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Electronic Supplementary Information (ESI)

Structural Investigation of Resorcinol based Symmetrical Banana Mesogens by XRD, NMR and Polarization measurements

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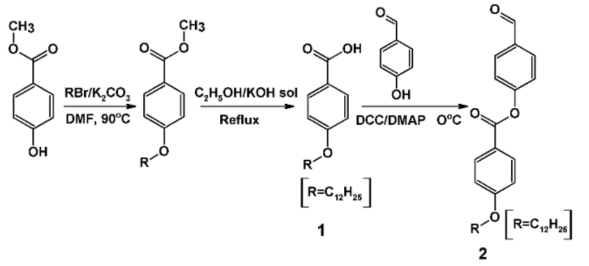

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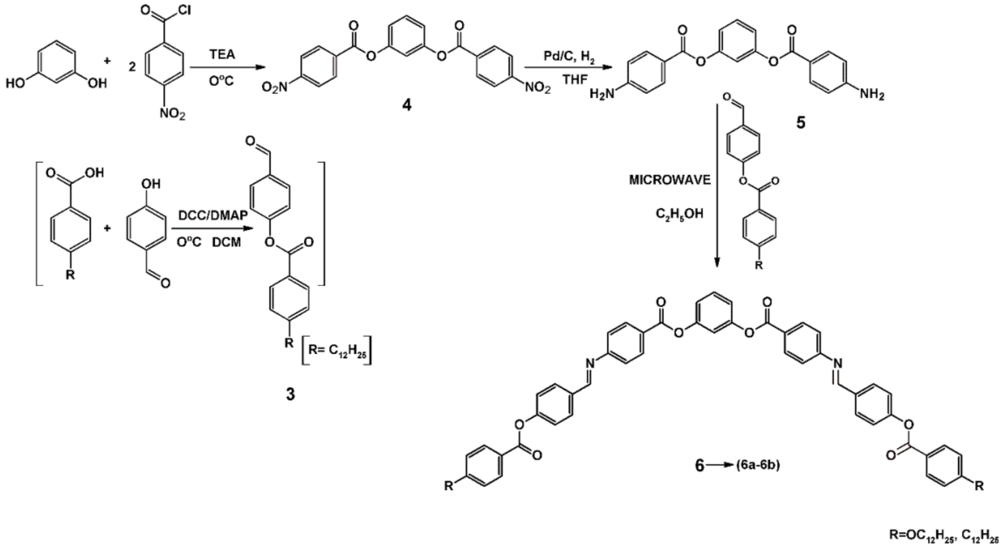
ESI-Scheme 1



Experimental Section

Materials

Resorcinol, 4-hydroxy benzaldehyde, n-bromododecane, 4-nitrobenzoyl chloride, 10% palladium on charcoal (Pd/C), N, N′-dicyclohexylcarbodiimide (DCC) and 4-dimethylamino pyridine (DMAP) were purchased from Aldrich (USA) and used without further purification. Triethylamine, N, N′-dimethylformamide (DMF), tetrahydrofuran (THF), methanol, isopropanol, ethanol and chloroform (SD Fine, Mumbai) were used as received. Dichloromethane (DCM), ethyl acetate, 1,4-dioxane, diethyl ether, toluene, n-hexane, acetone, n-heptane, glacial acetic acid, ethyl methyl ketone (EMK), anhydrous sodium sulphate, potassium hydroxide (pellets), sodium chloride, anhydrous potassium carbonate, sodium bicarbonate, celite-540 and hydrochloric acid were obtained from Merck (India) and used as such.

Synthesis of 4-dodecyloxy benzoic acid (1)

Synthesis of 4-dodecyloxy methyl benzoate

In a typical experiment, 4-hydroxy methylbenzoate (5 g, 0.033 mol) was placed in a 500 ml three necked round bottom flask equipped with stirrer and thermometer. To that, DMF (150 ml) and potassium carbonate (5.53 g, 0.04 mol) were added. The resulting mixture was stirred while maintaining the temperature at 90 °C, then n-bromododecane (7.92 ml, 0.033 mol) was added through a pressure equalizing dropping funnel over a period of 30 minutes and the stirring was continued for about 4 hours and then the reaction mixture was allowed to cool to room temperature, poured into a two liter beaker.[1] The contents were diluted with water (250 ml) and then transferred to a 500 ml separating funnel and diethyl ether was added. The ether layer collected was washed twice using

10% potassium hydroxide solution and followed by distilled water. The organic layer was dried with anhydrous sodium sulphate. Upon evaporation of ether, 4-dodecyloxy methyl benzoate resulted in as a liquid.

