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Supporting Information

**Thermotropic Liquid Crystals based on Extended 2,5-Disubstituted-1,3,4-Oxadiazoles:
Structure-Property Relationships, Variable-temperature Powder X-ray Diffraction and
Small-angle X-ray Scattering Studies**

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Synthesis and characterization

Scheme S1. Synthetic routes to the extended 2,5-di-substituted-1,3,4-oxadiazoles

Synthesis of **1a–1d** mesogens

(a) Preparation of **Ia–Id**

Synthetic routes for the compounds studied in this work are depicted in Scheme S1. *p*-Substituted benzoic acid R-PhCO₂H (10 mmol, 1.4–2.8 g) (R = C₁₀H₂₁O, CH₃O, (CH₃)₂N, F) was added to thionyl chloride SOCl₂ (10 mL) and refluxed for 6 h to give the corresponding *p*-substituted benzoyl chloride. Excessive SOCl₂ was removed by vacuum distillation and the reaction mixture was cooled to room temperature. *p*-Decyloxybenzoic hydrazide (10 mmol, 2.92 g) dissolved in pyridine (50 mL) was added dropwise over a period of 10 min to the as-formed *p*-substituted benzoyl chloride. The reaction mixture was stirred at 100 °C for 8 h. Crude solid was precipitated by pouring the reaction mixture into distilled water (100 mL). The crude solid was washed with distilled water and recrystallized from ethanol. Yield: 75–78 %. **Ia**: ¹H-NMR (CDCl₃): d = 9.23 (s, 2H), 7.81 (d, *J* = 8.6 Hz, 4H), 6.98 (d, *J* = 8.6 Hz, 4H), 4.01 (t, *J* = 6.6 Hz, 4H), 1.81 (m, 4H), 1.45 (m, 4H), 1.30 (m, 24H), 0.88 (t, *J* = 6.62 Hz, 6H). ¹³C-{¹H}-NMR (CDCl₃): 163.720, 162.679, 129.178, 123.432, 114.637, 68.416, 32.036, 31.097, 29.848, 29.698, 29.510, 29.461, 29.244, 26.123, 22.828, 14.271. MS (70eV, EI) *m/z* (*I* %): 552 (4.38) [M⁺]. HRMS Calcd. for C₃₄H₅₂N₂O₄: 552.3927; Found: 552.3927. **Ib**: ¹H-NMR (CDCl₃): d = 9.33 (q, 2H), 7.83 (q, 4H), 6.92 (q, 4H), 3.99 (t, *J* = 6.6 Hz, 2H), 3.86 (s, 3H), 1.81 (m, 2H), 1.45 (m, 2H), 1.30 (m, 12H), 0.88 (t, *J* = 6.62 Hz, 3H). ¹³C-{¹H}-NMR (CDCl₃): 164.360, 164.288, 162.996, 162.657, 129.340, 129.300, 123.867, 123.531, 114.588, 114.102, 68.419, 55.582, 32.033, 29.695, 29.510, 29.453, 29.259, 26.130, 22.816, 14.242. MS (70eV, EI) *m/z* (*I* %): 426 (1.22) [M⁺]. HRMS Calcd. for C₂₅H₃₄N₂O₄: 426.2518; Found: 426.2518. **Ic**: ¹H-NMR (CDCl₃): d = 9.31 (d, *J* = 6.6 Hz, 1H), 9.13 (d, *J* = 6.6 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 9 Hz, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.04 (s, 6H), 1.81 (m, 2H), 1.45 (m, 2H), 1.27 (m, 12H), 0.88 (t, *J* = 6.60 Hz, 3H). ¹³C-{¹H}-NMR (CDCl₃): 165.065, 164.386,

162.410, 153.049, 129.339, 129.079, 123.872, 118.252, 114.450, 111.186, 68.347, 40.185, 32.039, 29.703, 29.526, 29.460, 29.285, 26.246, 22.821, 14.250. MS (+ve FAB) m/z (I %): 439 (100) $[M]^+$. **Id**: ^1H -NMR (CDCl_3): d = 9.50 (d, J = 6.6 Hz, 1H), 9.22 (d, J = 6.6 Hz, 1H), 7.88 (q, J = 8.4 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.81 (m, 2H), 1.46 (m, 2H), 1.30 (m, 12H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3): 165.312, 164.824, 162.463, 161.433, 130.007, 129.059, 129.021, 124.394, 115.562, 114.062, 67.652, 31.205, 28.909, 28.859, 28.661, 28.597, 28.480, 25.376, 22.003, 13.851. MS (70eV, EI) m/z (I %): 414 (3.31) $[M]^+$. HRMS Calcd. for $\text{C}_{24}\text{H}_{31}\text{FN}_2\text{O}_3$: 414.2318; Found: 414.2318.

