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Supplementary Information

Alkyl Substituent-Dependent Systematic Change in Cold Crystallization of Azo Molecules

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Identification of 2,4-DM-4-C*n* and 2,4-DM-2-C*n*

2,4-DM-4-C2: Yield: 0.051 g (5.6%); elemental analysis for $C_{20}H_{20}N_2O$, Calc: C, 78.92; H, 6.62; N, 9.20%, Found: C, 78.74; H, 6.67; N, 9.25%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 8.99 (d, J = 8.4 Hz, $1H_{arom}$), 8.35 (d, J = 8.3 Hz, $1H_{arom}$), 7.86 (d, J = 8.4 Hz, $1H_{arom}$), 7.72 (d, J = 8.2 Hz, $1H_{arom}$), 7.66 (t, J = 7.6 Hz, $1H_{arom}$), 7.56 (t, J = 7.6 Hz, $1H_{arom}$), 7.16 (s, $1H_{arom}$), 7.11 (d, J = 8.1 Hz, $1H_{arom}$), 6.89 (d, J = 8.5 Hz, $1H_{arom}$), 4.30 (q, J = 7.0 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.59 (t, J = 7.0 Hz, 3H, C–CH_3); IR (KBr): ν 1580 cm^{-1} (C=C), 2881–2948 (C–H), 3019–3076 (C–H_{arom}).

2,4-DM-4-C3: Yield: 0.0051 g (0.53%); elemental analysis for $C_{21}H_{22}N_2O$, Calc: C, 79.21; H, 6.96; N, 8.80%, Found: C, 78.84; H, 6.62; N, 8.77%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 8.99 (d, J = 8.4 Hz, $1H_{arom}$), 8.35 (d, J = 8.3 Hz, $1H_{arom}$), 7.86 (d, J = 8.4 Hz, $1H_{arom}$), 7.72 (d, J = 7.9 Hz, $1H_{arom}$), 7.66 (t, J = 7.7 Hz, $1H_{arom}$), 7.56 (t, J = 7.6 Hz, $1H_{arom}$), 7.16 (s, $1H_{arom}$), 7.11 (d, J = 8.0 Hz, $1H_{arom}$), 6.90 (d, J = 8.5 Hz, $1H_{arom}$), 4.19 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.75 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 2.00 (sext, J = 7.0 Hz, 2H, C–CH_2–C), 1.17 (t, J = 7.4 Hz, 3H, C–CH_3); IR (KBr): ν 1578 cm^{-1} (C=C), 2872–2952 (C–H), 3018–3074 (C–H_{arom}).

2,4-DM-4-C5: Yield: 0.072 g (6.9%); elemental analysis for $C_{23}H_{26}N_2O$, Calc: C, 79.73; H, 7.56; N, 8.09%, Found: C, 79.62; H, 7.69; N, 8.04%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.4 Hz, $1H_{arom}$), 8.34 (d, J = 8.4 Hz, $1H_{arom}$), 7.86 (d, J = 8.4 Hz, $1H_{arom}$), 7.72 (d, J = 8.2 Hz, $1H_{arom}$), 7.66 (t, J = 7.6 Hz, $1H_{arom}$), 7.56 (t, J = 7.6 Hz, $1H_{arom}$), 7.16 (s, $1H_{arom}$), 7.11 (d, J = 8.2 Hz, $1H_{arom}$), 6.90 (d, J = 8.5 Hz, $1H_{arom}$), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.97 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.45 (sext, J = 7.2 Hz, 4H, C–CH_2–C), 0.98 (t, J = 7.2 Hz, 3H, C–CH_3); IR (KBr): ν 1581 cm^{-1} (C=C), 2864–2955 (C–H), 3014–3069 (C–H_{arom}).

2,4-DM-4-C6: Yield: 0.0056 g (0.52%); elemental analysis for $C_{24}H_{28}N_2O$, Calc: C, 79.96; H, 7.83; N, 7.77%, Found: C, 79.57; H, 7.84; N, 7.70%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.3 Hz, $1H_{arom}$), 8.34 (d, J = 8.0 Hz, $1H_{arom}$), 7.86 (d, J = 8.4 Hz, $1H_{arom}$), 7.72 (d, J = 8.1 Hz, $1H_{arom}$), 7.66 (t, J = 7.0 Hz, $1H_{arom}$), 7.56 (t, J = 7.0 Hz, $1H_{arom}$), 7.16 (s, $1H_{arom}$), 7.10 (d, J = 8.3 Hz, $1H_{arom}$), 6.90 (d, J = 8.5 Hz, $1H_{arom}$), 4.22 (t, J = 6.3 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.97 (quin, J = 6.9 Hz, 2H, O–C–CH_2–C), 1.43–1.29 (m, 6H, C–CH_2–C), 0.94 (t, J = 7.0 Hz, 3H, C–CH_3); IR (KBr): ν 1579 cm^{-1} (C=C), 2856–2937 (C–H), 3012–3064 (C–H_{arom}).

2,4-DM-4-C7: Yield: 0.084 g (7.5%); elemental analysis for $C_{25}H_{30}N_2O$, Calc: C, 80.17; H, 8.07; N, 7.48%, Found: C, 80.36; H, 8.24; N, 7.78%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.4 Hz, $1H_{arom}$), 8.34 (d, J = 8.2 Hz, $1H_{arom}$), 7.86 (d, J = 8.4 Hz, $1H_{arom}$), 7.72 (d, J = 8.2 Hz, $1H_{arom}$), 7.66 (t, J = 7.6 Hz, $1H_{arom}$), 7.56 (t, J = 7.6 Hz, $1H_{arom}$), 7.16 (s, $1H_{arom}$), 7.10 (d, J = 8.3 Hz, $1H_{arom}$), 6.89 (d, J = 8.5 Hz, $1H_{arom}$), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.97 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.45–1.26 (m, 8H, C–CH_2–C), 0.91 (t, J = 7.0 Hz, 3H, C–CH_3); IR (KBr): ν 1580 cm^{-1} (C=C), 2858–2961 (C–H), 3023–3076 (C–H_{arom}).

2,4-DM-4-C8: Yield: 0.030 g (2.5%); elemental analysis for $C_{26}H_{32}N_2O$, Calc: C, 80.37; H, 8.30; N, 7.21%, Found: C, 80.28; H, 8.50; N, 7.11%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.4 Hz,

$1H_{arom}$), 8.34 (d, J = 8.4 Hz, $1H_{arom}$), 7.86 (d, J = 8.4 Hz, $1H_{arom}$), 7.72 (d, J = 8.2 Hz, $1H_{arom}$), 7.66 (t, J = 7.6 Hz, $1H_{arom}$), 7.56 (t, J = 7.3 Hz, $1H_{arom}$), 7.16 (s, $1H_{arom}$), 7.10 (d, J = 8.1 Hz, $1H_{arom}$), 6.89 (d, J = 8.5 Hz, $1H_{arom}$), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.97 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.48–1.26 (m, 10H, C–CH_2–C), 0.90 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): ν 1577 cm^{-1} (C=C), 2856–2966 (C–H), 3031–3068 (C–H_{arom}).

2,4-DM-4-C9: Yield: 0.064 g (5.3%); elemental analysis for $C_{27}H_{34}N_2O$, Calc: C, 80.55; H, 8.51; N, 6.96%, Found: C, 80.45; H, 8.77; N, 6.96%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.4 Hz, $1H_{arom}$), 8.34 (d, J = 8.4 Hz, $1H_{arom}$), 7.86 (d, J = 8.4 Hz, $1H_{arom}$), 7.72 (d, J = 8.2 Hz, $1H_{arom}$), 7.66 (t, J = 7.6 Hz, $1H_{arom}$), 7.56 (t, J = 7.6 Hz, $1H_{arom}$), 7.16 (s, $1H_{arom}$), 7.10 (d, J = 8.3 Hz, $1H_{arom}$), 6.89 (d, J = 8.5 Hz, $1H_{arom}$), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.96 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.54–1.23 (m, 12H, C–CH_2–C), 0.89 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): ν 1579 cm^{-1} (C=C), 2846–2962 (C–H), 3019–3076 (C–H_{arom}).

2,4-DM-4-C10: Yield: 0.052 g (4.2%); elemental analysis for $C_{28}H_{36}N_2O$, Calc: C, 80.73; H, 8.71; N, 6.72%, Found: C, 80.55; H, 8.96; N, 6.89%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.3 Hz, $1H_{arom}$), 8.34 (d, J = 8.5 Hz, $1H_{arom}$), 7.86 (d, J = 8.4 Hz, $1H_{arom}$), 7.72 (d, J = 8.2 Hz, $1H_{arom}$), 7.66 (t, J = 7.3 Hz, $1H_{arom}$), 7.56 (t, J = 7.4 Hz, $1H_{arom}$), 7.16 (s, $1H_{arom}$), 7.10 (d, J = 8.3 Hz, $1H_{arom}$), 6.89 (d, J = 8.5 Hz, $1H_{arom}$), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.96 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.44–1.26 (m, 14H, C–CH_2–C), 0.89 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): ν 1579 cm^{-1} (C=C), 2848–2963 (C–H), 3021–3073 (C–H_{arom}).