Hydrolysis of 4-dodecyloxy methyl benzoate

4-dodecyloxy methylbenzoate (6.4g, 0.02 mol) was placed in a one liter single necked round bottom flask equipped with double wall water condenser. Ethanol (250 ml) and potassium hydroxide (2.8 g, 0.05 mol) dissolved in distilled water (250 ml) were added to the flask. The solution was refluxed for two hours and allowed to cool to room temperature and then neutralized with 10% hydrochloric acid to get a white precipitate.[1] It was purified by recrystallizing from methanol.

4-dodecyloxy benzoic acid (1)

Yield: 84%, m.p-96.2°C, FT-IR (KBr, cm^{-1}): 2921, 2851 ($C\text{-}H_{str}$), 2558 ($O\text{-}H_{str.}$of carboxylic acid), 1681 ($C{=}O_{str}$ of carboxylic acid), 1605, 1512 ($C{=}C_{str}$ aromatic), 1467, 1427 ($C\text{-}H_{ben}$), 1255, 1167 ($C\text{-}O\text{-}C_{asym\&symstr}$ ether); ^{1}H-NMR ppm ($CDCl_3$): 8.05 (d, 2H), 6.93 (d, 2H), 4.01 (t, 2H), 1.79 (m, 2H), 1.45 (m, 2H), 1.34 (m, 16H), 0.87 (t, 3H); ^{13}C-NMR ppm ($CDCl_3$): 171.91, 163.86, 132.42, 120.91, 114.27, 68.38, 32.02, 29.76, 29.73, 29.69, 29.65, 29.45, 29.17, 26.06, 22.79 and 14.23.

Synthesis of 4-formylphenyl 4-dodecyloxybenzoate (2, 3)

In a representative experiment, 4-dodecyloxy benzoic acid (5.2 g, 0.017 mol) and 4-hydroxy benzaldehyde (2.1 g, 0.017 mol) were placed in a 500 ml conical flask. To this, dichloromethane (100 ml) was added and the solution was stirred at room temperature on a magnetic stirrer. 4-dimethylamino pyridine (0.2 g, 0.0017 mol) was added as a catalyst to the reaction mixture. After 10 minutes, N, N^{1}-dicyclohexylcabodiimide (3.6 g, 0.0175 mol) was added to the flask[2] and the solution was allowed to stir for 12 hours. The precipitated N, N^1-dicyclohexyl urea was filtered off and washed with excess of dichloromethane (100 ml). The combined organic solution was taken into 500 ml separating funnel and then washed twice with 5% KOH solution and followed by distilled water, dried over anhydrous sodium sulphate. Then the solution collected was concentrated to get the solid which was purified by recrystallization from isopropyl alcohol.

For synthesizing other mesogen namely 4-formylphenyl 4-dodecylbenzoate, the above procedure was followed.

4-formylphenyl 4-dodecyloxybenzoate (2)

Yield: 70.7%, m.p-67 °C, FT-IR (KBr, cm^{-1}): 2920, 2851 (C-H$_{str}$), 2667 (-CH$_{str}$ of aldehyde), 1728 (C=O$_{str}$), 1682 (-HC=O), 1604, 1512 (C=C$_{str}$ aromatic), 1467, 1428, (C-H$_{ben}$), 1257, 1168 (C-O-C $_{asym\&symstr}$ of ester and ether); ^{1}H-NMR ppm ($CDCl_3$): 10.01 (s, 1H), 8.13 (d, 2H), 7.96 (d, 2H), 7.38 (d, 2H), 6.96 (d, 2H), 4.04 (t, 2H), 1.81 (m, 2H), 1.46 (m, 2H), 1.35 (m, 17H), 0.87 (t, 3H); ^{13}C-NMR ppm ($CDCl_3$): 191.16, 164.36, 163.97, 156.00, 133.95, 132.53, 131.35, 122.71, 120.86, 114.52, 68.48, 32.01, 29.75, 29.73, 29.68, 29.65, 29.44, 29.15, 26.05, 22.78 and 14.23.

