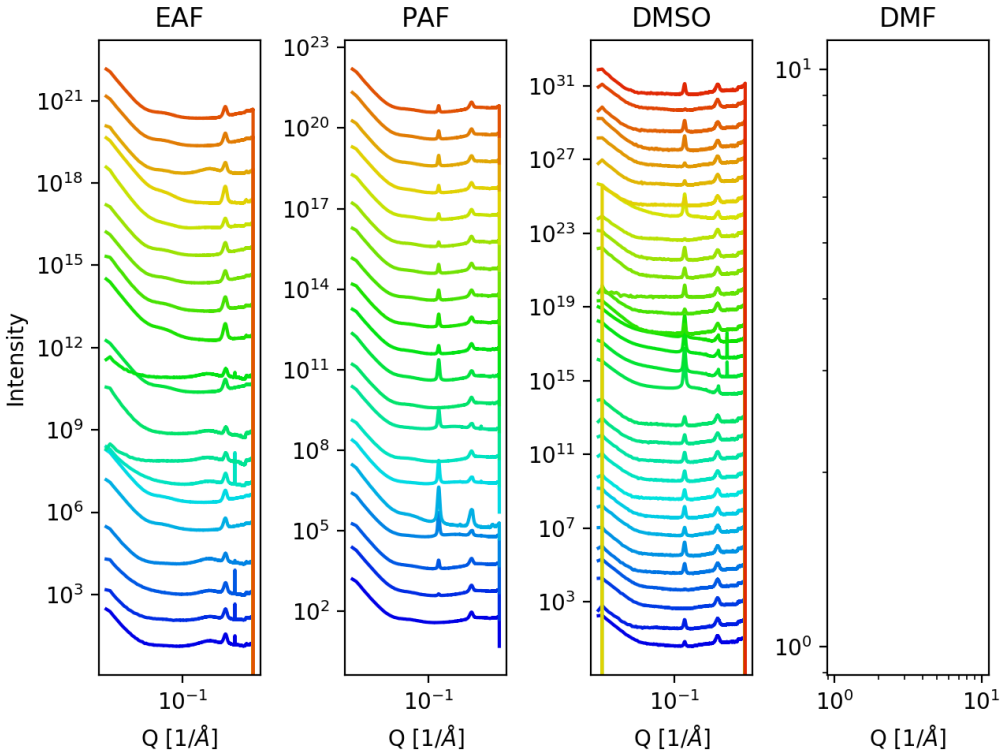

Figure 54. SAXS scattering patterns from AZO3-C18:1 in EAF, PAF, DMSO and DMF solvents after 20 minutes of UV exposure. The curves are ordered such that AZO3-C18:1 concentration increases from top to bottom.