2,4-DM-4-C11: Yield: 0.087 g (6.7%); elemental analysis for $C_{29}H_{38}N_2O$, Calc: C, 80.88; H, 8.89; N, 6.51%, Found: C, 80.92; H, 9.06; N, 6.55%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.4 Hz, $1H_{arom}$), 8.34 (d, J = 8.5 Hz, $1H_{arom}$), 7.86 (d, J = 8.4 Hz, $1H_{arom}$), 7.72 (d, J = 8.2 Hz, $1H_{arom}$), 7.66 (t, J = 7.3 Hz, $1H_{arom}$), 7.56 (t, J = 7.8 Hz, $1H_{arom}$), 7.16 (s, $1H_{arom}$), 7.10 (d, J = 8.0 Hz, $1H_{arom}$), 6.89 (d, J = 8.5 Hz, $1H_{arom}$), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.96 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.44–1.26 (m, 16H, C–CH_2–C), 0.88 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): ν 1578 cm^{-1} (C=C), 2851–2952 (C–H), 3021–3073 (C–H_{arom}).

2,4-DM-4-C12: Yield: 0.04 g (3.0%); elemental analysis for $C_{30}H_{38}N_2O$, Calc: C, 81.03; H, 9.07; N, 6.30%, Found: C, 81.33; H, 9.01; N, 6.19%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.4 Hz, $1H_{arom}$), 8.34 (d, J = 8.3 Hz, $1H_{arom}$), 7.86 (d, J = 8.4 Hz, $1H_{arom}$), 7.72 (d, J = 8.2 Hz, $1H_{arom}$), 7.66 (t, J = 7.4 Hz, $1H_{arom}$), 7.56 (t, J = 7.1 Hz, $1H_{arom}$), 7.16 (s, $1H_{arom}$), 7.10 (d, J = 8.3 Hz, $1H_{arom}$), 6.89 (d, J = 8.5 Hz, $1H_{arom}$), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.96 (quin, J = 7.1 Hz, 2H, O–C–CH_2–C), 1.44–1.22 (m, 18H, C–CH_2–C), 0.88 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): ν 1579 cm^{-1} (C=C), 2847–2954 (C–H), 3013–3069 (C–H_{arom}).

2,4-DM-4-C13: Yield: 0.099 g (7.2%); elemental analysis for $C_{31}H_{40}N_2O$, Calc: C, 81.17; H, 9.23; N, 6.11%, Found: C, 81.28; H, 9.14; N, 6.02%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.4 Hz, $1H_{arom}$), 8.34 (d, J = 8.4 Hz, $1H_{arom}$), 7.86 (d, J = 8.4 Hz, $1H_{arom}$), 7.72 (d, J = 8.2 Hz, $1H_{arom}$), 7.65 (t, J = 7.4 Hz, $1H_{arom}$), 7.56 (t, J = 7.2 Hz, $1H_{arom}$), 7.16 (s, $1H_{arom}$), 7.10 (d, J = 8.2 Hz, $1H_{arom}$), 6.89 (d, J = 8.5 Hz, $1H_{arom}$), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3),

1.96 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.44–1.21 (m, 20H, C–CH_2–C), 0.88 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): ν 1577 cm^{-1} (C=C), 2845–2950 (C–H), 3015–3072 (C–H_{arom}).

2,4-DM-4-C14: Yield: 0.019 g (1.4%); elemental analysis for $C_{32}H_{42}N_2O$, Calc: C, 81.31; H, 9.38; N, 5.93%, Found: C, 81.55; H, 9.22; N, 5.79%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.6 Hz, 1H_{arom}), 8.34 (d, J = 8.6 Hz, 1H_{arom}), 7.86 (d, J = 8.4 Hz, 1H_{arom}), 7.72 (d, J = 8.2 Hz, 1H_{arom}), 7.65 (t, J = 7.3 Hz, 1H_{arom}), 7.56 (t, J = 7.6 Hz, 1H_{arom}), 7.16 (s, 1H_{arom}), 7.10 (d, J = 8.1 Hz, 1H_{arom}), 6.89 (d, J = 8.5 Hz, 1H_{arom}), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.96 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.49–1.26 (m, 22H, C–CH_2–C), 0.88 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): ν 1578 cm^{-1} (C=C), 2848–2952 (C–H), 3016–3073 (C–H_{arom}).

2,4-DM-4-C15: Yield: 0.23 g (15%); elemental analysis for $C_{33}H_{44}N_2O$, Calc: C, 81.43; H, 9.53; N, 5.76%, Found: C, 81.35; H, 9.38; N, 5.69%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.3 Hz, 1H_{arom}), 8.34 (d, J = 8.4 Hz, 1H_{arom}), 7.86 (d, J = 8.4 Hz, 1H_{arom}), 7.72 (d, J = 8.2 Hz, 1H_{arom}), 7.65 (t, J = 7.6 Hz, 1H_{arom}), 7.56 (t, J = 7.1 Hz, 1H_{arom}), 7.16 (s, 1H_{arom}), 7.10 (d, J = 8.2 Hz, 1H_{arom}), 6.89 (d, J = 8.5 Hz, 1H_{arom}), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.96 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.49–1.26 (m, 24H, C–CH_2–C), 0.88 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): ν 1577 cm^{-1} (C=C), 2848–2951 (C–H), 3019–3070 (C–H_{arom}).

2,4-DM-4-C16: Yield: 0.093 g (6.2%); elemental analysis for $C_{34}H_{46}N_2O$, Calc: C, 81.55; H, 9.66; N, 5.59%, Found: C, 81.49; H, 9.71; N, 5.46%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.4 Hz, 1H_{arom}), 8.34 (d, J = 8.2 Hz, 1H_{arom}), 7.86 (d, J = 8.4 Hz, 1H_{arom}), 7.72 (d, J = 8.2 Hz, 1H_{arom}), 7.65 (t, J = 7.6 Hz, 1H_{arom}), 7.56 (t, J = 7.6 Hz, 1H_{arom}), 7.16 (s, 1H_{arom}), 7.10 (d, J = 8.1 Hz, 1H_{arom}), 6.89 (d, J = 8.5 Hz, 1H_{arom}), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.96 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.43–1.26 (m, 24H, C–CH_2–C), 0.88 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): ν 1577 cm^{-1} (C=C), 2847–2953 (C–H), 3016–3073 (C–H_{arom}).

2,4-DM-4-C17: Yield: 0.10 g (6.7%); elemental analysis for $C_{35}H_{48}N_2O$, Calc: C, 81.66; H, 9.79; N, 5.44%, Found: C, 81.43; H, 9.73; N, 5.41%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.4 Hz, 1H_{arom}), 8.34 (d, J = 8.3 Hz, 1H_{arom}), 7.86 (d, J = 8.4 Hz, 1H_{arom}), 7.72 (d, J = 8.2 Hz, 1H_{arom}), 7.65 (t, J = 7.4 Hz, 1H_{arom}), 7.56 (t, J = 7.6 Hz, 1H_{arom}), 7.16 (s, 1H_{arom}), 7.10 (d, J = 7.6 Hz, 1H_{arom}), 6.89 (d, J = 8.5 Hz, 1H_{arom}), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.96 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.50–1.26 (m, 28H, C–CH_2–C), 0.88 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): ν 1576 cm^{-1} (C=C), 2849–2951 (C–H), 3014–3072 (C–H_{arom}).

2,4-DM-4-C18 Yield: 0.078 g (4.9%); elemental analysis for $C_{36}H_{50}N_2O$, Calc: C, 81.77; H, 9.91; N, 5.30%, Found: C, 81.91; H, 9.80; N, 5.11%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.3 Hz, 1H_{arom}), 8.34 (d, J = 8.3 Hz, 1H_{arom}), 7.86 (d, J = 8.4 Hz, 1H_{arom}), 7.72 (d, J = 8.2 Hz, 1H_{arom}), 7.65 (t, J = 7.3 Hz, 1H_{arom}), 7.56 (t, J = 7.4 Hz, 1H_{arom}), 7.16 (s, 1H_{arom}), 7.10 (d, J = 8.2 Hz, 1H_{arom}), 6.89 (d, J = 8.5 Hz, 1H_{arom}), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.96 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.50–1.26 (m, 30H, C–CH_2–C), 0.88 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): ν 1580 cm^{-1} (C=C), 2851–2949 (C–H), 3016–3074 (C–H_{arom}).