(b) Preparation of Ia–Id

Compound **I** (5 mmol, 2.10–2.76 g) was added to SOCl_2 (5 mL) in dried benzene (50 mL). The reaction mixture was refluxed for 8 h and subsequently poured into an iced NaHCO_3 solution (1 M). The crude solid was collected and washed several times with de-ionized water and recrystallized from ethanol. Yield = 90–95 %. **1a**: ^1H -NMR (CDCl_3): d = 8.04 (d, J = 8.8 Hz, 4H), 7.01 (d, J = 8.8 Hz, 4H), 4.03 (t, J = 6.6 Hz, 4H), 1.83 (m, 4H), 1.47 (m, 4H), 1.32 (m, 24H), 0.88 (t, J = 6.6 Hz, 6H). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3): 164.289, 161.983, 128.701, 116.696, 115.113, 68.450, 32.049, 29.709, 29.526, 29.453, 29.306, 26.161, 22.828, 14.249. MS (70eV EI) m/z (I %): 534 (100) $[M]^+$. HRMS Calcd. for $\text{C}_{34}\text{H}_{50}\text{N}_2\text{O}_3$: 534.3821; Found: 534.3821. Elemental analysis: Calcd. (%) for $\text{C}_{34}\text{H}_{50}\text{N}_2\text{O}_3$ (534): C 76.42, H 9.36, N 5.24; Found: C 76.21, H 9.33, N 4.96. **1b**: ^1H -NMR (CDCl_3): d = 8.05 (m, 4H), 7.02 (m, 4H), 4.03 (t, J = 6.52 Hz, 2H), 3.89 (s, 3H), 1.82 (m, 2H), 1.45 (m, 2H), 1.32 (m, 12H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3): 164.325, 164.198, 162.363, 162.018, 128.738, 128.723, 116.807, 116.471, 115.115, 114.630, 68.442, 55.611, 32.037, 29.694, 29.514, 29.454, 29.287, 26.146, 22.817, 14.243. MS

(70eV EI) m/z (I %): 408 (17.11) $[M]^+$. HRMS Calcd. for $C_{25}H_{32}N_2O_3$: 408.2413; Found: 408.2412. Elemental analysis: Calcd. (%) for $C_{25}H_{32}N_2O_3$ (408): C 73.53, H 7.84, N 6.86; Found: C 73.27, H 8.04, N 6.73. **1c**: 1H -NMR ($CDCl_3$): δ = 8.03 (d, J = 8.8 Hz, 2H), 7.96 (d, J = 9.0 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 9.0 Hz, 2H), 4.02 (t, J = 6.52 Hz, 2H), 3.06 (s, 6H), 1.82 (m, 2H), 1.45 (m, 2H), 1.32 (m, 12H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C - $\{^1H\}$ -NMR ($CDCl_3$): 164.940, 163.718, 161.731, 152.374, 128.558, 128.358, 116.879, 115.014, 111.772, 111.430, 68.392, 40.289, 32.061, 29.707, 29.534, 29.474, 29.307, 26.161, 22.838, 14.276. MS (70eV EI) m/z (I %): 421 (100) $[M]^+$. HRMS Calcd. for $C_{26}H_{35}N_3O_2$: 421.2729; Found: 421.2729. Elemental analysis: Calcd. (%) for $C_{26}H_{35}N_3O_2$ (421): C 74.10, H 8.31, N 9.97. Found: C 74.20, H 8.30, N 9.72. **1d**: 1H -NMR ($CDCl_3$): δ = 8.12 (m, 2H), 8.04 (d, J = 8.64 Hz, 2H), 7.22 (m, 2H), 7.01 (d, J = 8.60 Hz, 2H), 4.03 (t, J = 6.52 Hz, 2H), 1.82 (m, 2H), 1.48 (m, 2H), 1.30 (m, 12H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C - $\{^1H\}$ -NMR ($CDCl_3$): 166.498, 163.472, 163.147, 162.193, 129.161, 128.821, 120.612, 116.663, 116.367, 115.165, 68.463, 32.034, 29.695, 29.508, 29.452, 29.270, 26.139, 22.817, 14.248. MS (70eV EI) m/z (I %): 396 (44.77) $[M]^+$. HRMS Calcd. for $C_{24}H_{29}FN_2O_2$: 396.2213; Found: 396.2213. Elemental analysis: Calcd. (%) for $C_{24}H_{29}FN_2O_2$ (396): C 72.73, H 7.32, N 7.07. Found: C 72.62, H 7.09, N 7.14.