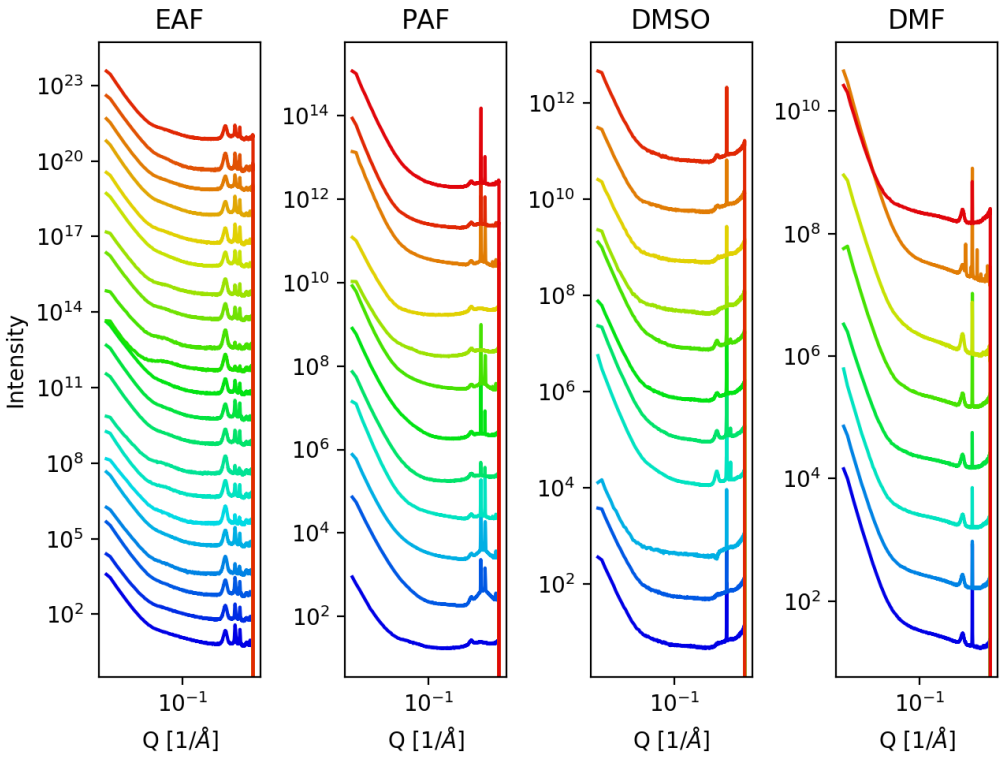

Figure 55. SAXS scattering patterns from AZO3-*i*C3 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-*i*C3 concentration increases from top to bottom.

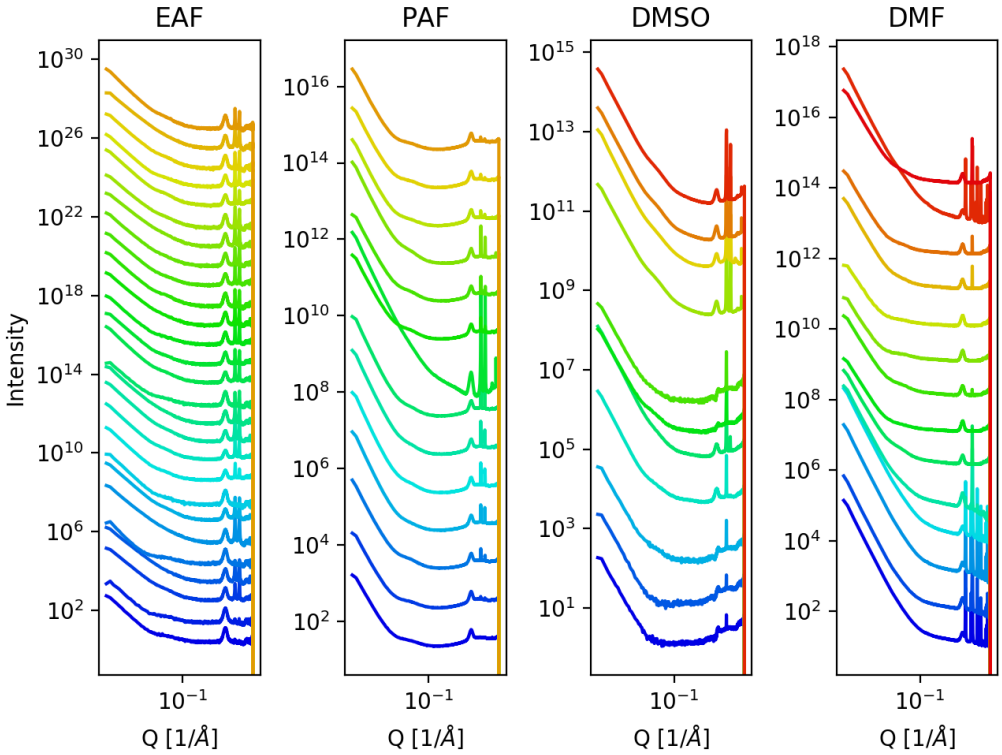

Figure 56. SAXS scattering patterns from AZO3-*i*C4 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-*i*C4 concentration increases from top to bottom.

