Electronic Supplementary Information (ESI)

Intramolecular Charge Transfer Interactions and Molecular Order of Rod like Mesogens

M. Guruprasad Reddy,[a] Nitin. P. Lobo,[b] E. Varathan,[c] S. Easwaramoorthi,[c] and T. Narasimhaswamy*[a]

[a] *Polymer Laboratory,* [b] *Chemical Physics Laboratory,* [c] *Chemical Laboratory, CSIR-Central Leather Research Institute, Adyar, Chennai, India-600020.*

Experimental Section

Materials

N,N-Dimethylaminobenzoic acid, 4-Hydroxy benzaldehyde, 4-Dimethylamino pyridine (DMAP), Dicyclohexylcarbodiimide (DCC), 10% Pd/C, Ammoniumformate ($HCOONH_4$), 4-Hydroxy acetanilide, n-bromoalkanes (C_2-C_{12}, even number carbons only) are used as received (Aldrich, USA). Sodium Phosphate Monobasic anhydrous (NaH_2PO_4), Sodium Chlorite ($NaClO_2$) Tetrahydrofuran (THF), Dichloromechane (DCM), Diethyl ether, Potassium hydroxide, Ethanol, Isopropyl alcohol, heptane are used without further purification (MERCK, India)

Synthesis of 4- formylphenyl 4-(dimethylamino) benzoate (1)

In a representative experiment, 4-(Dimethylamino) benzoic acid (4 g, 0.0242 mole) and 4-hydroxy benzaldehyde (2.2 g, 0.0242 mole) were placed in a 250 ml conical flask. To that 50 ml dichloromethane and 50 ml tetrahydrofuran were added and the solution was stirred with magnetic stirrer. After one hour, dicyclohexylcarbodiimide (4.9 g, 0.0242 mole) dissolved in 25 ml dichloromethane and catalytic amount of 4-dimethylamino pyridine (0.29 g, 0.0024 mole) were added to the reaction mixture.[1] The stirring was continued for 10 hours, then the reaction mixture was filtered and filtrate was concentrated by evaporating the solvent. The semi-solid obtained was re dissolved in dichloromethane and washed with 10%

HCl followed by 5 % KOH solution. The solid obtained was purified by recrystallization in isopropanol.

Yield: 68%, m.p-163.5 °C, FT-IR (KBR, cm^{-1}): 2928, 2851 (C-H_{str}), 1718 (C=O_{str}), 1692 (-HC=O), 1593, 1500 (C=C_{str} aromatic), 1409, 1356 (C-H_{bend}), 1261, 1206, (C-O-C $_{asym\ \&\ sym\ str}$ of ester and ether respectively); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (s, 1H), 7.97 (d, J = 7.9 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 7.7 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H), 3.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 164.7, 156.3, 153.9, 133.6, 132.1, 131.2, 122.7, 115.1, 110.9, 40.1.

Synthesis of 4-((4-(dimethylamino) benzoyl) oxy) benzoic acid (2)

In a representative experiment, 4- formylphenyl 4-(dimethylamino) benzoate (4 g, 0.0148 moles) and resorcinol (2.4 g, 0.0222 moles) dissolved in 140 ml tert-butyl alcohol. Independently, a mixture of sodium phosphate monobasic anhydrous (NaH_2PO_4) (5.3 g, 0.0445 moles) and sodium chlorite ($NaClO_2$) (8 g, 0.0888 moles) were dissolved in 30 ml water.[2] The aqueous solution was added in a drop wise manner into the tert-butyl alcohol solution over a 10-min period. The pale yellow reaction mixture was, then stirred at room temperature overnight. Volatile components were removed in vacuo and the residue was dissolved in 100 ml water. The aqueous solution was acidified to pH 3 by adding 1 N aqueous HCl solution. The liberated white precipitate was isolated, washed successively with water and hexane, and the solid was dried and recrystallized from 1-Propanol.

4-((4-(dimethylamino) benzoyl) oxy) benzoic acid (2)

Yield: 62%, m.p-223.1 °C FT-IR (KBr, cm^{-1}): 2921, 2851 (C-H_{str}), 2558 (O-$H_{str.}$ of carboxylic acid), 1725 (C=O_{str}), 1681 (C=O_{str} of carboxylic acid), 1605, 1512 (C=C_{str} aromatic), 1467, 1427 (C-H_{ben}), 1255, 1167 (C-O-C $_{asym\ \&\ sym\ str}$ of ester and ether); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.4

Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 3.06 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.1, 164.6, 154.9, 154.1, 132.0, 131.1, 128.4, 122.3, 114.6, 111.2, 40.0.

Synthesis of 1-(benzyloxy)-4-(dodecyloxy) benzene (3)

In a representative experiment, 4-(benzyloxy) phenol (4 g, 0.0199 moles) dissolved in 100 ml ethanol , KOH (2.8 g, 0.0499 moles) dissolved in 25 ml distilled water and kept reflux for half an hour and then 1-bromododecane (4.7 ml, 0.0199 moles) added drop by drop using pressure equalizing dropping funnel.[2] The reaction progress check by TLC. The reaction mixture was poured in distilled water the obtained solid was filtered and recrystallized by isopropanol.