2,4-DM-4-C20: Yield: 0.14 g (8.2%); elemental analysis for $C_{37}H_{52}N_2O$, Calc: C, 81.96; H, 10.14; N,

5.03%, Found: C, 81.73; H, 10.25; N, 4.78%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 9.00 (d, J = 8.4 Hz, 1H$_{arom}$), 8.34 (d, J = 8.4 Hz, 1H$_{arom}$), 7.86 (d, J = 8.4 Hz, 1H$_{arom}$), 7.72 (d, J = 8.2 Hz, 1H$_{arom}$), 7.65 (t, J = 7.6 Hz, 1H$_{arom}$), 7.56 (t, J = 7.0 Hz, 1H$_{arom}$), 7.16 (s, 1H$_{arom}$), 7.10 (d, J = 7.8 Hz, 1H$_{arom}$), 6.89 (d, J = 8.5 Hz, 1H$_{arom}$), 4.22 (t, J = 6.4 Hz, 2H, O–CH_2–C), 2.74 (s, 3H, C_{arom}–CH_3), 2.40 (s, 3H, C_{arom}–CH_3), 1.96 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.49–1.26 (m, 34H, C–CH_2–C), 0.88 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): ν 1578 cm^{-1} (C=C), 2850–2952 (C–H), 3017–3073 (C–H$_{arom}$).

2,4-DM-2-C2: Yield: 0.0081 g (0.89%); elemental analysis for $C_{20}H_{20}N_2O$, Calc: C, 78.92; H, 6.62; N, 9.20%, Found: C, 78.87; H, 6.64; N, 9.24%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 8.41 (d, J = 8.5 Hz, 1H$_{arom}$), 7.82 (d, J = 9.0 Hz, 1H$_{arom}$), 7.81 (d, J = 7.9 Hz, 1H$_{arom}$), 7.68 (d, J = 8.1 Hz, 1H$_{arom}$), 7.50 (t, J = 7.9 Hz, 1H$_{arom}$), 7.41 (t, J = 6.9 Hz, 1H$_{arom}$), 7.38 (d, J = 9.0 Hz, 1H$_{arom}$), 7.19 (s, 1H$_{arom}$), 7.12 (d, J = 8.7 Hz, 1H$_{arom}$), 4.24 (q, J = 7.0 Hz, 2H, O–CH_2–C), 2.72 (s, 3H, C_{arom}–CH_3), 2.41 (s, 3H, C_{arom}–CH_3), 1.43 (t, J = 7.0 Hz, 3H, C–CH_3) ; IR (KBr): ν 1596 cm^{-1} (C=C), 2858–2933 (C–H), 3014–3049 (C–H$_{arom}$).

2,4-DM-2-C3: Yield: 0.21 g (21%); elemental analysis for $C_{21}H_{22}N_2O$, Calc: C, 79.21; H, 6.96; N, 8.80%, Found: C,79.30 ; H,6.96 ; N,8.89 %. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 8.40 (d, J = 8.5 Hz, 1H$_{arom}$), 7.82 (d, J = 9.0 Hz, 1H$_{arom}$), 7.81 (d, J = 7.9 Hz, 1H$_{arom}$), 7.68 (d, J = 8.2 Hz, 1H$_{arom}$), 7.50 (t, J = 7.7 Hz, 1H$_{arom}$), 7.40 (t, J = 7.5 Hz, 1H$_{arom}$), 7.38 (d, J = 9.1 Hz, 1H$_{arom}$), 7.19 (s, 1H$_{arom}$), 7.12 (d, J = 8.7 Hz, 1H$_{arom}$), 4.13 (t, J = 6.5 Hz, 2H, O–CH_2–C), 2.72 (s, 3H, C_{arom}–CH_3), 2.41 (s, 3H, C_{arom}–CH_3), 1.82 (sext, J = 7.1 Hz, 2H, C–CH_2–C), 1.00 (t, J = 7.4 Hz, 3H, C–CH_3); IR (KBr): ν 1594 cm^{-1} (C=C), 2857–2940 (C–H), 3018–3058 (C–H$_{arom}$).

2,4-DM-2-C6: Yield: 0.11 g (10%); elemental analysis for $C_{24}H_{28}N_2O$, Calc: C, 79.96; H, 7.83; N, 7.77%, Found: C, 79.76; H, 7.59; N, 7.85%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 8.40 (d, J = 8.6 Hz, 1H$_{arom}$), 7.82 (d, J = 9.0 Hz, 1H$_{arom}$), 7.81 (d, J = 8.5 Hz, 1H$_{arom}$), 7.68 (d, J = 8.2 Hz, 1H$_{arom}$), 7.51 (t, J = 8.1 Hz, 1H$_{arom}$), 7.40 (t, J = 7.4 Hz, 1H$_{arom}$), 7.38 (d, J = 9.1 Hz, 1H$_{arom}$), 7.19 (s, 1H$_{arom}$), 7.11 (d, J = 8.3 Hz, 1H$_{arom}$), 4.16 (t, J = 6.5 Hz, 2H, O–CH_2–C), 2.72 (s, 3H, C_{arom}–CH_3), 2.41 (s, 3H, C_{arom}–CH_3), 1.79 (quin, J = 7.1 Hz, 2H, O–C–CH_2–C), 1.47–1.27 (m, 6H, C–CH_2–C), 0.85 (t, J = 6.9 Hz, 3H, C–CH_3); IR (KBr): ν 1592 cm^{-1} (C=C), 2856–2947 (C–H), 3024–3055 (C–H$_{arom}$).

2,4-DM-2-C7: Yield: 0.48 g (43%); elemental analysis for $C_{25}H_{30}N_2O$, Calc: C, 80.17; H, 8.07; N, 7.48%, Found: C, 80.17; H, 8.26; N, 7.49%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 8.40 (d, J = 8.6 Hz, 1H$_{arom}$), 7.82 (d, J = 9.0 Hz, 1H$_{arom}$), 7.81 (d, J = 8.1 Hz, 1H$_{arom}$), 7.68 (d, J = 8.2 Hz, 1H$_{arom}$), 7.49 (t, J = 8.1 Hz, 1H$_{arom}$), 7.40 (t, J = 7.3 Hz, 1H$_{arom}$), 7.38 (d, J = 9.1 Hz, 1H$_{arom}$), 7.19 (s, 1H$_{arom}$), 7.12 (d, J = 8.1 Hz, 1H$_{arom}$), 4.15 (t, J = 6.5 Hz, 2H, O–CH_2–C), 2.72 (s, 3H, C_{arom}–CH_3), 2.41 (s, 3H, C_{arom}–CH_3), 1.78 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.46–1.21 (m, 8H, C–CH_2–C), 0.85 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): ν 1592 cm^{-1} (C=C), 2857–2945 (C–H), 3020–3053 (C–H$_{arom}$).

2,4-DM-2-C8: Yield: 0.082 g (7.1%); elemental analysis for $C_{26}H_{32}N_2O$, Calc: C, 80.37; H, 8.30; N, 7.21%, Found: C, 80.40; H, 8.60; N, 7.21%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 8.40 (d, J = 8.6 Hz, 1H$_{arom}$), 7.82 (d, J = 9.0 Hz, 1H$_{arom}$), 7.80 (d, J = 8.0 Hz, 1H$_{arom}$), 7.68 (d, J = 8.2 Hz, 1H$_{arom}$), 7.50 (t, J

= 7.7 Hz, $1H_{arom}$), 7.40 (t, *J* = 7.0 Hz, $1H_{arom}$), 7.38 (d, *J* = 9.1 Hz, $1H_{arom}$), 7.19 (s, $1H_{arom}$), 7.12 (d, *J* = 8.4 Hz, $1H_{arom}$), 4.15 (t, *J* = 6.5 Hz, 2H, O–CH_2–C), 2.72 (s, 3H, C_{arom}–CH_3), 2.41 (s, 3H, C_{arom}–CH_3), 1.78 (quin, *J* = 7.1 Hz, 2H, O–C–CH_2–C), 1.46–1.22 (m, 10H, C–CH_2–C), 0.86 (t, *J* = 6.9 Hz, 3H, C–CH_3); IR (KBr): *ν* 1594 cm^{-1} (C=C), 2856–2946 (C–H), 3015–3040 (C–H_{arom}).

2,4-DM-2-C9: Yield: 0.16 g (13%); elemental analysis for $C_{27}H_{34}N_2O$, Calc: C, 80.55; H, 8.51; N, 6.96%, Found: C, 80.40; H, 8.76; N, 6.83%. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si): *δ* 8.40 (d, *J* = 8.7 Hz, $1H_{arom}$), 7.82 (d, *J* = 9.0 Hz, $1H_{arom}$), 7.80 (d, *J* = 8.0 Hz, $1H_{arom}$), 7.68 (d, *J* = 8.2 Hz, $1H_{arom}$), 7.50 (t, *J* = 7.7 Hz, $1H_{arom}$), 7.40 (t, *J* = 7.4 Hz, $1H_{arom}$), 7.38 (d, *J* = 9.1 Hz, $1H_{arom}$), 7.19 (s, $1H_{arom}$), 7.12 (d, *J* = 8.1 Hz, $1H_{arom}$), 4.15 (t, *J* = 6.5 Hz, 2H, O–CH_2–C), 2.72 (s, 3H, C_{arom}–CH_3), 2.41 (s, 3H, C_{arom}–CH_3), 1.78 (quin, *J* = 7.0 Hz, 2H, O–C–CH_2–C), 1.46–1.22 (m, 12H, C–CH_2–C), 0.87 (t, *J* = 6.9 Hz, 3H, C–CH_3); IR (KBr): *ν* 1594 cm^{-1} (C=C), 2854–2954 (C–H), 3012–3058 (C–H_{arom}).

