



Journal Name

Electronic Supplementary Information (ESI)

A Room-Temperature Liquid Crystal Polymer Based on Discotic 1,3,4-Oxadizole

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Fig. S1. TGA thermographs of **MOXD**, **DOXD** and **POXD** under nitrogen gas at a heating rate of 10.0 °C min⁻¹.

Fig. S2. TGA thermographs of **MOXD**, **DOXD** and **POXD** under nitrogen gas at a heating rate of 10.0 °C min⁻¹.

Reference

Experimental

General

^1H NMR spectra were collected on a Bruker AV400 (400MHz) spectrometer. The chemical shifts (in ppm) are relative to the protons of tetramethylsilane ($\delta = 0$ ppm). Proton decoupled ^{13}C NMR spectra were recorded at 101 MHz on the same spectrometer. High-resolution mass spectra (HRMS) were obtained with an FTICR-MS mass spectrometer. Gel permeation chromatography (GPC) was carried out on a Waters 515 GPC instrument using THF as an eluent at 35 °C. The GPC calibration curve was obtained with linear polystyrene standards.

The temperature and enthalpy changes of phase transitions were determined by a NETZSCH DSC 204 differential scanning calorimeter at a heating rate of 10 °C/min and pre-calibrated with a pure indium sample. The optical textures of mesophases were observed on a polarized-light optical microscope (OLYMPUS BX53) equipped with a temperature-controlled hot stage. Thermogravimetric analyses were performed by NETZSCH TG 209 under a stream of flowing N_2 . The X-ray diffractographs were recorded on a Bruker D8 ADVANCE diffractometer with CuK_α X-ray radiation ($\lambda = 1.54146$ Å, rated at 1.6 kW) equipped with a modular temperature chamber attachment (Material Research Instruments) with a scan range of 1.5 – 30° (2 θ).

UV-visible electronic absorption spectra were recorded on a Perkin-Elmer Lambda 19 UV/Vis spectrophotometer. Steady-state emission spectra were recorded on a Cary Eclipse spectrophotometer. The emission quantum yields were determined using the method of Demas and Crosby with quinine sulphate as standard ($\Phi = 0.546$ in 1N H_2SO_4).¹

Synthesis and Characterization

All chemicals were commercially available and used as received. Dichloromethane used for photoluminescence studies was of HPLC grade, the other solvents were of analytical grade.

Synthesis of 3,4-didecyloxy-5-hydroxymethylbenzoate **2** and methyl 3,4,5-tridecyloxy benzoate **3**. To a 100 mL round-bottom flask was added methyl gallate (2.0 g, 10.9 mmol),

K₂CO₃ powder (3.0 g), KI (catalytic amount), 1-bromodecane (6.0 g, 27.2 mmol) and DMF (20 mL). The reaction mixture was heated at 70°C for 3h with stirring, then it was cooled to room temperature and K₂CO₃ was filtered. The filtrate was dissolved in H₂O (150 mL) and was extracted three times with CH₂Cl₂ (150 mL). The combined organic phase was washed four times with saturated NaCl solution, separated and dried over MgSO₄. The solvent was evaporated and the crude products were separated and purified by column chromatography on silica gel (eluent, Petroleum ether : EtOAc, 15 : 1 v/v) to yield 2.24 g of **2** and 2.91 g of **3**. The overall yield of **2** and **3** is 88%.

3,4-Didecyloxy-5-hydroxymethylbenzoate **2**: ¹H NMR (400MHz, CDCl₃) δ = 7.28 (d, *J* = 2.0 Hz, 1H), 7.17 (d, *J* = 2.0 Hz, 1H), 5.86 (s, 1H), 4.16 (t, *J* = 6.8 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 3.88 (s, 3H), 1.82 – 1.70 (m, 4H), 1.45 – 1.26 (m, 28H), 0.88 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ = 166.8, 151.3, 149.1, 138.6, 125.2, 109.4, 106.4, 73.6, 68.9, 52.2, 31.9, 30.2, 29.6, 29.6, 29.4, 29.3, 26.2, 25.9, 22.7, 14.1. HRMS (M+H)⁺ (C₂₈H₄₈O₅): 464.3502 (calculated), 464.3528 (found).