4-formylphenyl 4-dodecylbenzoate (3)

Yield: 67.6%, m.p-63°C, FT-IR (KBr, cm^{-1}): 2956, 2918, 2847 (C-H$_{str}$), 1739 (C=O$_{str}$), 1698 (-HC=O), 1601, 1504 (C=C$_{str}$ aromatic), 1461, 1389 (C-H$_{ben}$), 1265, 1158 (C-O-C $_{asym\&symstr}$ of ester and ether); ^{1}H-NMR ppm ($CDCl_3$): 9.99 (s, 1H), 8.10 (d, 2H), 7.95 (d, 2H), 7.39 (d, 2H), 7.32 (d, 2H), 2.69 (t, 2H), 1.64 (m, 2H), 1.36 (m, 18H), 0.8 (t, 3H); ^{13}C-NMR ppm ($CDCl_3$): 191.13, 164.66, 155.92, 150.05, 134.04, 131.36, 130.45, 128.90, 126.35, 122.68, 46.08, 36.20, 32.01, 29.75, 29.73, 29.65, 29.54, 29.44, 29.34, 22.78 and 14.22.

Synthesis of 1, 3-phenylene bis (4-nitrobenzoate) (4)

In a typical experiment, resorcinol (1.5 g, 0.0135mol) dissolved in EMK (20 ml) was placed in a 250 ml two neck round bottom flask equipped with stirrer and was placed in an ice bath. Triethylamine (3.79 ml, 0.027mol) dissolved in EMK (15 ml) was added to the flask at 0°C. 4-nitrobenzoyl chloride (5 g, 0.027 mol) dissolved in 1, 4-dioxane (75 ml) was slowly added through a pressure equalizing dropping funnel for about 45 minutes while maintaining temperature at 0°C and stirred for about 5 hours. The precipitated triethylamine salt was filtered and the solution was concentrated to get white solid. It was washed twice with 5% aqueous $NaHCO_3$ and followed by distilled water, dried in vacuum oven. Then it was recrystallized twice from toluene.

Yield: 67.3%, m.p-192°C, FT-IR (KBr, cm^{-1}): 3079, 3058 (aromatic $C\text{-}H_{str}$), 2945, 2857 ($C\text{-}H_{str}$), 1737 ($C{=}O_{str}$), 1609, 1599, 1527 ($C{=}C_{str}$ aromatic), 1449, 1381 ($C\text{-}H_{ben}$), 1350 ($\text{-}NO_{2str}$), 1281, 1243, 1164 (C-O-C $_{asym\&symstr}$ of ester and ether); ^{1}H-NMR ppm ($CDCl_3$): 8.37 (s, 8H), 7.54 (t, 1H), 7.25 (t, 1H), 7.23(dd, 2H); ^{13}C-NMR ppm ($CDCl_3$): 163.03, 154.08, 151.09, 134.60, 131.45, 130.40, 123.91, 119.58 and 115.54.

Synthesis of 1, 3-phenylene bis (4-aminobenzoate) (5)

The 1, 3-phenylene bis (4-nitrobenzoate) (5 g, 0.012 mol) was placed in 250 ml three neck round bottom flask fixed on a magnetic stirrer and THF (150 ml) was added to the flask. 10% Pd/C (0.5 g) was slowly added while stirring the solution.[3] The stirring was continued at room temperature in an atmosphere of hydrogen while the progress of the reaction was monitored by TLC. The mixture was filtered using celite-540 and the solution so obtained was concentrated to get a solid.

Yield: 71.5%, m.p-189.2°C, FT-IR (KBr, cm^{-1}): 3472, 3374, 3226 (NH_{2str}), 3067 (aromatic C-H_{str}), 2963 (C-H_{str}), 1712 (C=O_{str}), 1624 (NH_{ben}), 1599, 1516 (C=C_{str} aromatic), 1484, 1391 (C-H_{ben}), 1260, 1173, 1126 (C-O-C $_{asym\&symstr}$ of ester and ether); ^{1}H-NMR ppm (DMSO-d_6): 7.76 (d, 4H), 7.42 (t, 1H), 7.04 (t, 1H), 7.04(dd , 2H) 6.61 (d, 4H), 6.08 (s, 4H), ^{13}C-NMR ppm ($CDCl_3$): 165.07, 154.75, 151.93, 132.52, 130.35, 119.77, 116.73, 114.83 and 113.43.