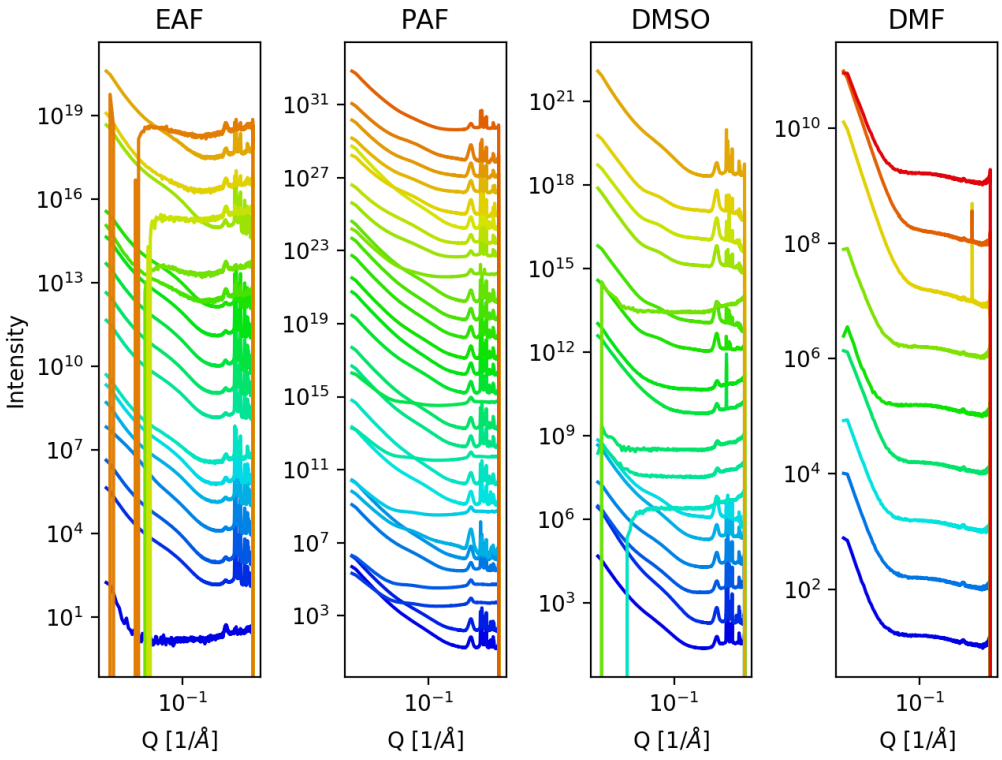

Figure 57. SAXS scattering patterns from AZO3-*t*C4 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-*t*C4 concentration increases from top to bottom.

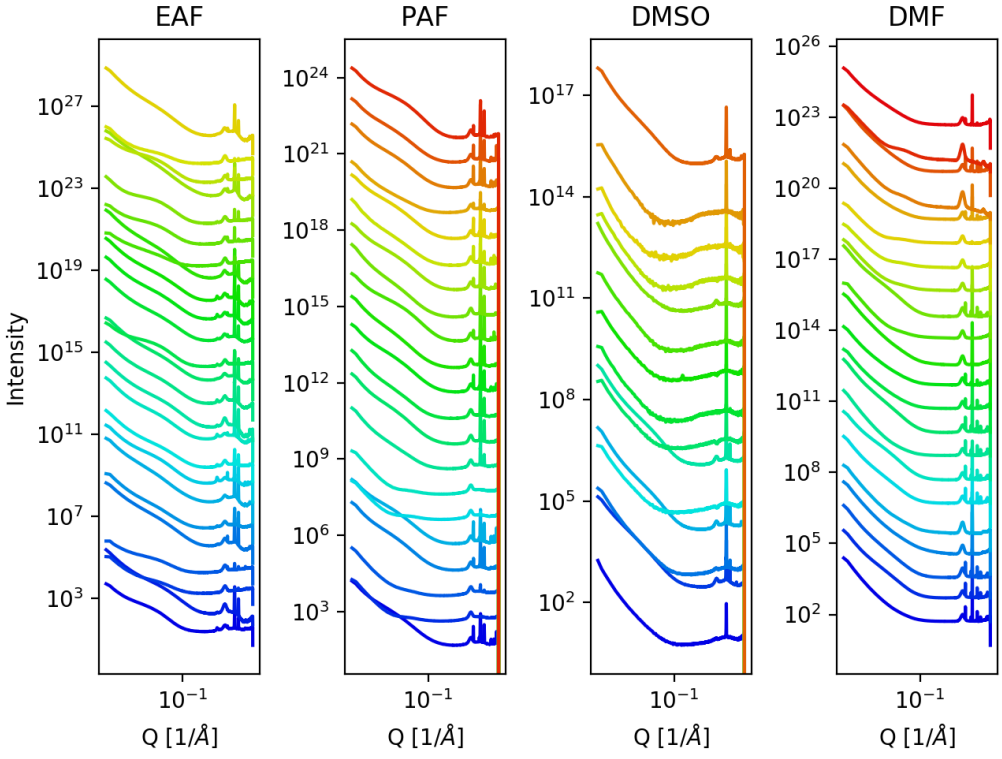

Figure 58. SAXS scattering patterns from AZO3-*t*C8 in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-*t*C8 concentration increases from top to bottom.