Synthesis of **2a–2d**

(c) Preparation of **IIa–IIc**

To the *p*-substituted benzoyl chloride (10 mmol) (see previous section (a)), *p*-iodobenzylhydrazide (10 mmol, 2.62 g) dissolved in pyridine (50 mL) was added dropwise over a period of 10 min. The reaction mixture was stirred at 100 °C for 8 h, and then poured into de-

ionized water (100 mL). The precipitate was washed with de-ionized water and recrystallized from ethanol. Yield = 66–77%.

IIa: ^1H -NMR (CDCl_3): d = 9.50 (d, J = 6.6 Hz, 1H), 9.22 (d, J = 6.6 Hz, 1H), 7.88 (q, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.81 (m, 2H), 1.46 (m, 2H), 1.28 (m, 12H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C - $\{^1\text{H}\}$ -NMR (d^6 -DMSO): 165.246, 165.173, 161.485, 137.401, 132.053, 131.872, 129.429, 114.123, 99.534, 67.201, 31.265, 28.971, 28.920, 28.720, 28.659, 28.541, 25.434, 22.064, 13.924. MS (70eV EI) m/z (I %): 522 (2.16) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{24}\text{H}_{31}\text{IN}_2\text{O}_3$: 522.1379; Found: 522.1379. **IIb:** ^1H -NMR (d^6 -DMSO): d = 9.51 (s, 1H), 10.36 (s, 1H), 7.90 (d, J = 8.4 Hz, 4H), 7.70 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.3 Hz, 2H), 3.83 (s, 3H). ^{13}C - $\{^1\text{H}\}$ -NMR (d^6 -DMSO): 165.922, 165.828, 162.665, 138.048, 132.688, 132.515, 129.956, 125.251, 114.357, 110.185, 56.021. MS (70eV EI) m/z (I %): 396 (5.05) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{15}\text{H}_{13}\text{IN}_2\text{O}_3$: 395.9970; Found: 395.9970. **IIc:** ^1H -NMR (d^6 -DMSO): d = 10.40 (s, 1H), 10.11 (s, 1H), 7.90 (d, J = 8.36 Hz, 2H), 7.78 (d, J = 8.84 Hz, 2H), 7.68 (d, J = 8.32 Hz, 2H), 6.73 (d, J = 8.96 Hz, 2H), 2.97 (s, 6H). ^{13}C - $\{^1\text{H}\}$ -NMR (d^6 -DMSO): 166.375, 165.940, 153.013, 137.891, 132.831, 129.931, 129.506, 119.511, 111.335, 99.796, 40.292. MS (70eV EI) m/z (I %): 409 (5.77) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{16}\text{H}_{16}\text{IN}_3\text{O}_2$: 409.0287; Found: 409.0287. **IId:** ^1H -NMR (d^6 -DMSO): d = 10.57 (s, 2H), 7.98 (m, 2H), 7.92 (d, J = 8.01 Hz, 2H), 7.70 (d, J = 6.75 Hz, 2H), 7.38 (d, J = 8.85 Hz, 2H). ^{13}C - $\{^1\text{H}\}$ -NMR (d^6 -DMSO): 165.882, 165.378, 163.196, 138.075, 132.544, 132.544, 130.842, 129.956, 129.550, 116.310, 116.020, 100.291. MS (70eV EI) m/z (I %): 384 (18.93) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{14}\text{H}_{10}\text{FIN}_2\text{O}_2$: 383.9771; Found: 383.9771.

(d) Preparation of **IIIa–III d**

Compounds **III** were prepared similarly according to (b). Yield = 86–91%. **IIIa**: ^1H -NMR (d^6 -DMSO): δ = 8.04 (d, J = 9.65 Hz, 2H), 7.86 (m, 4H), 7.01 (d, J = 8.88 Hz, 2H), 4.03 (t, 6.53 Hz, 2H), 1.82 (m, 2H), 1.45 (m, 2H), 1.32 (m, 12H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3): 164.990, 163.686, 162.270, 138.464, 128.888, 128.300, 123.735, 116.081, 115.184, 98.361, 68.477, 32.031, 29.688, 29.506, 29.449, 29.268, 26.138, 22.814, 14.243. MS (70eV EI) m/z (I %): 504 (53.24) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{24}\text{H}_{29}\text{IN}_2\text{O}_2$: 504.1273; Found: 504.1273. **IIIb**: ^1H -NMR (d^6 -DMSO): δ = 8.03 (m, 4H), 7.88 (d, J = 7.24 Hz, 2H), 7.16 (d, J = 8.28 Hz, 2H), 3.86 (s, 3H). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3): 164.032, 162.861, 161.888, 137.697, 128.080, 127.515, 122.822, 115.405, 114.027, 97.781, 54.924. MS (70eV EI) m/z (I %): 378 (100) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{15}\text{H}_{11}\text{IN}_2\text{O}_2$: 377.9865; Found: 377.9865. **IIIc**: ^1H -NMR (d^6 -DMSO): δ = 7.97 (m, 2H), 7.86 (m, 4H), 6.76 (d, J = 7.14 Hz, 2H), 3.05 (s, 6H). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3): 165.623, 163.041, 152.579, 138.349, 128.512, 128.182, 124.028, 111.726, 110.813, 97.916, 40.208. MS (70eV EI) m/z (I %): 391 (78.71) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{16}\text{H}_{14}\text{IN}_3\text{O}$: 391.0181; Found: 391.0181. **IIId**: ^1H -NMR (d^6 -DMSO): δ = 8.22–8.18 (m, 2H), 8.03–7.89 (m, 4H), 7.51–7.45 (m, 2H). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3): 166.721, 164.198, 163.360, 129.361, 128.354, 123.373, 120.183, 116.792, 116.496, 98.811. MS (70eV EI) m/z (I %): 366 (100) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{14}\text{H}_8\text{FIN}_2\text{O}$: 365.9665; Found: 365.9665.