Synthesis of 1, 3-phenylene bis{4-[4-(4-n-dodecyloxybenzoyloxy)benzylideneamino]benzoate} (DBPPDO) (6a)

In a representative experiment, 1, 3-phenylene bis (4-aminobenzoate) (0.42 g, 0.0012 mol) and (1 g, 0.0024 mol) of 4-formylphenyl 4-dodecyloxybenzoate were placed in a 100 ml conical flask. By adding a few drops of ethanol, the material was made into pasty and the flask was kept in a microwave oven (power: 40 W) for about 15 minutes.[4] Then it was allowed to cool to room temperature, washed with methanol and recrystallized twice from ethyl methyl ketone.

Yield: 66.9%, mp: 151.6 °C, FT-IR (KBr, cm^{-1}): 2955, 2920, 2872 (C-H_{str}), 1730 (C=O_{str}), 1626 (-C=N_{str}), 1596, 1510 (C=C_{str} aromatic), 1468, 1393, (C-H_{ben}), 1256, 1134, 1101 (C-O-C $_{asym\&symstr}$ of ester and ether); ^{1}H-NMR ppm ($CDCl_3$): 8.37 (s, 2H), 8.15 (d, 4H), 8.05 (d, 4H), 7.89 (d, 4H), 7.40 (t, 1H), 7.26 (d, 4H), 7.17 (d, 4H), 7.13 (t, 1H), 7.08 (dd, 2H), 6.88 (d, 4H), 3.97 (t, 4H), 1.71 (m, 4H), 1.24 (m, 36H), 0.79 (t, 6H); ^{13}C-NMR ppm ($CDCl_3$):164.55, 163.81, 160.77, 156.94, 154.07, 151.59, 133.31, 132.41, 131.62, 131.24, 130.40, 129.84, 126.48, 122.45,121.16, 120.96, 119.24, 115.92, 114.44, 68.42, 31.94, 29.67, 29.66, 29.61, 29.58, 29.38, 29.12, 26.0, 22.71 and 14.13.

Synthesis of 1, 3-phenylene bis{4-[4-(4-n-dodecylbenzoyloxy)benzylideneamino]benzoate} (DBPPD) (6b)

In a representative experiment, a mixture of 1, 3-phenylene bis (4-aminobenzoate) (0.44 g, 0.0012 mol) and 4-formylphenyl 4-dodecylbenzoate (1 g, 0.0025 mol) was taken into a 100 ml conical flask. A few drops of ethanol were added to make it pasty and the flask was kept in a microwave oven (power: 40 W) for about 15 minutes.[4] Then it was cooled to room temperature, washed with methanol and recrystallized twice from ethyl acetate.

Yield: 64.5%, m.p-157.7 °C, FT-IR (KBr, cm^{-1}): 2956, 2920, 2850 (C-H$_{str}$), 1733 (C=O$_{str}$), 1631 (-C=N$_{str}$), 1604, 1597, 1508 (C=C$_{str}$ aromatic), 1468, 1362 (C-H$_{ben}$), 1276, 1162, 1142 (C-O-C $_{asym\&symstr}$ of ester and ether); ^{1}H-NMR ppm (CDCl$_3$): 8.46 (s, 2H), 8.24 (d, 4H), 8.13 (d, 4H), 8.01 (d, 4H), 7.48 (t, 1H), 7.37 (d, 4H), 7.34 (d, 4H), 7.27 (d, 4H), 7.23 (t, 1H), 7.18 (dd, 2H), 2.70 (t, 4H), 1.66 (m, 4H), 1.27 (m, 36H), 0.89 (t, 6H); ^{13}C-NMR ppm (CDCl$_3$): 164.87, 164.56, 160.75, 156.92, 153.99, 151.58, 149.79, 133.40, 131.62, 130.43, 130.36, 129.86, 128.78, 126.61, 126.49, 122.42, 120.96, 119.25, 115.92, 36.14, 31.94, 31.14, 29.68, 29.65, 29.58, 29.48, 29.37, 29.27, 22.71 and 14.27.