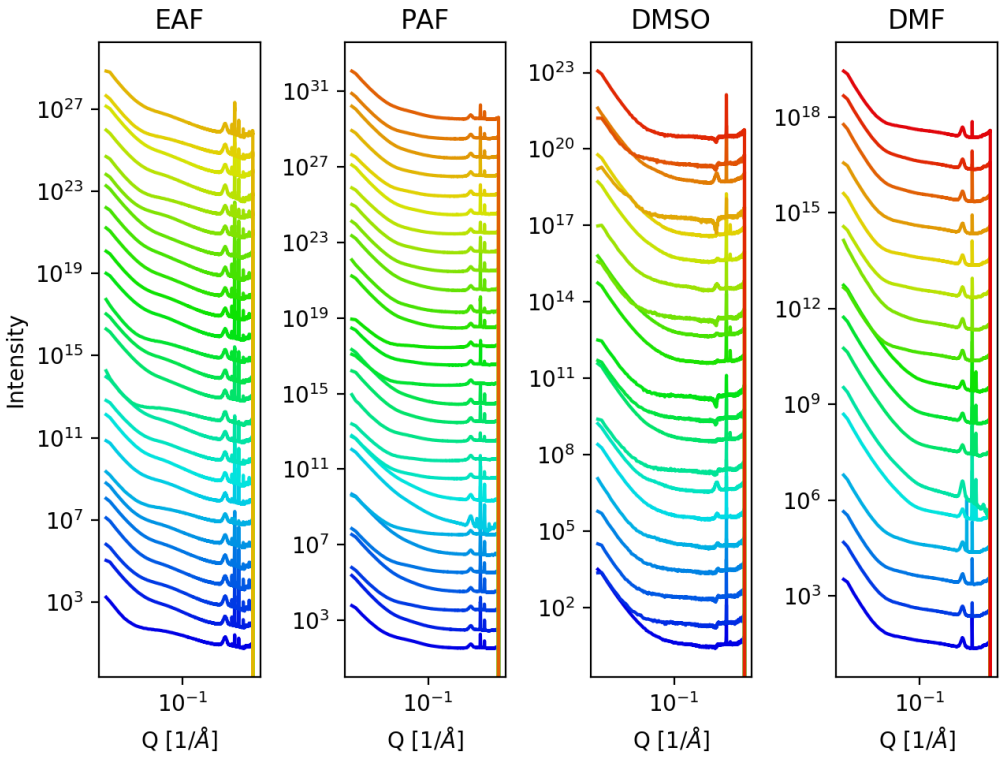

Figure 59. SAXS scattering patterns from AZO3-EtOH in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-EtOH concentration increases from top to bottom.