(e) Preparation of IVa–IVd

A mixture of compound **III** (2 mmol), trimethylsilylacetylene (2.4 mmol, 0.237 g), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.02 mmol, 0.014 g) and CuI (0.02 mmol, 0.004 g) in a solution of dry THF (50 mL) and triethyl amine (10 mL) was stirred at room temperature under Ar for 12 h. The reaction mixture was evaporated in vacuo and the solid residue was extracted into CH_2Cl_2 (50 mL). The extract solution was washed with aqueous sodium cyanide solution and brine solution, dried over

anhydrous MgSO_4 and filtered, and then evaporated in vacuo to afford crude solid that was purified by flash column chromatography using silica gel and ethyl acetate/hexane (v/v: = 1:4) as eluent. Yield = 85%. **IVa**: ^1H -NMR (CDCl_3): d = 8.09–8.04 (m, 4H), 7.63–7.56 (m, 2H), 7.03–6.97 (m, 2H), 4.03 (t, J = 6.54 Hz, 2H), 1.82 (m, 2H), 1.45 (m, 2H), 1.28 (m, 12H), 0.88 (t, J = 6.62 Hz, 3H), 0.27 (s, 9H). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3): 164.905, 163.747, 162.219, 132.668, 128.871, 126.849, 126.682, 123.844, 116.118, 115.150, 104.188, 97.714, 68.451, 32.039, 29.695, 29.513, 29.460, 29.272, 26.143, 22.824, 14.260, -0.008. MS (70eV EI) m/z (I %): 474 (17.35) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{29}\text{H}_{38}\text{N}_2\text{O}_2\text{Si}$: 474.2702; Found: 474.2702. **IVb**: ^1H -NMR (CDCl_3): d = 8.09–8.05 (m, 4H), 7.60 (d, J = 8.28 Hz, 2H), 7.03 (d, J = 8.78 Hz, 2H), 3.90 (s, 3H), 0.27 (s, 9H). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3): 164.823, 163.802, 162.596, 132.668, 128.895, 126.686, 126.533, 123.797, 116.431, 114.690, 104.181, 97.755, 55.616, -0.008. MS (70eV EI) m/z (I %): 348 (100) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2\text{Si}$: 348.1294; Found: 348.1294. **IVc**: ^1H -NMR (CDCl_3): d = 8.05 (d, J = 8.24 Hz, 2H), 7.97 (d, J = 8.82 Hz, 2H), 7.59 (d, J = 8.19 Hz, 2H), 6.76 (d, 8.87 Hz, 2H), 3.07 (s, 6H), 0.27 (s, 9H). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3): 165.606, 163.205, 152.601, 132.616, 128.543, 126.560, 126.149, 124.184, 111.763, 110.954, 104.331, 97.456, 40.229, 0.008. MS (70eV EI) m/z (I %): 361 (88.34) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{OSi}$: 361.1610; Found: 361.1610. Elemental analysis: Calcd. (%) for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{OSi}$ (362): C 69.83, H 6.41, N 11.63, Found: C 69.80, H 6.46, N 11.40. **IVd**: ^1H -NMR (CDCl_3): d = 8.16–8.13 (m, 2H), 8.07 (m, 2H), 7.61 (d, J = 8.60 Hz, 2H), 7.22 (d, J = 8.76 Hz, 2H), 0.27 (s, 9H). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3): 166.306, 164.419, 164.322, 132.746, 129.386, 126.812, 123.516, 120.301, 116.763, 116.531, 104.070, 98.034, 0.011. MS (70eV EI) m/z (I %): 336 (48.74) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{19}\text{H}_{17}\text{FN}_2\text{OSi}$: 336.1094; Found: 336.1094.