2,4-DM-2-C10: Yield: 0.016 g (1.3%); elemental analysis for $C_{28}H_{36}N_2O$, Calc: C, 80.73; H, 8.71; N, 6.72%, Found: C, 80.83; H, 8.90; N, 6.63%. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si): *δ* 8.40 (d, *J* = 8.6 Hz, $1H_{arom}$), 7.82 (d, *J* = 9.0 Hz, $1H_{arom}$), 7.80 (d, *J* = 7.8 Hz, $1H_{arom}$), 7.68 (d, *J* = 8.2 Hz, $1H_{arom}$), 7.50 (t, *J* = 8.0 Hz, $1H_{arom}$), 7.40 (t, *J* = 7.1 Hz, $1H_{arom}$), 7.38 (d, *J* = 9.1 Hz, $1H_{arom}$), 7.19 (s, $1H_{arom}$), 7.12 (d, *J* = 7.7 Hz, $1H_{arom}$), 4.15 (t, *J* = 6.5 Hz, 2H, O–CH_2–C), 2.72 (s, 3H, C_{arom}–CH_3), 2.41 (s, 3H, C_{arom}–CH_3), 1.78 (quin, *J* = 7.0 Hz, 2H, O–C–CH_2–C), 1.46–1.22 (m, 14H, C–CH_2–C), 0.88 (t, *J* = 6.9 Hz, 3H, C–CH_3); IR (KBr): *ν* 1594 cm^{-1} (C=C), 2855–2945 (C–H), 3016–3037 (C–H_{arom}).

2,4-DM-2-C11: Yield: 0.46 g (35%); elemental analysis for $C_{29}H_{38}N_2O$, Calc: C, 80.88; H, 8.89; N, 6.51%, Found: C, 80.80; H, 8.53; N, 6.60%. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si): *δ* 8.40 (d, *J* = 8.5 Hz, $1H_{arom}$), 7.82 (d, *J* = 9.1 Hz, $1H_{arom}$), 7.80 (d, *J* = 7.7 Hz, $1H_{arom}$), 7.68 (d, *J* = 8.2 Hz, $1H_{arom}$), 7.50 (t, *J* = 7.7 Hz, $1H_{arom}$), 7.40 (t, *J* = 7.5 Hz, $1H_{arom}$), 7.38 (d, *J* = 9.1 Hz, $1H_{arom}$), 7.19 (s, $1H_{arom}$), 7.12 (d, *J* = 8.2 Hz, $1H_{arom}$), 4.15 (t, *J* = 6.5 Hz, 2H, O–CH_2–C), 2.72 (s, 3H, C_{arom}–CH_3), 2.41 (s, 3H, C_{arom}–CH_3), 1.78 (quin, *J* = 7.0 Hz, 2H, O–C–CH_2–C), 1.46–1.22 (m, 16H, C–CH_2–C), 0.88 (t, *J* = 6.9 Hz, 3H, C–CH_3); IR (KBr): *ν* 1594 cm^{-1} (C=C), 2847–2947 (C–H), 3021–3052 (C–H_{arom}).

2,4-DM-2-C12: Yield: 0.12 g (9.3%); elemental analysis for $C_{30}H_{38}N_2O$, Calc: C, 81.03; H, 9.07; N, 6.30%, Found: C, 81.12; H, 9.33; N, 6.25%. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si): *δ* 8.40 (d, *J* = 8.4 Hz, $1H_{arom}$), 7.82 (d, *J* = 9.0 Hz, $1H_{arom}$), 7.80 (d, *J* = 7.9 Hz, $1H_{arom}$), 7.68 (d, *J* = 8.2 Hz, $1H_{arom}$), 7.50 (t, *J* = 8.1 Hz, $1H_{arom}$), 7.40 (t, *J* = 7.3 Hz, $1H_{arom}$), 7.38 (d, *J* = 9.0 Hz, $1H_{arom}$), 7.19 (s, $1H_{arom}$), 7.12 (d, *J* = 8.3 Hz, $1H_{arom}$), 4.15 (t, *J* = 6.5 Hz, 2H, O–CH_2–C), 2.72 (s, 3H, C_{arom}–CH_3), 2.41 (s, 3H, C_{arom}–CH_3), 1.78 (quin, *J* = 7.1 Hz, 2H, O–C–CH_2–C), 1.46–1.22 (m, 18H, C–CH_2–C), 0.88 (t, *J* = 6.9 Hz, 3H, C–CH_3); IR (KBr): *ν* 1593 cm^{-1} (C=C), 2849–2948 (C–H), 3014–3042 (C–H_{arom}).

2,4-DM-2-C14: Yield: 0.076 g (5.4%); elemental analysis for $C_{32}H_{42}N_2O$, Calc: C, 81.31; H, 9.38; N, 5.93%, Found: C, 81.65; H, 9.60; N, 5.91%. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si): *δ* 8.40 (d, *J* = 8.6 Hz, $1H_{arom}$), 7.82 (d, *J* = 9.0 Hz, $1H_{arom}$), 7.80 (d, *J* = 7.6 Hz, $1H_{arom}$), 7.68 (d, *J* = 8.2 Hz, $1H_{arom}$), 7.50 (t, *J* = 8.2 Hz, $1H_{arom}$), 7.40 (t, *J* = 7.5 Hz, $1H_{arom}$), 7.38 (d, *J* = 9.1 Hz, $1H_{arom}$), 7.19 (s, $1H_{arom}$), 7.11 (d, *J* = 8.2 Hz, $1H_{arom}$), 4.15 (t, *J* = 6.5 Hz, 2H, O–CH_2–C), 2.72 (s, 3H, C_{arom}–CH_3), 2.41 (s, 3H, C_{arom}–CH_3), 1.78 (quin, *J* = 7.0 Hz, 2H, O–C–CH_2–C), 1.40–1.22 (m, 22H, C–CH_2–C), 0.88 (t, *J* = 6.8 Hz, 3H, C–

CH_3); IR (KBr): *v* 1596 cm^{-1} (C=C), 2850–2954 (C–H), 3017–3053 (C–H_{arom}).

2,4-DM-2-C16: Yield: 0.42 g (21%); elemental analysis for $C_{34}H_{46}N_2O$, Calc: C, 81.55; H, 9.66; N, 5.59%, Found: C, 81.35; H, 9.80; N, 5.33%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 8.40 (d, J = 8.9 Hz, 1H_{arom}), 7.82 (d, J = 9.0 Hz, 1H_{arom}), 7.80 (d, J = 8.2 Hz, 1H_{arom}), 7.68 (d, J = 8.2 Hz, 1H_{arom}), 7.49 (t, J = 7.0 Hz, 1H_{arom}), 7.40 (t, J = 8.1 Hz, 1H_{arom}), 7.38 (d, J = 9.0 Hz, 1H_{arom}), 7.19 (s, 1H_{arom}), 7.11 (d, J = 7.4 Hz, 1H_{arom}), 4.15 (t, J = 6.5 Hz, 2H, O–CH_2–C), 2.72 (s, 3H, C_{arom}–CH_3), 2.41 (s, 3H, C_{arom}–CH_3), 1.78 (quin, J = 7.1 Hz, 2H, O–C–CH_2–C), 1.44–1.22 (m, 26H, C–CH_2–C), 0.88 (t, J = 6.9 Hz, 3H, C–CH_3); IR (KBr): *v* 1596 cm^{-1} (C=C), 2849–2955 (C–H), 3017–3053 (C–H_{arom}).