Methyl 3,4,5-tridecyloxybenzoate **3**: ¹H NMR (400MHz, CDCl₃) δ = 7.25 (s, 2H), 4.01 (t, *J* = 6.6 Hz, 6H), 3.89 (s, 3H), 1.83 – 1.72 (m, 6H), 1.47 – 1.27 (m, 36H), 0.88 (t, *J* = 6.6 Hz, 9H). HRMS (M+H)⁺ (C₃₈H₆₈O₅): 604.5067 (calculated), 604.5023 (found).

Synthesis of 3,4-Didecyloxy-5-(1-hydroxydecan)methylbenzoate **4**. To a 50 mL round-bottom flask was added compound **2** (0.50 g, 1.48 mmol), 1-bromodecane (0.67g, 3.01 mmol), K₂CO₃ powder (0.82 g), KI (catalytic amount) and DMF (15 mL). The mixture was stirred at 70 °C for 3h. After which the reaction mixture was cooled to room temperature and extracted three

times with CH_2Cl_2 (150 mL). The combined organic phase was washed four times with saturated NaCl solution and dried over MgSO_4 . The solvent was evaporated and the crude product was purified by column chromatography on silica gel (eluent, CH_2Cl_2 : EtOAc, 20 : 1 v/v) to yield 0.51g (57%) of **4** as white solid. ^1H NMR (400 MHz, CDCl_3) δ = 7.24 (s, 2H), 4.01 (t, J = 6.6 Hz, 6H), 3.88 (s, 3H), 3.63 (t, J = 6.4 Hz, 2H), 1.82 – 1.68 (m, 8H), 1.47 – 1.26 (m, 40H), 0.87 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ = 167.0, 152.8, 142.3, 124.6, 107.9, 73.5, 69.1, 63.0, 52.1, 29.6, 29.6, 29.5, 29.4, 29.4, 29.4, 29.3, 26.1, 22.7, 14.1. HRMS ($\text{M}+\text{H}$) $^+$: 620.5016 (calculated), 620.4932 (found).

Synthesis of 3,4-Didecyloxy-5-(1-hydroxydecan)benzoic acid **5**. To a solution of the ester **4** (0.51g, 0.82 mmol) in EtOH (10 mL), KOH (0.34 g, in 0.6 mL of H_2O) was added and the resulting solution was refluxed for 3h. Then the solution was cooled to room temperature and acidified with dilute HCl under. The precipitate was collected by filtration, washed two times with EtOH (20 mL) and dried to yield 0.46 g (94%) of **5** as white solid. ^1H NMR (400 MHz, CDCl_3) δ = 7.29 (s, 2H), 4.28 (t, J = 6.2Hz, 2H), 4.20 (t, J = 6.6 Hz, 2H), 4.02 (t, J = 6.4 Hz, 4H), 1.83– 1.68 (m, 8H), 1.45 –1.26 (m, 40H), 0.88 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ = 171.2, 152.9, 152.8, 143.1, 123.7, 108.5, 73.6, 69.2, 63.1, 32.0, 31.9, 29.7, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 22.7, 14.2. HRMS ($\text{M}+\text{H}$) $^+$: 606.4859 (calculated), 606.4821 (found).

Synthesis of 3,4-Didecyloxy-5-(1-methacryloyloxydecan)benzoic acid **6**. To a 100 mL flask, **5** (0.45 g, 0.74 mmol), dry CH_2Cl_2 (10 mL), and dry pyridine (0.3 mL) were added. Methacryloyl chloride (0.16 g, 1.5 mmol) was added dropwise with constant pressure drop funnel at 0°C and the reaction was stirred at room temperature for 3h. To the reaction