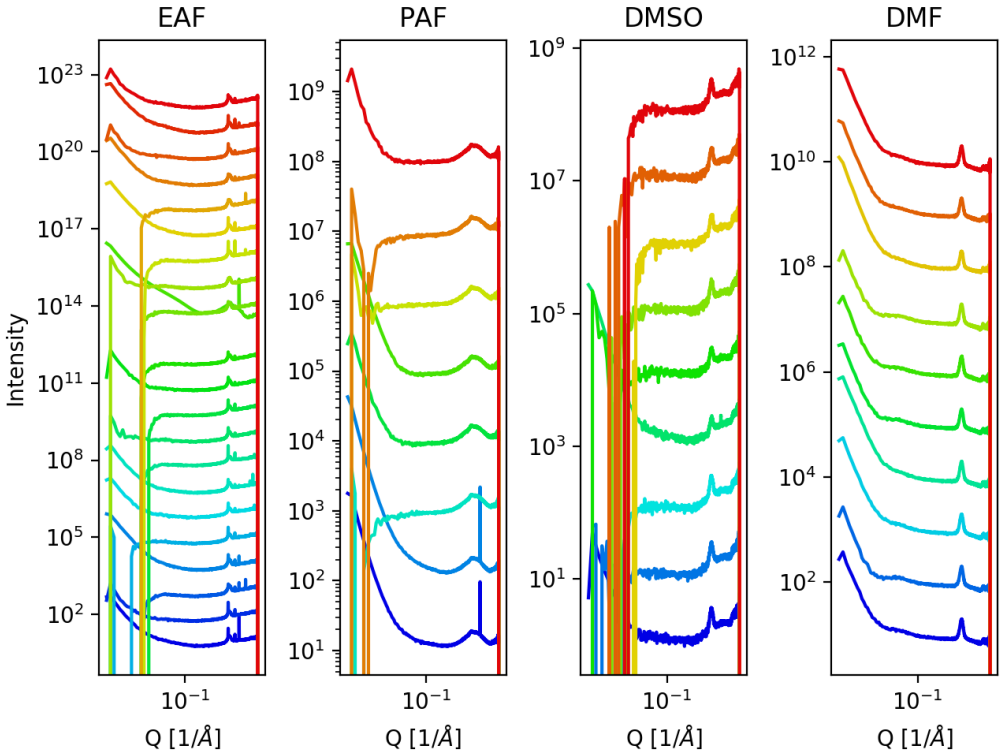

Figure 60. SAXS scattering patterns from AZO3-EH in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-EH concentration increases from top to bottom.

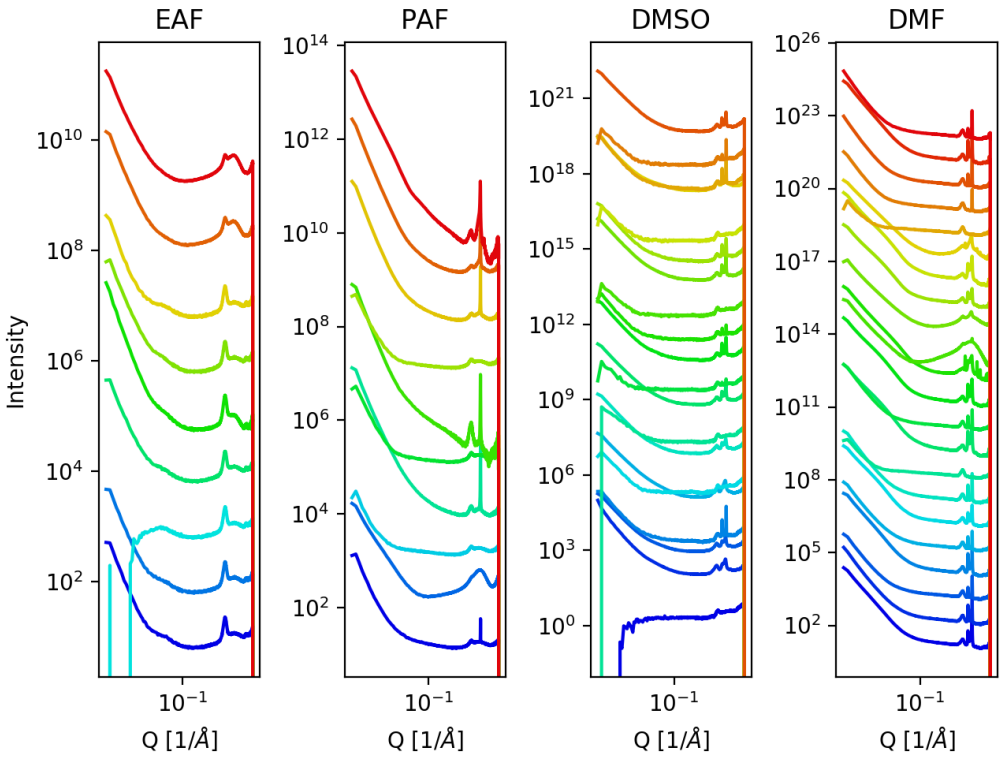

Figure 61. SAXS scattering patterns from AZO3-CE in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-CE concentration increases from top to bottom.