(f) Preparation of Va–Vd

To a methanolic solution (50 mL) of compound **IV** (1 mmol) was added anhydrous K_2CO_3 (1 mmol, 0.138 g). The reaction mixture was stirred at RT for 4 h and was evaporated in vacuo. The solid residue was dissolved in CH_2Cl_2 (50 mL) and the solution was washed with de-ionized water and brine and dried over anhydrous $MgSO_4$. Crude product was obtained by evaporation of solution, which was purified by flash column chromatography on silica gel using ethyl acetate/hexane mixture (v:v = 1:3) as eluent. Yield ~ 91-96%. **Va**: 1H -NMR ($CDCl_3$): δ = 8.12–8.04 (m, 4H), 7.66–7.62 (m, 2H), 7.02 (d, J = 8.81 Hz, 2H), 4.04 (t, J = 6.55 Hz, 2H), 3.24 (s, 1H), 1.84 (m, 2H), 1.45 (m, 2H), 1.30 (m, 12H), 0.88 (t, J = 6.66 Hz, 3H). ^{13}C - $\{^1H\}$ -NMR ($CDCl_3$): 164.945, 163.616, 162.228, 132.850, 128.851, 126.751, 125.432, 124.244, 116.087, 115.136, 82.901, 80.070, 68.434, 32.029, 29.839, 29.693, 29.507, 29.483, 29.265, 26.129, 22.817, 14.257. MS (70eV EI) m/z (I %): 402 (58.0) $[M]^+$. HRMS Calcd. for $C_{26}H_{30}N_2O_2$: 402.2307; Found: 402.2307. **Vb**: 1H -NMR ($CDCl_3$): δ = 8.09–8.05 (m, 4H), 7.63 (d, J = 8.39 Hz, 2H), 7.02 (d, J = 8.90 Hz, 2H), 3.89 (s, 3H), 3.25 (s, 1H). ^{13}C - $\{^1H\}$ -NMR ($CDCl_3$): 164.932, 163.631, 162.232, 132.867, 128.909, 126.777, 125.495, 124.254, 116.410, 114.706, 82.911, 80.080, 55.623. MS (70eV EI) m/z (I %): 276 (100) $[M]^+$. HRMS Calcd. for $C_{17}H_{12}N_2O_2$: 276.0898; Found: 276.0898. Elemental analysis: Calcd. (%) for $C_{17}H_{12}N_2O_2$ (276): C 73.95, H 4.38, N 10.14; Found: C 73.63, H 4.44, N 10.27. **Vc**: 1H -NMR ($CDCl_3$): δ = 8.07 (d, J = 8.57 Hz, 2H), 7.98 (d, J = 9.06 Hz, 2H), 7.62 (d, J = 8.57 Hz, 2H), 6.76 (d, J = 9.06 Hz, 2H), 3.24 (s, 1H), 3.07 (s, 6H). ^{13}C - $\{^1H\}$ -NMR ($CDCl_3$): 165.651, 163.038, 152.570, 132.792, 128.519, 126.626, 125.082, 124.598, 111.724, 110.817, 93.040, 79.880, 40.190. MS (70eV EI) m/z (I %): 289 (86.47) $[M]^+$. HRMS Calcd. for $C_{18}H_{15}N_3O$: 289.1215; Found: 289.1215. **Vd**: 1H -NMR ($CDCl_3$): δ = 8.17–8.08 (m, 4H), 7.65 (d, J = 8.26 Hz, 2H), 7.22 (m, 2H), 3.26 (s, 1H). ^{13}C - $\{^1H\}$ -NMR ($CDCl_3$): 166.322, 164.201, 163.802, 132.941, 129.490, 126.941, 125.938, 123.909, 116.772,

116.549, 82.823, 80.292. MS (70eV EI) m/z (I %): 264 (100) $[M]^+$. HRMS Calcd. for $C_{16}H_9FN_2O$: 264.0698; Found: 264.0698.