mixture was added water, and the product was extracted with CH_2Cl_2 . The solution was dried over MgSO_4 and the solvent was distilled in vacuum. The resulting product was heated for 10 minutes in pyridine (10 mL) and water (3 mL). Then the reaction mixture was acidified with dilute HCl, and extracted by Et_2O . The organic layer was washed with saturated NaHCO_3 solution and dried over MgSO_4 . The solvent was distilled in vacuum to give 0.34g (72%) of **6**. ^1H NMR (400 MHz, CDCl_3) δ = 7.33 (s, 1H), 7.30 (s, 1H), 6.10 (s, 1H), 5.55 (s, 1H), 4.14 (t, J = 6.6 Hz, 2H), 4.04 (t, J = 6.6 Hz, 6H), 1.94 (s, 3H), 1.84 – 1.20 (m, 48H), 0.84 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ = 167.6, 155.8, 136.5, 125.2, 108.5, 100.0, 73.5, 69.1, 64.9, 48.3, 31.9, 29.8, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 26.1, 22.7, 14.1. HRMS ($\text{M}+\text{H}$) $^+$: 642.5223 (calculated), 642.5180 (found).

Synthesis of 3,4,5-Tridecyloxybenzoic acid hydrazide **7**. A mixture of **3** (2.0 g, 3.31 mmol), hydrazine hydrate (10 mL) and EtOH (20 mL) was refluxed in a 100 mL round-bottom flask for 2h. Then the reaction mixture was cooled to room temperature and then white waxy solid precipitated. The precipitate was collected by filtration and the crude product was purified by recrystallization from ethanol, 1.87 g (94%) of **7** as white solid was obtained. ^1H NMR (400 MHz, CDCl_3) δ = 6.92 (s, 2H), 4.00 (t, J = 6Hz, 6H), 1.82 – 1.71 (m, 6H), 1.47 – 1.27 (m, 42H), 0.88 (t, J = 6.4 Hz, 9H). HRMS ($\text{M}+\text{H}$) $^+$: 604.5179 (calculated), 604.5157 (found).

Synthesis of 2-(3,4,5-Tri-decyloxyphenyl)-5-[3,4-didecyloxy-5-(1-methacryloyl-n-decan-1-yloxy) phenyl]-1,3,4-oxadiazole **MOXD**. Into a round-bottom flask, **6** (0.4 g, 0.62 mmol) was dissolved in SOCl_2 (15 mL). The reaction mixture was refluxed for 2h. After which the solution was cooled to room temperature and the solvent was removed under vacuum to

give the acid chloride, which was used immediately in the next step without further purification. The as-formed acid chloride was dissolved in dry pyridine (10 mL) and then slowly added to a solution of **7** (0.38 g, 0.62 mmol) in dry pyridine (10 mL). The reaction mixture was stirred at room temperature for 12h and refluxed for 2h. After removing the solvent under vacuum, the residue as the crude product **8** was dissolved in POCl₃ (10 mL) and then refluxed for 6h. After cooling, the resulting mixture was poured slowly into ice water with stirring. The product in water was extracted with CH₂Cl₂ (100 mL) and washed three times with saturated NaHCO₃ and three times with H₂O. The organic phase was dried over MgSO₄ and the solvent was removed under vacuum. The crude product was purified by column chromatography (eluent, CH₂Cl₂ : EtOAc, 30:1 v/v) to yield 0.5 g (65%) of **MOXD**. ¹H NMR (400 MHz, CDCl₃) δ = 7.30 (s, 4H), 6.10 (s, 1H), 5.54 (t, *J* = 1.6 Hz, 1H), 4.15–4.02 (m, 14H), 1.95 (s, 3H), 1.85 – 1.64 (m, 14H), 1.50 – 1.20 (m, 82H), 0.85 (m, 15H). ¹³C NMR (100 MHz, CDCl₃) δ = 164.6, 153.6, 153.2, 141.8, 136.5, 125.2, 118.6, 105.7, 105.6, 69.5, 69.2, 64.8, 32.0, 31.9, 30.4, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 26.1, 26.0, 22.7, 14.1. HRMS (M+H)⁺: 1244.0089 (calculated), 1244.0158 (found).