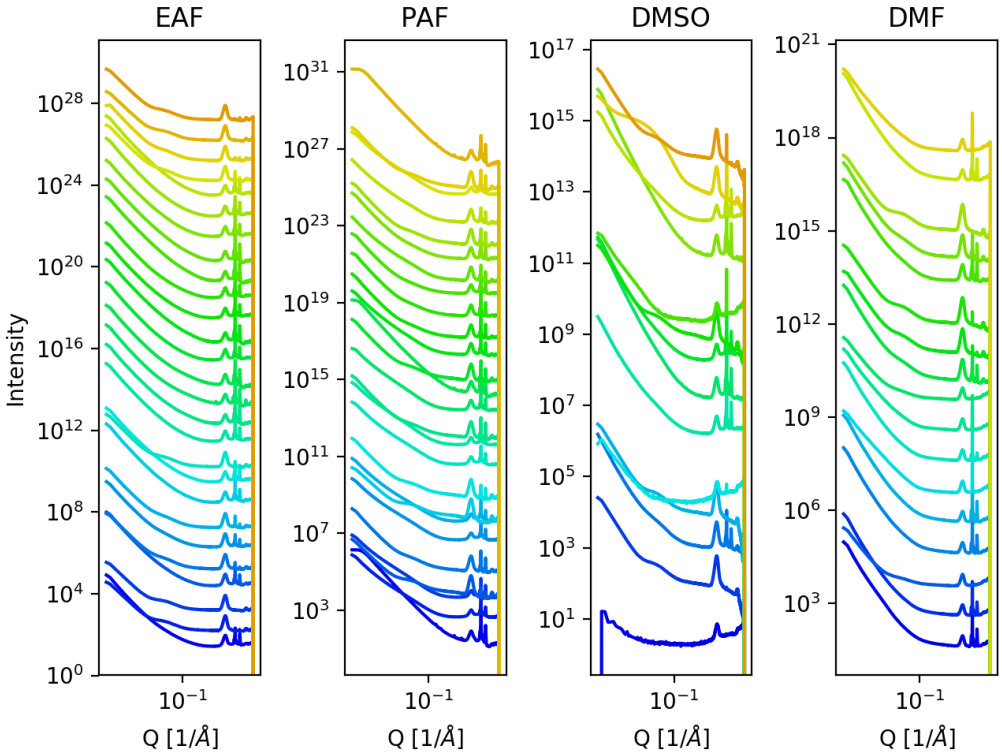

Figure 62. SAXS scattering patterns from AZO3-THP in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-THP concentration increases from top to bottom.

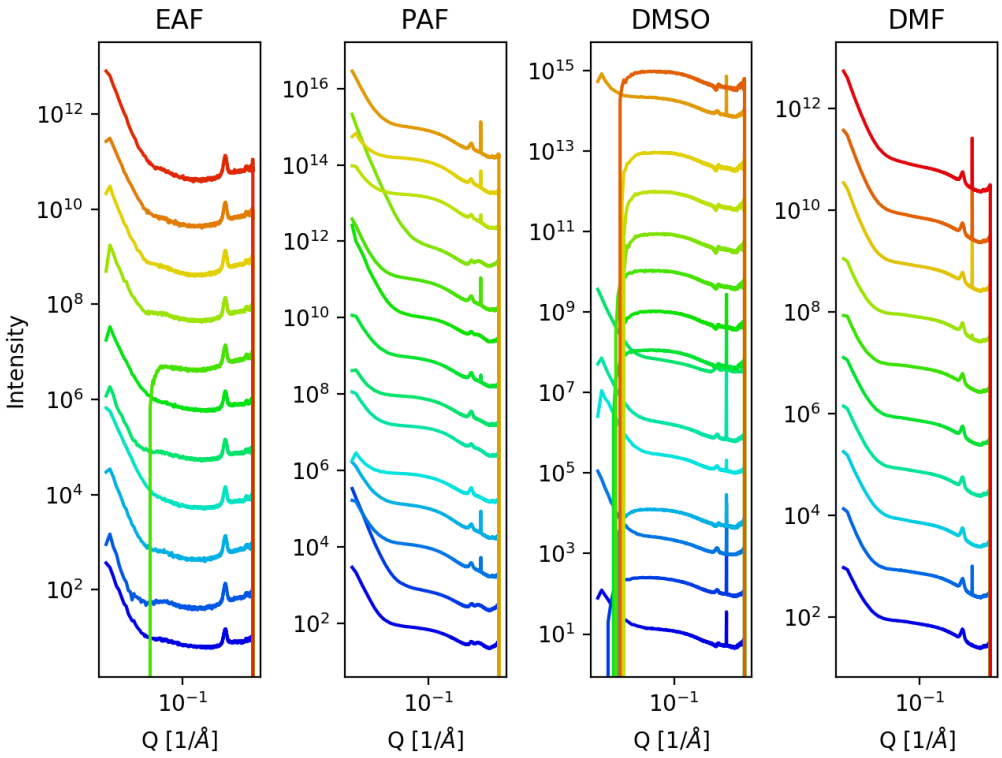

Figure 63. SAXS scattering patterns from AZO3-BTFMB in EAF, PAF, DMSO and DMF solvents. The curves are ordered such that AZO3-BTFMB concentration increases from top to bottom.