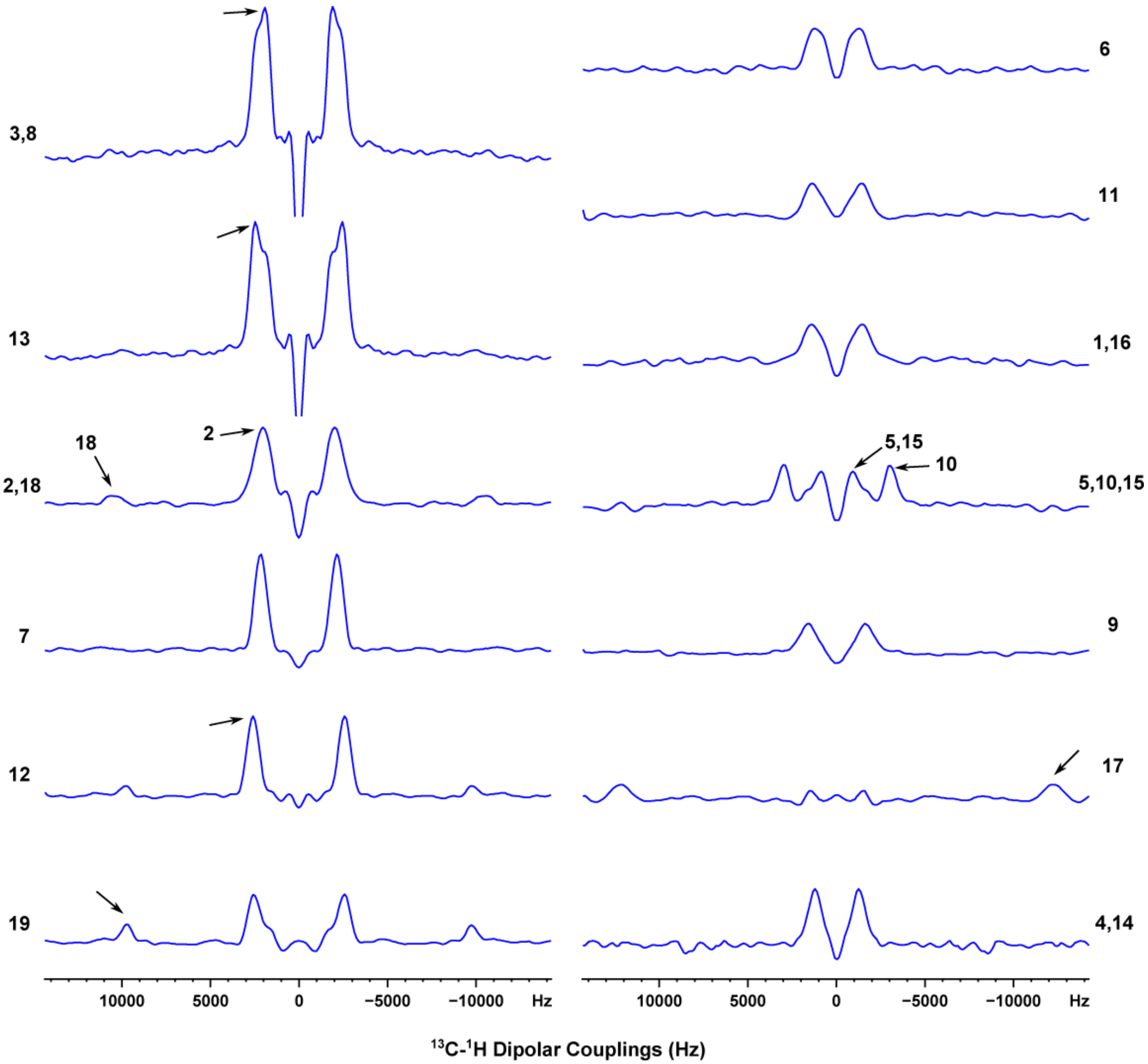


Figure S1: Dipolar cross sections from 2D SAMPI-4 spectrum for all carbon resonances of DBPPD in B_2 phase at 190˚C.

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