(g) *Preparation of 2a–2d*

Similar Pd-catalyzed C–C bond coupling reactions of compound **V** (1 equiv) with 1-iodo-4-decyloxybenzene (2 mmol, 0.72 g) were carried out at RT for 12 h under Ar (See section (e)). **2a**: 1H -NMR ($CDCl_3$): δ = 8.09 (d, J = 8.36 Hz, 2H), 8.06 (d, J = 8.76 Hz, 2H), 7.65 (d, J = 8.16 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 8.68 Hz, 2H), 6.88 (d, J = 8.56 Hz, 2H), 4.03 (t, J = 6.48 Hz, 4H), 1.82 (m, 4H), 1.44 (m, 4H), 1.28 (m, 24H), 0.88 (t, J = 6.6 Hz, 6H). ^{13}C - $\{^1H\}$ -NMR ($CDCl_3$): 164.842, 163.907, 162.211, 159.803, 133.364, 132.076, 128.862, 127.192, 126.806, 123.217, 116.242, 115.170, 114.802, 114.660, 92.766, 87.576, 68.469, 68.297, 32.041, 29.845, 29.703, 29.522, 29.334, 29.287, 26.157, 22.822, 14.246. MS (70eV EI) m/z (I %): 635 (100) $[M]^+$. HRMS Calcd. for $C_{42}H_{54}N_2O_3$: 634.4134; Found: 634.4134. Elemental analysis: Calcd. (%) for $C_{42}H_{54}N_2O_3$ (634): C 79.51, H 8.52, N 4.41. Found: C 79.18, H 8.67, N 4.32. **2b**: 1H -NMR ($CDCl_3$): δ = 8.11–8.07 (m, 4H), 7.64 (d, J = 8.52 Hz, 2H), 7.47 (d, J = 8.79 Hz, 2H), 7.04 (d, J = 8.94 Hz, 2H), 6.88 (d, J = 8.85 Hz, 2H), 3.98 (t, J = 6.54 Hz, 2H), 3.90 (s, 3H), 1.80 (m, 2H), 1.45 (m, 2H), 1.27 (m, 12H), 0.88 (t, J = 6.62 Hz, 3H). ^{13}C - $\{^1H\}$ -NMR ($CDCl_3$): 164.784, 163.975, 162.592, 159.816, 133.375, 132.094, 128.911, 127.242, 126.830, 123.184, 114.814, 114.714, 114.657, 92.799, 87.570, 68.308, 55.640, 32.045, 29.847, 29.701, 29.529, 29.462, 29.336, 26.167, 22.825, 14.250. MS (70eV EI) m/z (I %): 508 (100) $[M]^+$. HRMS Calcd. for $C_{33}H_{36}N_2O_3$: 508.2726; Found: 508.2726. Elemental analysis: Calcd. (%) for $C_{33}H_{36}N_2O_3$ (508): C 77.96, H 7.08, N 5.51. Found: C 77.72, H 7.23, N 5.36. **2c**: 1H -NMR ($CDCl_3$): δ = 8.08 (d, J = 8.31 Hz, 2H), 7.98 (d, J = 8.97 Hz, 2H), 7.63 (d, J = 8.34 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.76 Hz, 2H), 6.76 (d, J = 8.97 Hz, 2H), 4.00 (t, J = 6.5 Hz, 2H), 3.08 (s, 6H),

1.82 (m, 2H), 1.45 (m, 2H), 1.27 (m, 12H), 0.88 (t, $J = 6.6$ Hz, 3H). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3): 165.540, 163.344, 159.766, 152.587, 133.354, 132.032, 128.535, 126.832, 126.688, 123.553, 114.801, 114.742, 111.779, 111.033, 92.542, 87.672, 68.301, 40.238, 32.047, 29.849, 29.704, 29.533, 29.464, 29.342, 26.169, 22.828, 14.252. MS (70eV EI) m/z (I %): 521 (100) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{34}\text{H}_{39}\text{N}_3\text{O}_2$: 521.3042; Found: 521.3042. Elemental analysis: Calcd. (%) for $\text{C}_{34}\text{H}_{39}\text{N}_3\text{O}_2$ (521): C 78.33; H 7.48, N 8.06. Found: C 78.16, H 7.52, N 7.99. **2d**: ^1H -NMR (CDCl_3): d = 8.17–8.09 (m, 4H), 7.65 (d, $J = 8.48$ Hz, 2H), 7.48 (d, $J = 8.8$ Hz, 2H), 7.22 (d, $J = 8.76$ Hz, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 3.98 (t, $J = 6.56$ Hz, 2H), 1.79 (m, 2H), 1.46 (m, 2H), 1.30 (m, 12H), 0.88 (t, $J = 6.6$ Hz, 3H). ^{13}C - $\{^1\text{H}\}$ -NMR (CDCl_3): 166.678, 163.989, 163.319, 159.840, 133.377, 132.127, 129.454, 129.335, 127.545, 126.912, 122.843, 116.716, 116.466, 114.804, 93.008, 87.475, 68.293, 32.032, 29.688, 29.516, 29.450, 29.318, 26.151, 22.814, 14.241. MS (70eV EI) m/z (I %): 496 (100) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{32}\text{H}_{33}\text{FN}_2\text{O}_2$: 496.2526; Found: 496.2526. Elemental analysis: Calcd. (%) for $\text{C}_{32}\text{H}_{33}\text{FN}_2\text{O}_2$ (496): C 77.45, H 6.65, N 5.64. Found: C 77.32, H 6.54, N 5.48.