The similar procedure was used for 1-(benzyloxy)-4-(ethoxy)benzene, 1-(benzyloxy)-4-(butoxy)benzene, 1-(benzyloxy)-4-(hexyloxy)benzene, 1-(benzyloxy)-4-(octyloxy) benzene and 1-(benzyloxy)-4-(decyloxy)benzene.

1-(benzyloxy)-4-(dodecyloxy) benzene (3f)

Yield: 63%, m.p-80.5 °C, FT-IR (KBr, cm^{-1}): 2998, 2889 (C-H_{str}), 1559, 1512 (C=C_{str} aromatic), 1460, 1430 (C-H_{ben}), 1245, 1160 (C-O-$C_{asym\ \&\ sym\ str}$ of ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 9.1 Hz, 2H), 6.82 (d, *J* = 9.1 Hz, 2H), 5.01 (s, 2H), 3.89 (t, *J* = 6.7 Hz, 2H), 1.80 (m, 2H), 1.52 – 1.08 (m, 18H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 152.9, 137.4, 128.6, 127.9, 127.5, 115.8, 115.4, 70.7, 68.9, 32.0, 29.7, 29.7, 29.7, 29.7, 29.5, 29.4, 29.4, 26.1, 22.8, 14.2.

Synthesis of 4-(dodecyloxy)phenol (4)

In typical experiment, 1-(benzyloxy)-4-(dodecyloxy)benzene (2 g, 0.0054 mole) and ammonium formate (2.67 g, 0.054 mole) dissolved in 100 ml THF and 10% Pd/C (0.2 g) was added and stirred at room temperature 12 hrs. under nitrogen atmosphere.[3] The product purity

was check by TLC. After completion of the reaction the solid Pd/C was filtered by celite powder.

The similar procedure was used for making other compounds homologues namely 4-(ethoxy)phenol, 4-(butoxy)phenol, 4-(hexyloxy)phenol, 4-(octyloxy)phenol and 4-(decyloxy)phenol.

4-dodecyloxyphenol (4f)

Yield: 63%, m.p-80.9°C, FT-IR (KBr, cm^{-1}): 3458 (-O-H_{str}), 2959, 2916 (C-H_{str}), 1601, 1510 (C-C_{str} aromatic), 1441, 1315 (C-H_{ben}), 1167,1129 (C-O-$C_{asym\ \&\ sym\ str}$ of ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.71 (q, *J* = 9.0 Hz, 4H), 5.44 (s, 1H), 3.89 (t, *J* = 6.7 Hz, 2H), 1.80 (m, 2H), 1.52 – 1.08 (m, 18H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CHCl_3$) δ 153.2, 149.5, 116.1, 115.8, 68.9, 32.0, 29.7, 29.7, 29.7, 29.7, 29.5, 29.4, 29.4, 26.1, 22.8, 14.2.

4-((4-(dodecyloxy)phenoxy)carbonyl)phenyl4-(dimethylamino)benzoate(DdPCPDB) (5f)

In a representative experiment, 4-((4-(dimethylamino)benzoyl)oxy) benzoic acid (0.5 g, 0.0017 mole) and 4-dodecyloxyphenol (0.48 g, 0.0017 mole) were placed in a 100 ml conical flask. To that 10 ml dichloromethane and 10 ml tetrahydrofuran were added and the solution was stirred with magnetic stirrer. After one hour, dicyclohexylcarbodiimide (0.36 g, 0.0017 mole) dissolved in 5 ml dichloromethane and catalytic amount of 4-dimethylamino pyridine (0.036 g, 0.00017 mole) were added to the reaction mixture.[1] The stirring was continued for 10 hours, then the reaction mixture was filtered and filtrate was concentrated by evaporating the solvent. The semisolid obtained was re dissolved in dichloromethane and washed with 10% HCl followed by 5 % KOH solution. The solid obtained was purified by recrystallization in heptane.

4-((4-(dodecyloxy)phenoxy)carbonyl)phenyl4-(dimethylamino)benzoate(DdPCPDB) (5f)

Yield: 60%, m.p-113.1°C, FT-IR (KBR, cm^{-1}): 2995, 2869 (C-H_{str}), 1719 (C=O_{str}), 1623 and 1579 (C=C_{str} aromatic), 1419, 1354 (C-H_{bend}), 1260, 1203, (C-O-$C_{asym\ \&\ sym\ str}$ of ester and ether respectively); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 3.89 (t, *J* = 6.7 Hz, 2H), 3.01 (s, 6H), 1.81 – 1.65 (m, 2H), 1.52 – 1.08 (m, 18H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 164.8, 156.9, 155.6, 153.7, 144.2, 132.1, 131.6, 126.7, 122.4, 122.1, 115.6, 115.1, 111.0, 68.4, 40.2, 31.9, 29.6, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 26.0, 22.7, 14.1.