Synthesis of poly{2-(3,4,5-Tri-decyloxyphenyl)-5-[3,4-didecyloxy-5-(1-methacryloyl-n-decan-1-yloxy)phenyl]-1,3,4-oxadiazole}: **POXD**. The monomer **MOXD** (200 mg, 0.40 mmol), AIBN (0.2 mg, 0.1%) and dry THF (5mL) were added into a Schlenk tube. The solution was degassed by vacuum pump and filled with N₂. The reaction mixture was heated at 60 °C for 18h. The resulting polymer was diluted with CH₂Cl₂ and purified from the unconverted

monomer **MOXD** by silica gel column chromatography (eluent, CH₂Cl₂ : EtOAc, 15:1 v/v) to yield 90 mg of **POXD**; $M_n = 61711$, $M_w/M_n = 3.74$ (GPC with polystyrene standards).

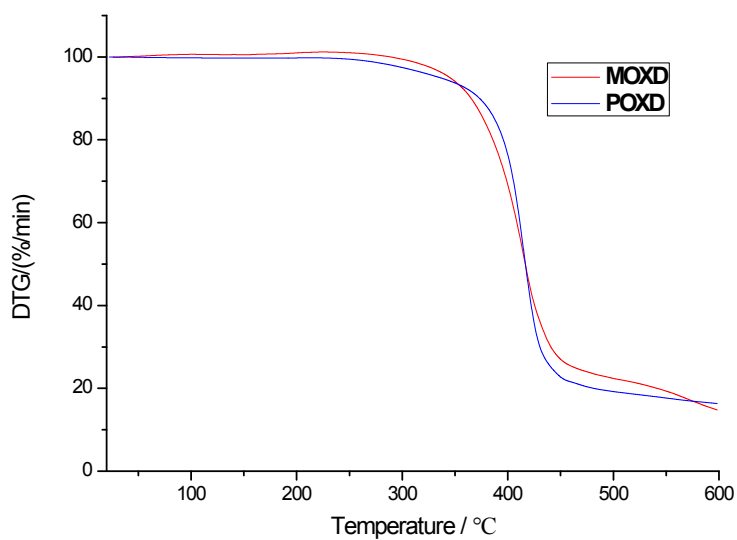


Fig. S1 TGA thermographs of **MOXD**, **DOXD** and **POXD** under nitrogen gas at a heating rate of 10.0 °C min⁻¹.

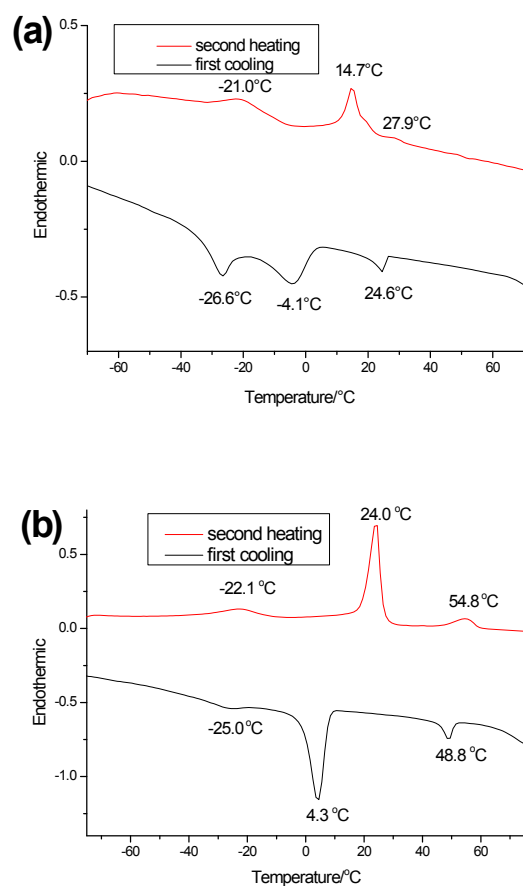


Fig. S2 DSC thermograms for the second heating and the first cooling cycles of (a) **MOXD**, (b) **POXD**.

Reference

- 1 G. A. Crosby and J. N. Demas, *J. Phys. Chem.*, 1971, 75, 991.