Syntheses of **3a–3b**

Extended mesogens **3a–3b** were prepared by the aforementioned Pd/Cu^I-catalyzed coupling reaction between 2,5-diphenylethynyl-1,3,4-oxadiazole (0.5 mmol, 0.135 g) and two molar equivalents of 1-iodo-4-decyloxybenzene (1 mmol, 0.360 g) (or 1-iodo-4-methoxybenzene (1 mmol, 0.234 g) for **3b**). **3a**: ^1H -NMR (CDCl_3): d = 8.11 (d, $J = 8.43$ Hz, 4H), 7.65 (d, $J = 8.40$ Hz, 4H), 7.48 (d, $J = 8.73$ Hz, 4H), 6.88 (d, $J = 8.79$ Hz, 4H), 3.99 (t, $J = 6.48$ Hz, 4H), 1.79 (m, 4H), 1.46–1.28 (m, 28H), 0.88 (t, $J = 6.6$ Hz, 6H). The ^{13}C -NMR spectra for the compounds **3a** and **3b** were not available due to their poor solubility in many organic solvents. MS (70eV EI) m/z (I %): 734 (100) $[\text{M}]^+$. HRMS Calcd. for $\text{C}_{50}\text{H}_{58}\text{N}_2\text{O}_3$: 734.4447; Found: 734.4447.

Elemental analysis: Calcd. (%) for $C_{50}H_{58}N_2O_3$ (734): C 81.77, H 7.96, N 3.81. Found: C 81.44, H 8.07, N 3.79. **3b**: 1H -NMR ($CDCl_3$): δ = 8.11 (d, J = 8.43 Hz, 4H), 7.65 (d, J = 8.40 Hz, 4H), 7.48 (d, J = 8.73 Hz, 4H), 6.88 (d, J = 8.79 Hz, 4H), 3.84 (s, 6H). MS (70eV EI) m/z (I %): 482 (100) $[M]^+$. HRMS Calcd. for $C_{32}H_{22}N_2O_3$: 482.1630; Found: 482.1630. Elemental analysis: Calcd. (%) for $C_{32}H_{22}N_2O_3$ (482): C 79.71, H 4.60, N 5.81. Found: C 79.38, H 4.82, N 5.63.

Structure determination by powder X-ray diffraction

The chemical structures of **2b** and **3a** have been established by ^1H and ^{13}C -NMR and MS data. Based on the models shown in Scheme 2, the molecular orientations and crystal packing were investigated by structure determination using powder X-ray diffraction data. These models were first created by using ISIS DRAW version 2.14 program and later were transformed into sets of fractional coordinates written in the Z-matrix format by using program Babel (<http://www.eyeopen.com/babel/>) or OPENBABEL (<http://openbabel.sourceforge.net>). The program can be downloaded free of charge. The following bond distances ($\text{\AA}$) and angles ($^\circ$) restraints were used: $\text{C}(\text{sp}^2/\text{sp}^3)\text{-H}$ 0.96, $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^2)$ 1.38, $\text{C}=\text{C}$ 1.20, $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ 1.54, $\text{C}(\text{sp}^2)\text{-O}$ 1.48, $\text{N-C}(\text{sp}^2)$ 1.35, N-N 1.39, the C-C-C angles of 120 and 109.5° are adopted for those sp^2 and sp^3 hybridized carbons respectively, C-N-O , C-O-C and C-N-N angles of the pentagonal oxadiazole ring are 107° , and the angle C-C=C motif is 180° . Automatic indexing using DICVOL program^[a] gave initial sets of lattice parameters. Due to the limited resolution of dataset for **2b** and **3a**, only 17 peaks were used and gave moderate figure of merits $M(17)/F(17)$ are 10.5/25.3 and 12.3/28.9 for **2b** and **3a** respectively. According to the unit cell volume ($2673 \text{ \AA}^3$ for **2b** and $4013 \text{ \AA}^3$ for **3a**), $Z = 4$ are expected for both cases to adopt the monoclinic symmetry with the calculated density $\sim 1.20\text{--}1.25 \text{ g cm}^{-3}$. The low calculated density is typical for organic solids or inclusions of solvent molecules. However the latter case is not likely as revealed by elemental analyses and TGA curves. Followed space group assignment was performed by a probability (trial and error) approach in which the systematic absences of the extracted intensities were evaluated by Pawley fit algorithm.^[b] The choices of space groups $\text{P2}_1/\text{c}$ and Pc and P2_1 were suggested. Space group $\text{P2}_1/\text{c}$ was chosen because of its frequent occurrence whereas the other two are less common and P2_1 was only restricted to the enantiopure compounds. Based on the