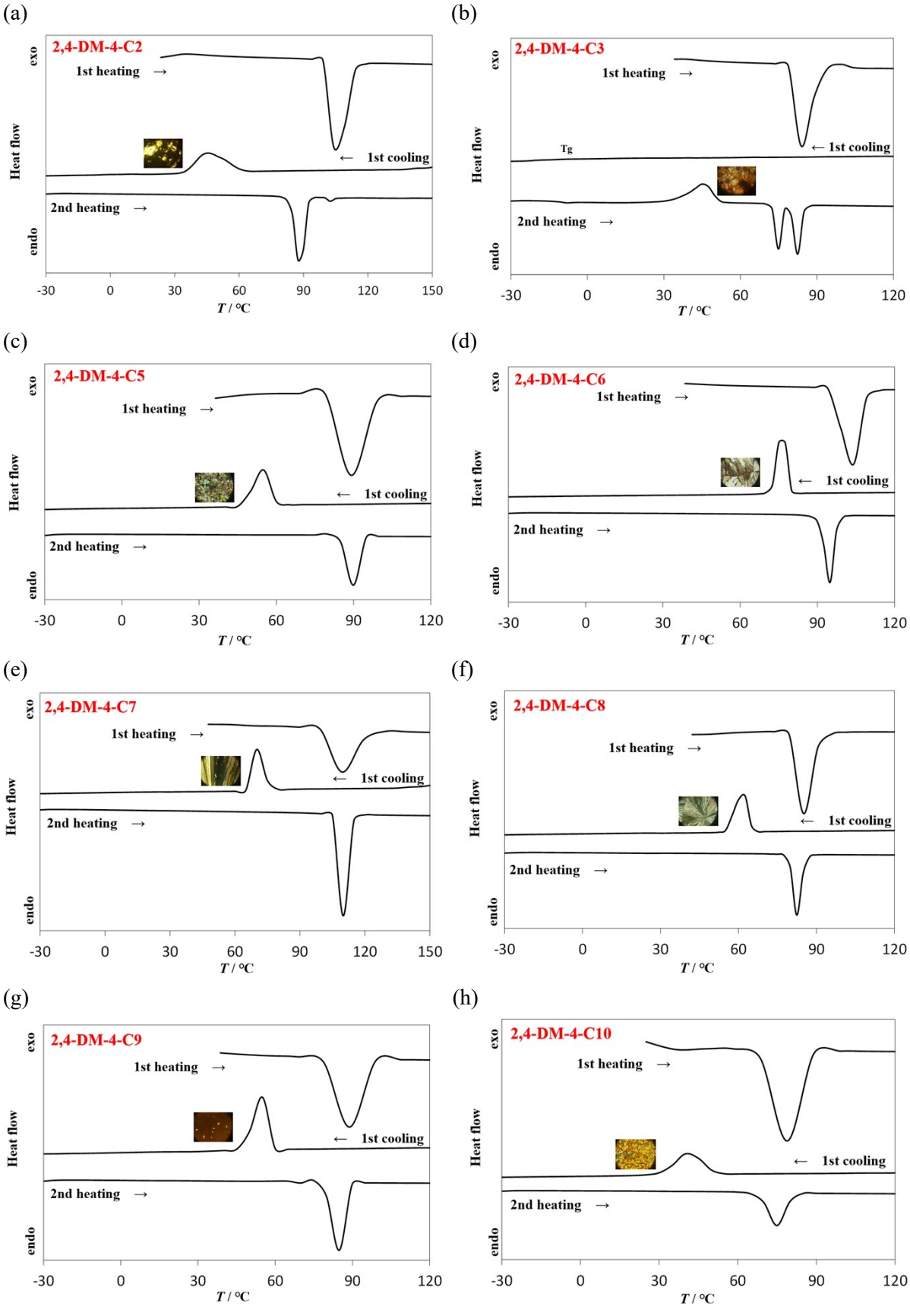
2,4-DM-2-C18: Yield: 0.20 g (12%); elemental analysis for $C_{36}H_{50}N_2O$, Calc: C, 81.77; H, 9.91; N, 5.30%, Found: C, 81.87; H, 10.21; N, 5.19%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 8.40 (d, J = 8.7 Hz, 1H_{arom}), 7.82 (d, J = 9.0 Hz, 1H_{arom}), 7.80 (d, J = 7.7 Hz, 1H_{arom}), 7.68 (d, J = 8.2 Hz, 1H_{arom}), 7.49 (t, J = 7.7 Hz, 1H_{arom}), 7.40 (t, J = 7.1 Hz, 1H_{arom}), 7.38 (d, J = 9.0 Hz, 1H_{arom}), 7.19 (s, 1H_{arom}), 7.11 (d, J = 8.5 Hz, 1H_{arom}), 4.15 (t, J = 6.5 Hz, 2H, O–CH_2–C), 2.72 (s, 3H, C_{arom}–CH_3), 2.41 (s, 3H, C_{arom}–CH_3), 1.78 (quin, J = 7.0 Hz, 2H, O–C–CH_2–C), 1.48–1.22 (m, 30H, C–CH_2–C), 0.88 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): *v* 1596 cm^{-1} (C=C), 2848–2949 (C–H), 3017–3053 (C–H_{arom}).

2,4-DM-2-C20: Yield: 0.043 g (2.6%); elemental analysis for $C_{37}H_{52}N_2O$, Calc: C, 81.96; H, 10.14; N, 5.03%, Found: C, 81.67; H, 10.36; N, 4.68%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 8.40 (d, J = 8.4 Hz, 1H_{arom}), 7.82 (d, J = 9.0 Hz, 1H_{arom}), 7.80 (d, J = 8.3 Hz, 1H_{arom}), 7.68 (d, J = 8.2 Hz, 1H_{arom}), 7.49 (t, J = 7.7 Hz, 1H_{arom}), 7.40 (t, J = 7.7 Hz, 1H_{arom}), 7.38 (d, J = 9.1 Hz, 1H_{arom}), 7.19 (s, 1H_{arom}), 7.11 (d, J = 8.6 Hz, 1H_{arom}), 4.15 (t, J = 6.5 Hz, 2H, O–CH_2–C), 2.72 (s, 3H, C_{arom}–CH_3), 2.41 (s, 3H, C_{arom}–CH_3), 1.78 (quin, J = 7.1 Hz, 2H, O–C–CH_2–C), 1.44–1.22 (m, 34H, C–CH_2–C), 0.88 (t, J = 6.8 Hz, 3H, C–CH_3); IR (KBr): *v* 1596 cm^{-1} (C=C), 2849–2950 (C–H), 3013–3053 (C–H_{arom}).

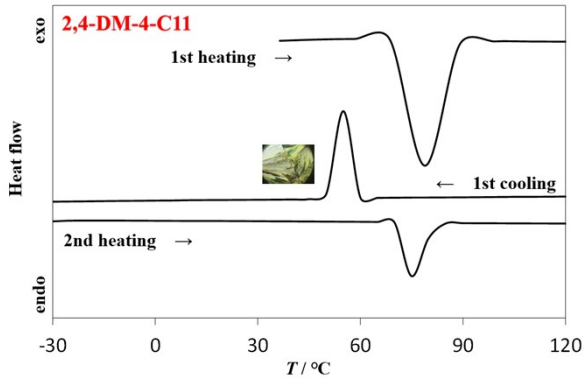
Table S1. Crystallographic data of 2,4-DM-4-C8

		2,4-DM-4-C8
Formula		$C_{26}H_{32}N_2O$
Fw		388.53
T / K		173
Crystal system		Monoclinic
Space group		$P2_1/n$
Unit cell	a / Å	8.4288(6)
	b / Å	19.7044(13)
	c / Å	14.1559(10)
	α / deg	90
	β / deg	105.4650(10)
	γ / deg	90
Volume / Å^3		2266.0(3)
Z		4
δ_{calc} / Mgm^{-3}		1.139
GOF		1.096
Final R	$R1$	0.0452
Indices [$I > 2\sigma(I)$]	$wR2$	0.1274
R indices	$R1$	0.0518
(all data)	$wR2$	0.1340

Thermal behavior of 2,4-DM-4-C*n*



(i)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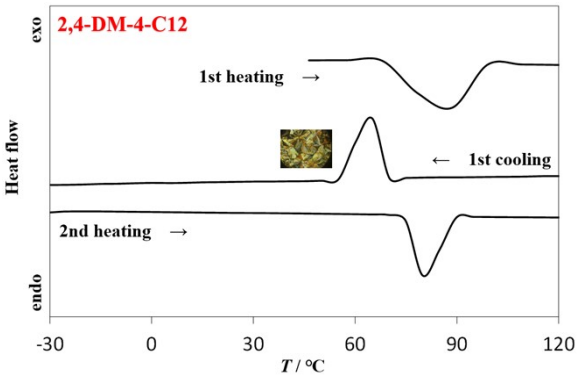
← 1st cooling
2nd heating →
endo
Heat flow
-30
0
30
60
90
120
T / °C

(j)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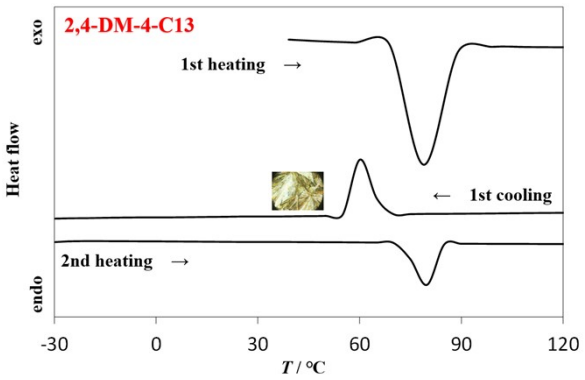
← 1st cooling
2nd heating →
endo
Heat flow
-30
0
30
60
90
120
T / °C

(k)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2nd heating →
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Heat flow
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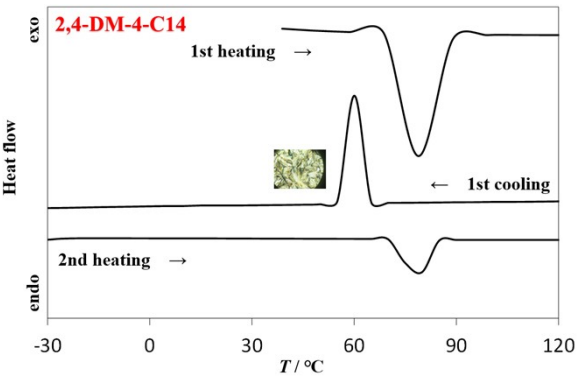
30
60
90
120
T / °C