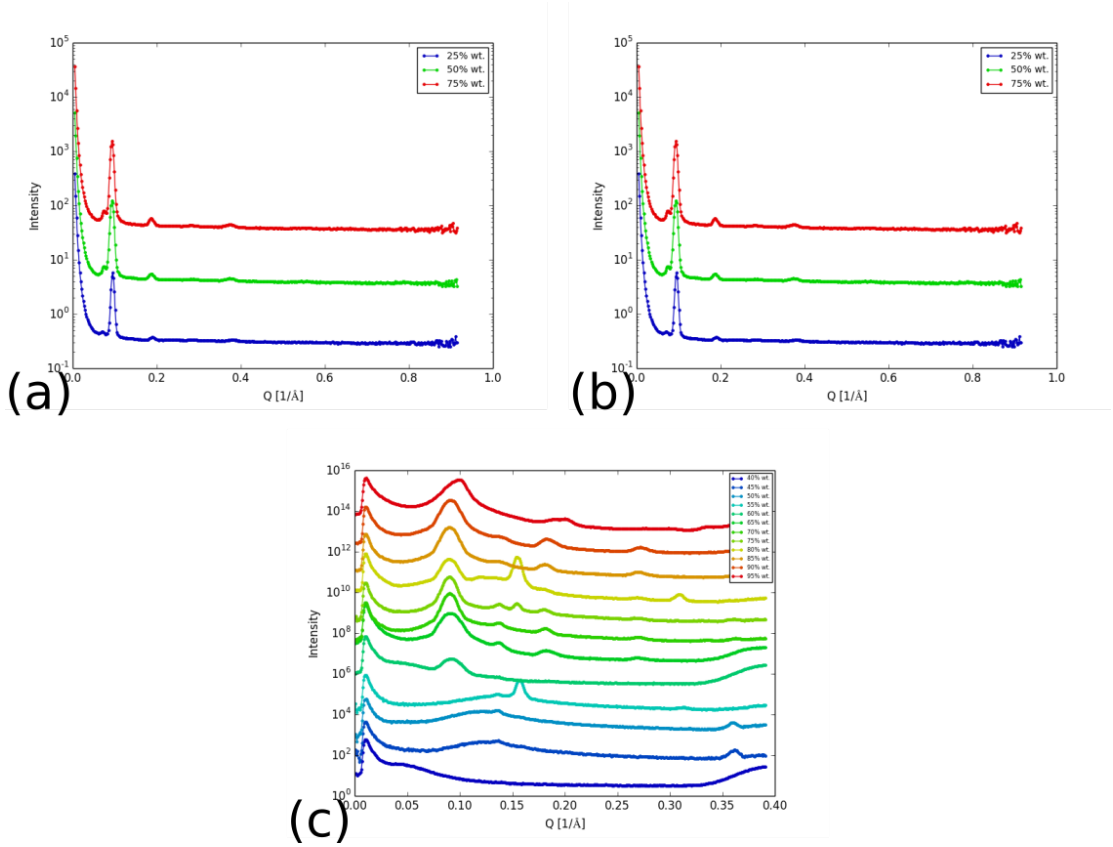

Figure 64. SANS scattering patterns from AZO1-C18:1 in (a) EAF, (b) PAF and (c) DMSO solvents. The curves are ordered such that the AZO1-C18:1 concentration increased from the bottom to the top.