unit cell volumes, one molecule **2b** or **3a** per asymmetric unit of the unit cell was needed for structure solution searches by simulated annealing implemented in DASH^[c] program or parallel tempering employed in FOX program.^[d] Using the default settings, structure solution search by varying all related parameters was not satisfactory to give chemically sensible solutions (even lower profile R_p and R_{wp} and χ^2 factors were attained), unless the search range for the molecular orientation angles: [Q1 (0.17 – 0.19), Q2 (0.48 – 0.52), Q3(-0.50 – -0.48) and Q4 (0.65 – 0.68)] were used and the three transitional freedoms and all torsion angles were fixed or were allowed to vary by $\pm 10\%$ of their mean values. When the profile χ^2 and R-factors (R_p and R_{wp}) converged to the minimal values, the selected structure solutions were examined and judged based on educated chemical and physical knowledge as well as the graphical fit of difference plot between the calculated and experimental diffractograms. No preferred orientation correction for both cases was made for the above structure solution calculations. Prior to the structural refinement, the chemically sensible structure solution was selected and manually pre-adjusted so as to remove those unrealistic close contacts by applying the appropriate sets of non-bonded distance restraints (minimum non-bonded distances of 2.0 Å and 2.5 Å for H...H and H...C respectively). For instance, when those bad contacts were disappeared then the corresponding weighing factors were reduced accordingly. The model adjustment process was repeated many times until there are no overlapped atoms or unrealistic bad contacts for non-bonded atoms. Subsequent Rietveld profile refinement^[e] using the full matrix least squares was carried out by GSAS/EXPGUI^[f, g] suite programs. Overall scale factor and the coefficients of the linear interpolation background function were refined. Profile shape parameters (Pseudo-Voigt function)^[h, i]; instrumental parameters (S/L) and (H/L), sample displacement (shft) and sample transparency (trns), Gaussian peak width (GW) and the Lorentzian peak broadening factor due to the microstrain effect of

crystallites (LY) were sequentially refined. Absorption correction for the surface roughness using Suortti function^[f] was applied for both cases and the constrained thermal parameters U_{iso} of atoms were also refined until positive values of U_{iso} were obtained. The effect of preferred orientation on the measured diffraction intensity of the datasets for **2b** and **3a** was apparent, evidenced by the March-Dollase coefficients^[j,k] (0.57(1) and 0.77(1) along their crystallographic {100} direction for **2b** and **3a** respectively). This indicates needle-like crystal habit for these two cases. When the refinement of all these non-structural parameters became converged with a negligible (shift/esd)² value, the model-biased profile refinement for **2b** and **3a** were switched in which the unit cell parameters (a, b, c and β), atomic coordinates, background, peak profile parameters were refined together to give the final R_p , R_{wp} , R_{exp} and R_F factors (Table 1). Final refinement plots for the solids **2b** and **3a** are listed in Figure S1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 616625 & 616626. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

References

- [a] A. Boultif, D. Louer, *J. Appl. Crystallogr.* **1991**, 24, 987-993.
- [b] G. S. Pawley, *J. Appl. Crystallogr.* **1981**, 14, 357-361.
- [c] W. I. F. David, K. Shankland, *DASH, Program for Structure Solution from Powder Diffraction Data*, Cambridge Crystallographic Data Center, Cambridge **2001**, (License agreement No: D/1023/2002).
- [d] V. Favre-Nicolin, R. Cerny, *J. Appl. Crystallogr.* **2002**, 35, 734-743. FOX, “free objects for crystallography”: A modular approach to *ab initio* structure determination from powder diffraction.
- [e] H. M. Rietveld, *J. Appl. Crystallogr.* **1969**, 2, 65-71.
- [f] A. C. Larson, R. B. Von Dreele, “General Structure Analysis System (GSAS)”, *Los Alamos National Laboratory Report LAUR 86-748* **2004**.
- [g] B. H. Toby, *EXPGUI, A Graphical User Interface for GSAS*, *J. Appl. Crystallogr.* **2001**, 34, 210-221.
- [h] P. Thompson, D. E. Cox, J. B. Hastings, *J. Appl. Crystallogr.* **1987**, 20, 79–83.
- [i] L. W. Finger, D. E. Cox, A. P. Jephcoat, *J. Appl. Crystallogr.* **1994**, 27, 892–900.
- [j] A. March, *Z. Kristallogr.* **1932**, 81, 285–297.
- [k] W. A. Dollase, *J. Appl. Crystallogr.* **1986**, 19, 267–272.

Figure S1. Final Rietveld refinement plots for **2b** (upper) and **3a** (lower) (crossed signs = observed data points, line = calculated profile, vertical ticks = Bragg peak positions). The difference plot between the experimental and calculated powder diffraction profile is shown at the bottom of each plot.

Figure S2. TGA curves for solids **1b**, **1d**, **2b**, **2d**, **3a** in N₂ atmosphere.

Figure S3. X-ray diffractograms for the solid **2b** (lower) and the annealed solid (top).