(l)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2nd heating →
endo
Heat flow
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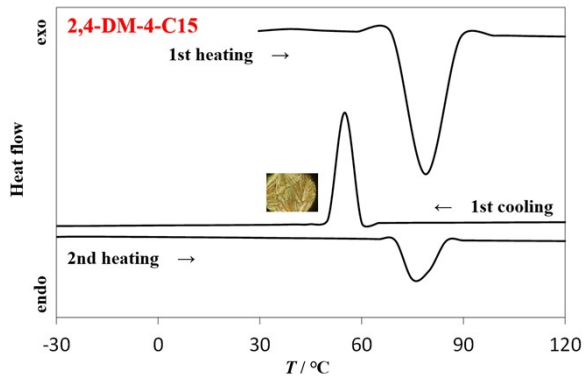
30
60
90
120
T / °C

(m)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2nd heating →
endo
Heat flow
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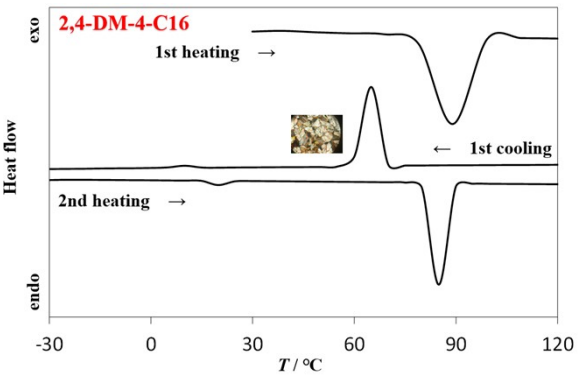
0
30
60
90
120
T / °C

(n)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endo
Heat flow
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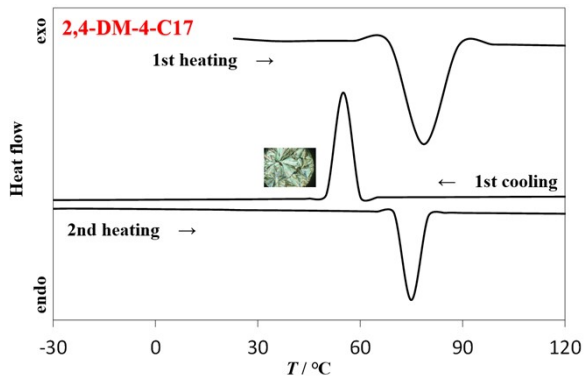
30
60
90
120
T / °C

(o)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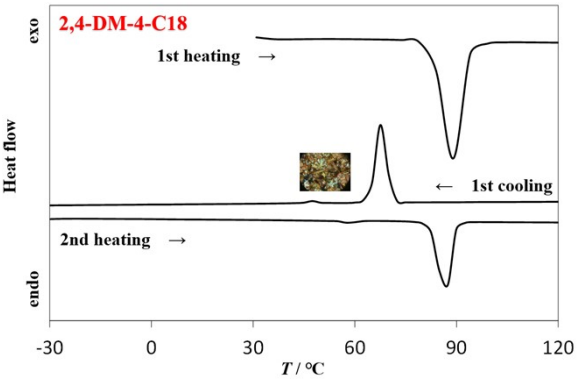
← 1st cooling
2nd heating →
endo
Heat flow
-30
0
30
60
90
120
T / °C

(p)


2,4-DM-4-C18
exo
1st heating →
← 1st cooling
2nd heating →
endo
Heat flow
-30
0
30
60
90
120
T / °C

(q)

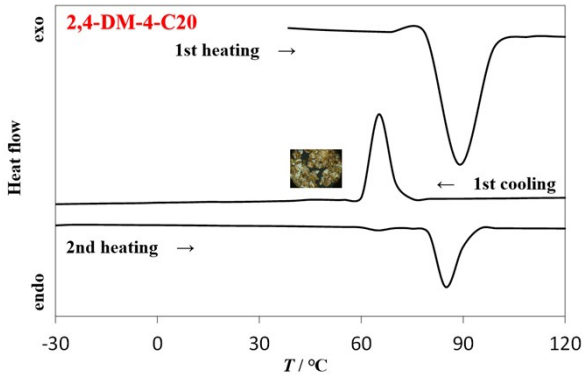
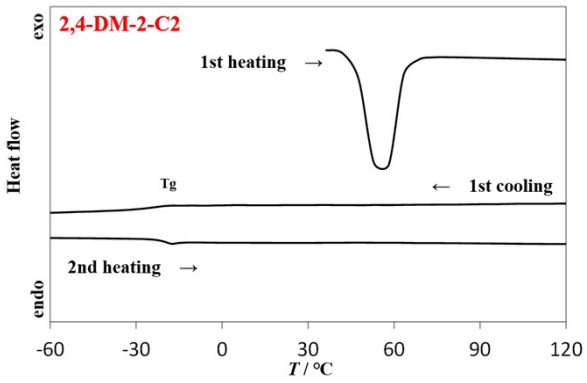


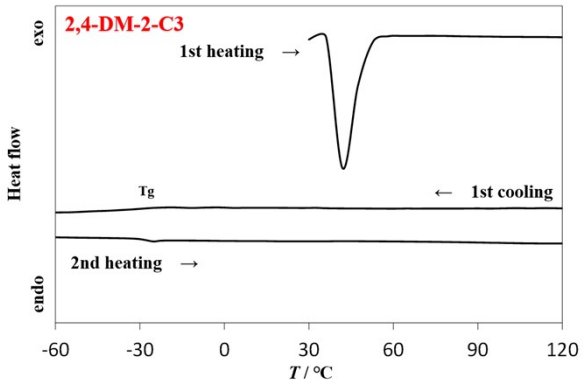
Fig. S1 DSC diagrams and POM images of (a) 2,4-DM-4-C2, (b) 2,4-DM-4-C3, (c) 2,4-DM-4-C5, (d) 2,4-DM-4-C6, (e) 2,4-DM-4-C7, (f) 2,4-DM-4-C8, (g) 2,4-DM-4-C9, (h) 2,4-DM-4-C10, (i) 2,4-DM-4-C11, (j) 2,4-DM-4-C12, (k) 2,4-DM-4-C13, (l) 2,4-DM-4-C14, (m) 2,4-DM-4-C15, (n) 2,4-DM-4-C16, (o) 2,4-DM-4-C17, (p) 2,4-DM-4-C18, and (q) 2,4-DM-4-C20.

Thermal behavior of 2,4-DM-2-C*n*

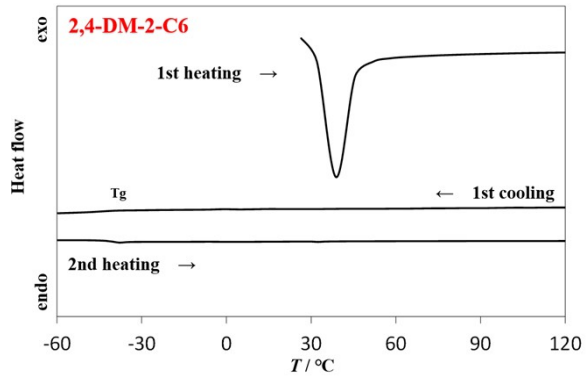
(a)



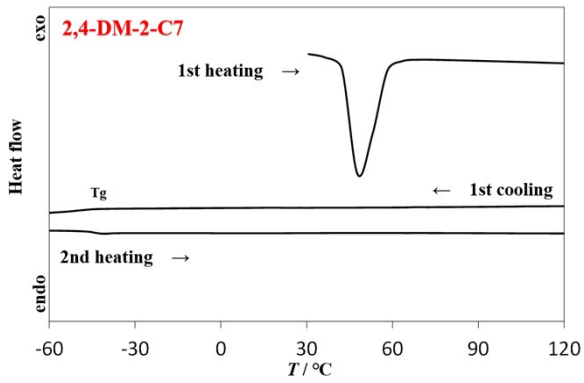
(b)



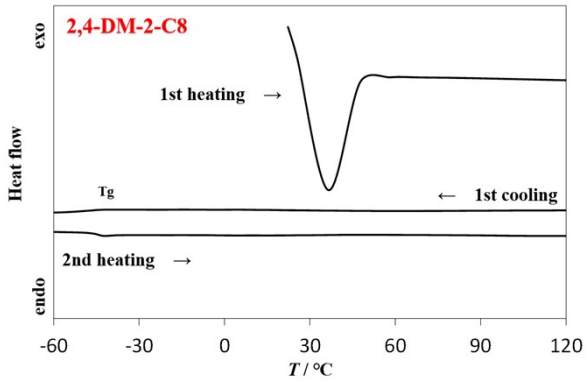
(c)