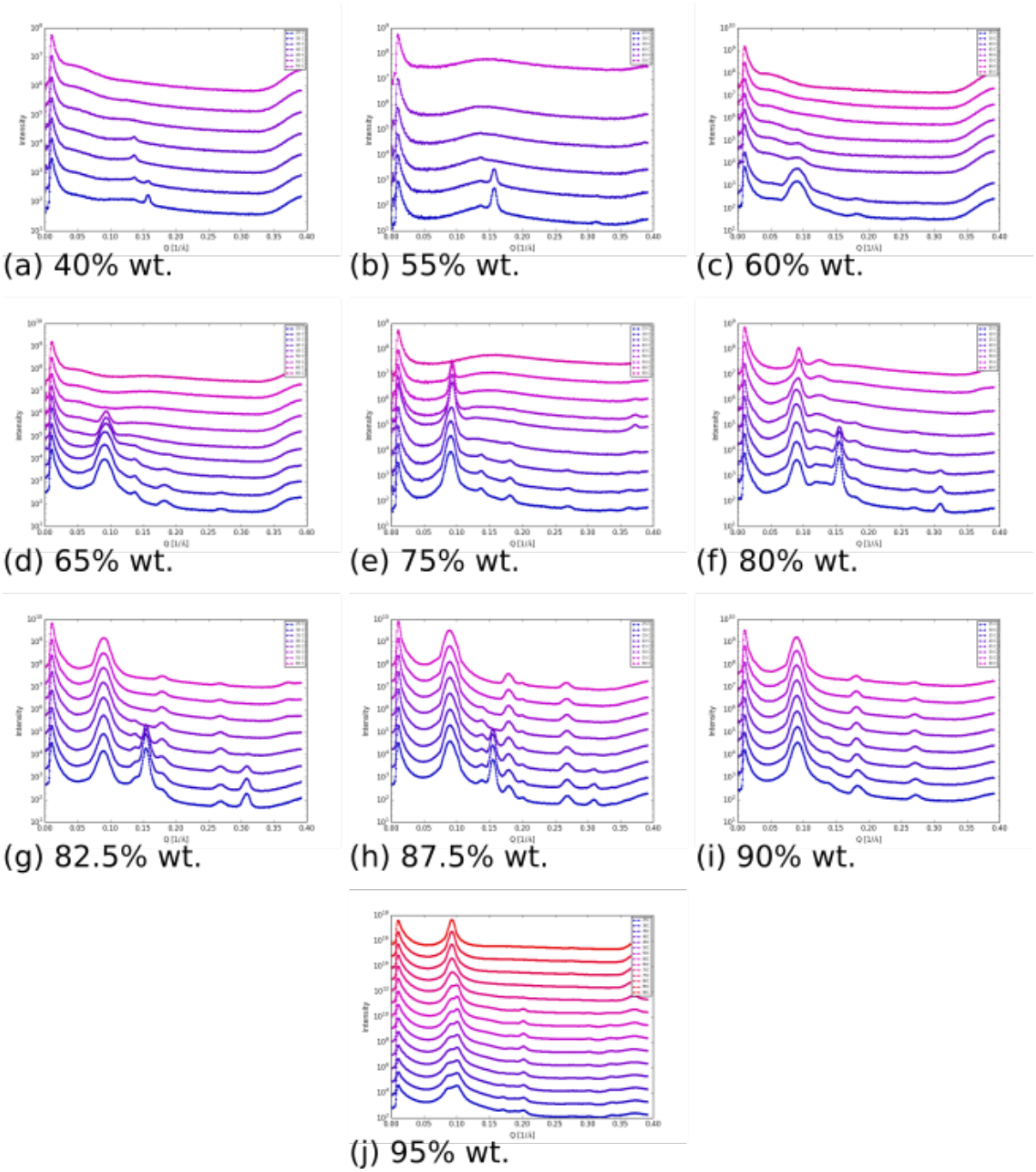

Figure 65. Benchtop SAXS scattering patterns for AZO1-C18:1 in DMSO concentration and temperature. a) 40% wt. AZO1-C18:1. b) 55% wt. AZO1-C18:1. c) 60% wt. AZO1-C18:1. d) 65% wt. AZO1-C18:1. e) 75% wt. AZO1-C18:1. f) 80% wt. AZO1-C18:1. g) 82.5% wt. AZO1-C18:1. h) 87.5% wt. AZO1-C18:1. i) 90% wt. AZO1-C18:1. j) 95% wt. AZO1-C18:1.

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1. A. Sokolova, J. Christoforidis, A. Eltobaji, J. Barnes, F. Darmann, A. E. Whitten and L. de Campo, *Neutron News*, 2016, **27**, 9-13.
2. A. S. Tremsin, A. V. Sokolova, F. Salvemini, V. Luzin, A. Paradowska, O. Muransky, H. J. Kirkwood, B. Abbey, C. M. Wensrich and E. H. Kisi, *Rev. Sci. Instrum.*, 2019, **90**, 035114.