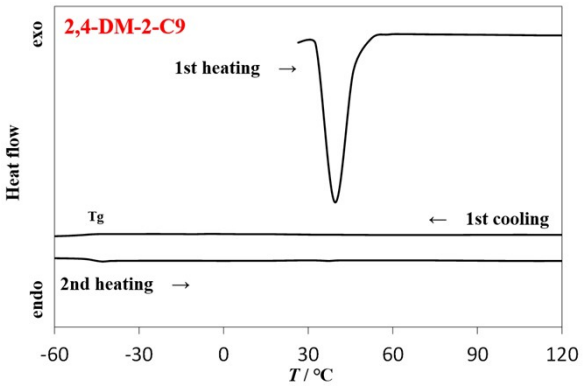
(d)



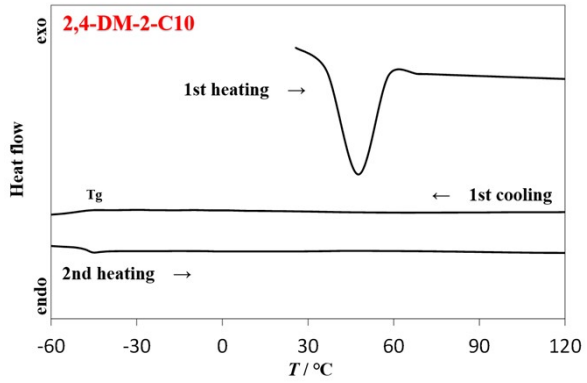
(e)



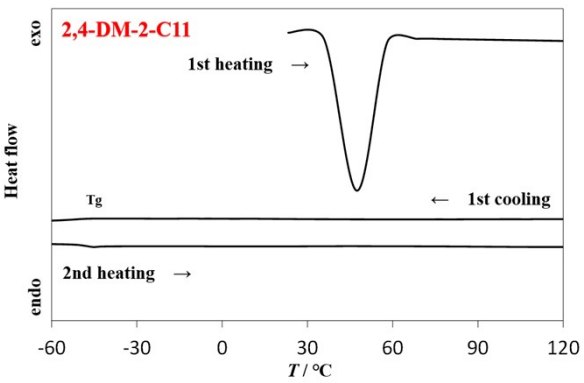
(f)



(g)



(h)



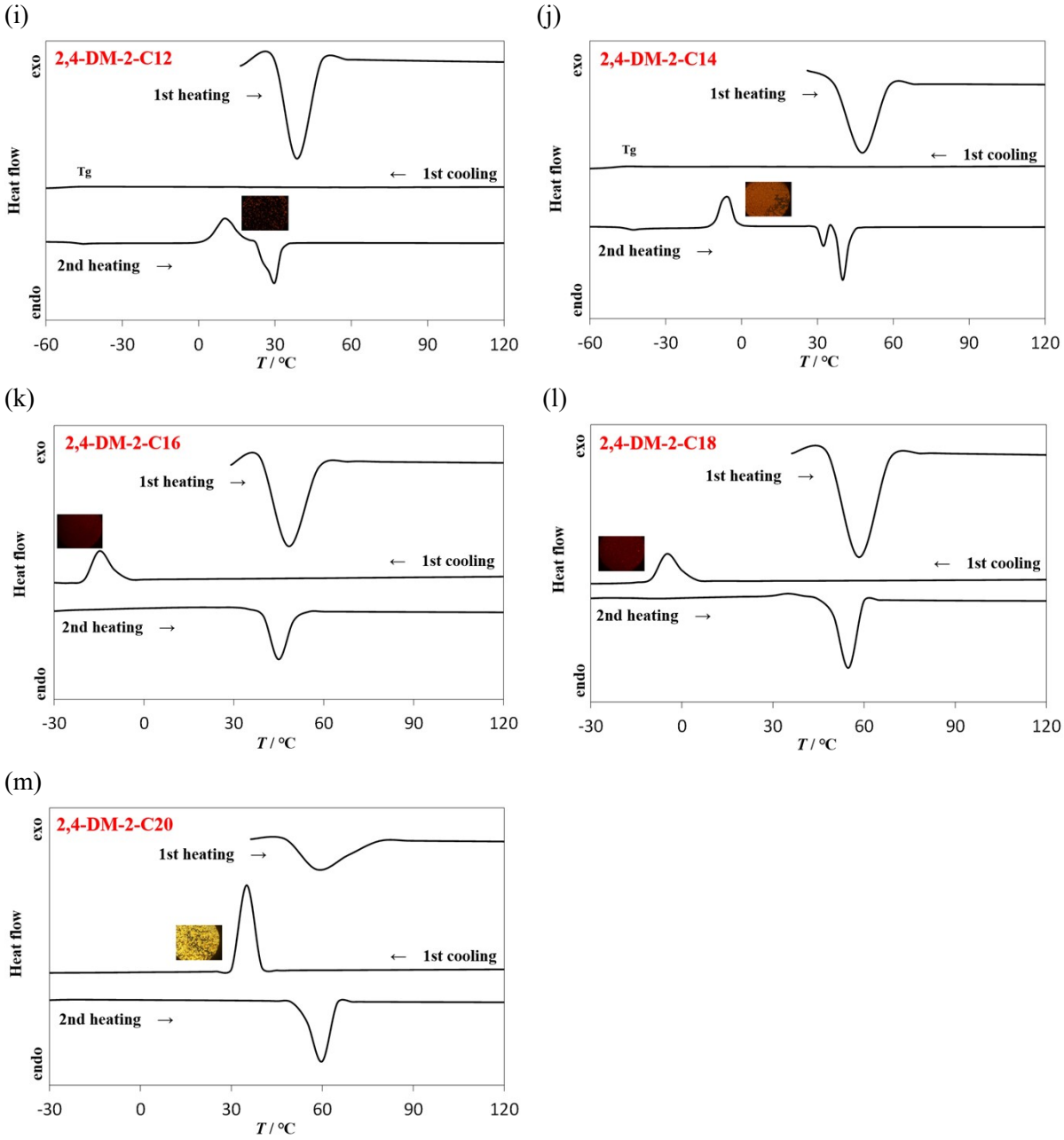


Fig. S2 DSC diagrams and POM images of (a) 2,4-DM-2-C2, (b) 2,4-DM-2-C3, (c) 2,4-DM-2-C6, (d) 2,4-DM-2-C7, (e) 2,4-DM-2-C8, (f) 2,4-DM-2-C9, (g) 2,4-DM-2-C10, (h) 2,4-DM-2-C11, (i) 2,4-DM-2-C12, (j) 2,4-DM-2-C14, (k) 2,4-DM-2-C16, (l) 2,4-DM-2-C18, (m) 2,4-DM-2-C20.

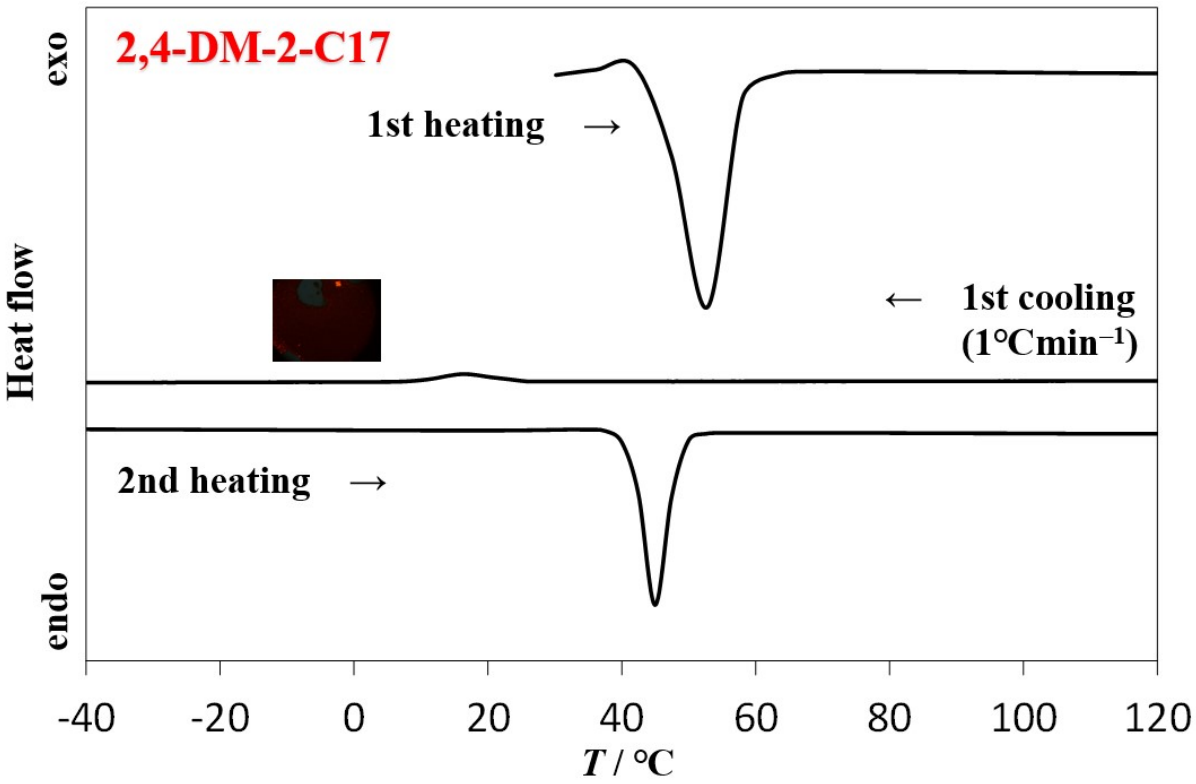


Fig. S3 DSC diagram and POM image of 2,4-DM-2-C17 with the cooling rate of 1°Cmin^{-1}.

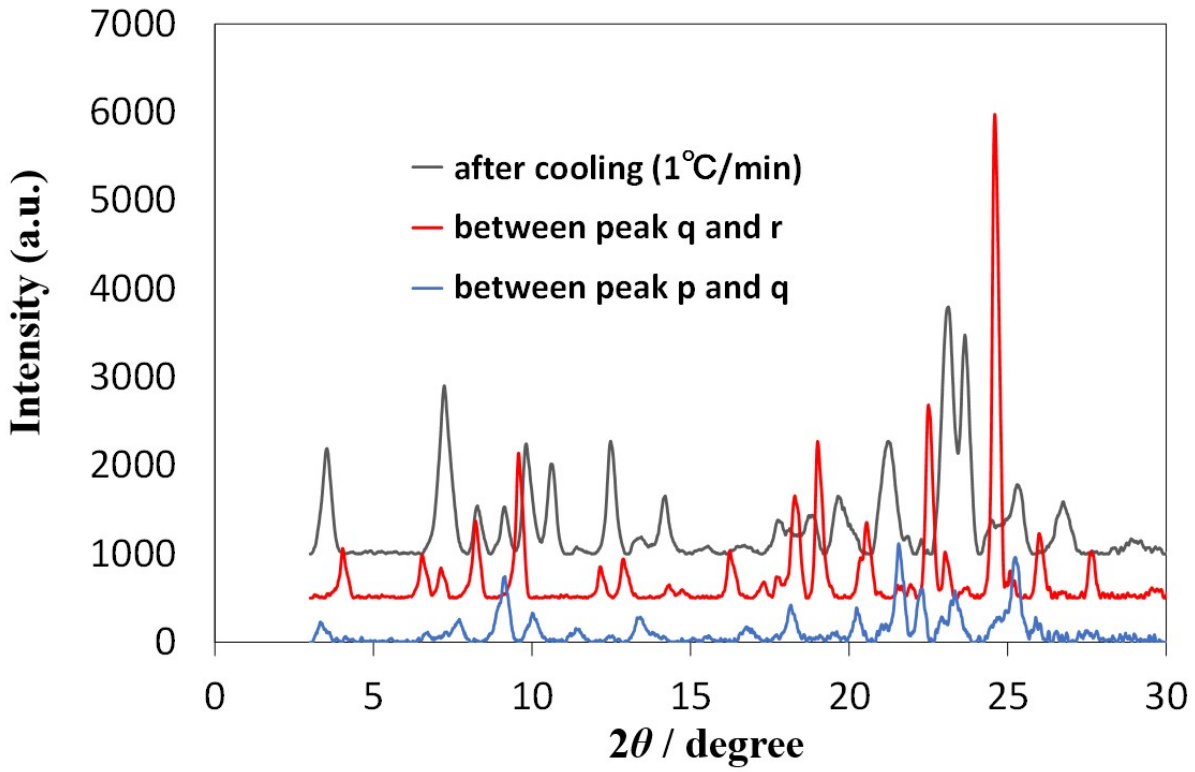
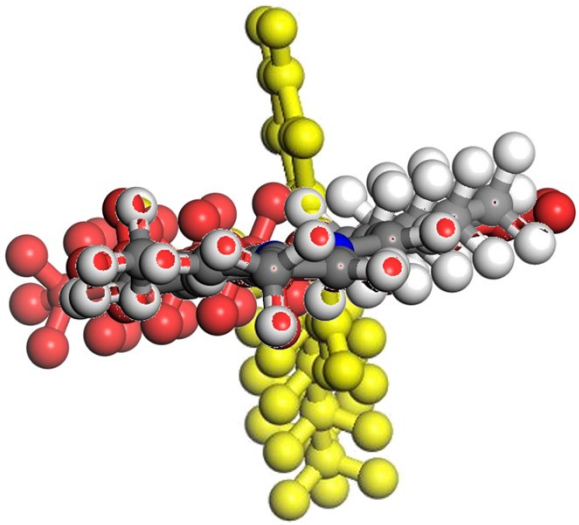


Fig. S4 Powder XRD patterns of 2,4-DM-2-C17. Blue line: measured at room temperature after cooling (between peak p and q in Figure 4d). Red line: measured at 30°C (between peak q and r in Figure 4d). Gray line: crystallized sample with slow cooling rate (1°Cmin^{-1}).

(a)



(b)

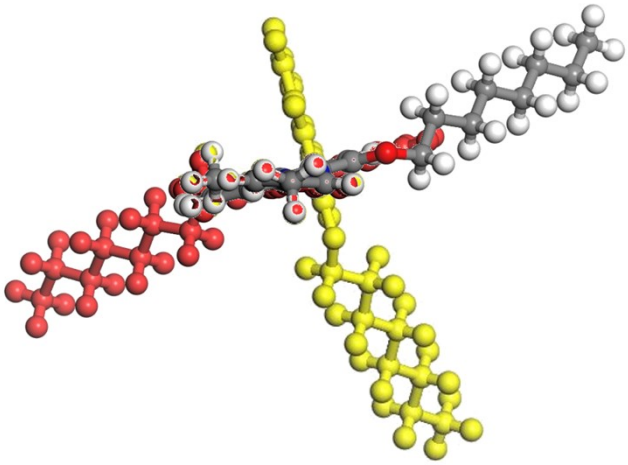


Fig. S5 Rotation model around azo group of (a) 2,4-DM-4-C*n* and (b) 2,4-DM-2-C*n*. The gray molecule is the calculated structure optimized by using DFT calculation. The yellow molecule is 90° rotated view, and the red molecule is 180° rotated view.

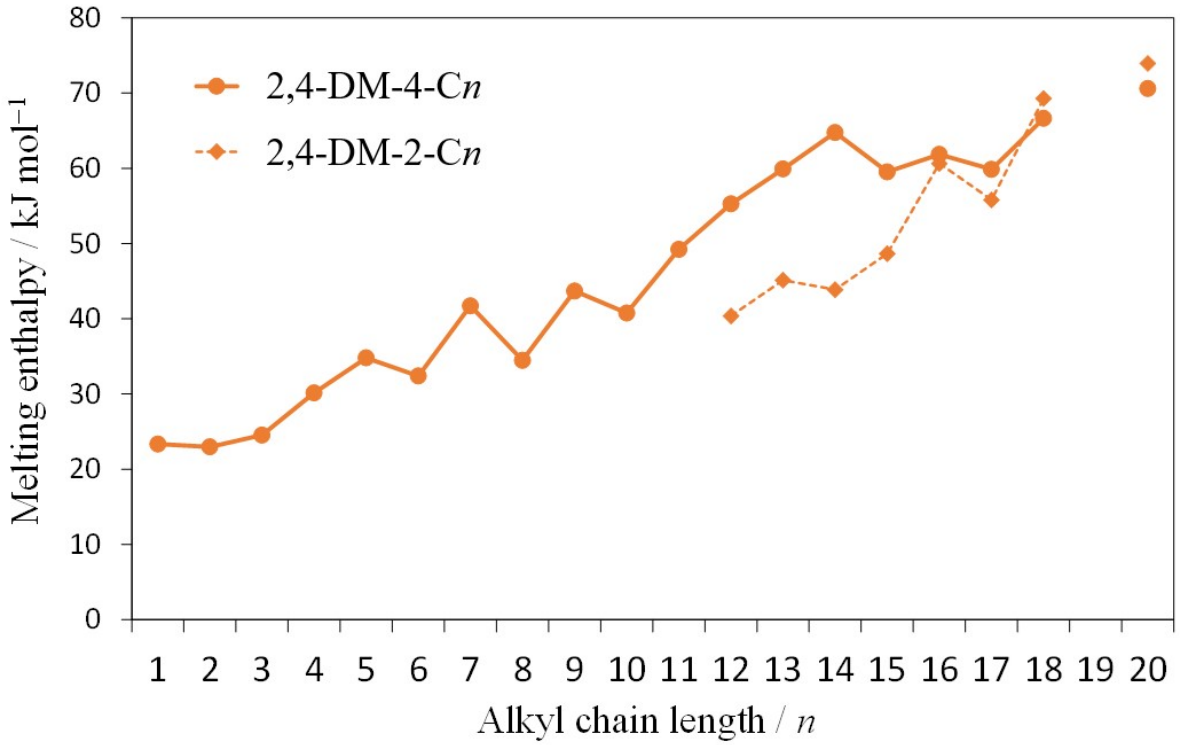


Fig. S6 Melting enthalpies of 2,4-DM-4-C*n* (orange circles) and 2,4-DM-2-C*n* (orange squares).