4-((4-ethoxyphenoxy)carbonyl)phenyl 4-(dimethylamino)benzoate (EPCPDB) (5a)

Yield: 65%, m.p-197.4°C, FT-IR (KBR, cm^{-1}): 2990, 2860 (C-H_{str}), 1727 (C=O_{str}), 1603 and 1574 (C=C_{str} aromatic), 1409, 1356 (C-H_{bend}), 1261, 1206, (C-O-$C_{asym\ \&\ sym\ str}$ of ester and ether respectively); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 2H), 8.06 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.6 Hz, 2H), 4.04 (q, *J* = 6.9 Hz, 2H), 3.09 (s, 6H), 1.43 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.9, 156.7, 155.7, 153.9, 144.2, 132.1, 131.6, 126.6, 122.4, 122.1, 115.2, 115.1, 110.8, 63.8, 40.1, 14.8.

4-((4-butoxyphenoxy)carbonyl)phenyl 4-(dimethylamino)benzoate (BPCPDB) (5b)

Yield: 66%, m.p- 158.7°C, FT-IR (KBR, cm^{-1}): 2995, 2872 (C-H_{str}), 1725 (C=O_{str}), 1614 and 1570 (C=C_{str} aromatic), 1415, 1359 (C-H_{bend}), 1260, 1204, (C-O-$C_{asym\ \&\ sym\ str}$ of ester and ether respectively); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.8 Hz, 2H), 8.06 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.70 (d, *J* = 8.2 Hz, 2H), 3.97 (t, *J* = 6.3 Hz, 2H), 3.09 (s, 6H), 1.84 – 1.72 (m, 2H), 1.50 (dd, *J* = 14.7, 7.4 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.9, 156.7, 155.7, 153.9, 144.2, 132.1, 131.6, 126.6, 122.4, 122.1, 115.2, 115.1, 110.8, 68.1, 40.0, 31.3, 19.2, 13.9.

4-((4-(hexyloxy)phenoxy)carbonyl)phenyl 4-(dimethylamino)benzoate (HPCPDB) (5c)

Yield: 63%, m.p-127.9°C, FT-IR (KBR, cm^{-1}): 2990, 2860 (C-H_{str}), 1720 (C=O_{str}), 1603 and 1574 (C=C_{str} aromatic), 1409, 1356 (C-H_{bend}), 1261, 1206, (C-O-C $_{asym\ \&\ sym\ str}$ of ester and ether respectively); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.1 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 3.89 (t, *J* = 6.5 Hz, 2H), 3.03 (s, 6H), 1.80 – 1.66 (m, 2H), 1.36 (m, 6H), 0.84 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 164.7, 156.9, 155.6, 153.5, 144.2, 132.1, 131.6, 126.7, 122.4, 122.1, 116.0, 115.1, 111.3, 68.4, 40.3, 31.6, 29.2, 25.7, 22.6, 14.0.

4-((4-(octyloxy)phenoxy)carbonyl)phenyl 4-(dimethylamino)benzoate (OPCPDB) (5d)

Yield: 61%, m.p-120.2°C, FT-IR (KBR, cm^{-1}): 2998, 2869 (C-H_{str}), 1728 (C=O_{str}), 1612 and 1570 (C=C_{str} aromatic), 1429, 1350 (C-H_{bend}), 1260, 1216, (C-O-C $_{asym\ \&\ sym\ str}$ of ester and ether respectively); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 2H), 8.06 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 3.96 (t, *J* = 6.5 Hz, 2H), 3.09 (s, 6H), 1.85 – 1.72 (m, 2H), 1.52 – 1.17 (m, 10H), 0.89 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.9, 156.9, 155.7, 153.9, 144.2, 132.1, 131.6, 126.6, 122.4, 122.1, 115.2, 115.1, 110.8, 68.8, 40.1, 31.9, 29.6, 29.5, 29.4, 29.3, 22.7, 14.1.

4-((4-(decyloxy)phenoxy)carbonyl)phenyl 4-(dimethylamino)benzoate (DPCPDB) (5e)

Yield: 67%, m.p-119.1°C, FT-IR (KBR, cm^{-1}): 2989, 2895 (C-H_{str}), 1722 (C=O_{str}), 1623 and 1571 (C=C_{str} aromatic), 1411, 1353 (C-H_{bend}), 1259, 1207, (C-O-C $_{asym\ \&\ sym\ str}$ of ester and ether respectively); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.3 Hz, 2H), 8.06 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 8.6 Hz, 2H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.09 (s, 6H), 1.86 – 1.71 (m, 2H), 1.53 – 1.17 (m, 14H), 0.89 (t, *J* = 6.3 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.9, 156.9,

155.7, 153.9, 144.2, 132.1, 131.6, 126.6, 122.4, 122.1, 115.2, 115.1, 110.8, 68.4, 40.1, 31.9, 29.6, 29.6, 29.4, 29.3, 29.3, 26.0, 22.7, 14.1.

Table S_1: Single crystal data for BPCPDB

Identification code	BPCPDB
Empirical formula	$C_{26}H_{27}NO_5$
Formula weight	433.49
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 9.8058(2) A alpha = 64.9330(10) deg. b = 15.4400(3) A beta = 83.4090(10) deg. c = 16.9339(3) A gamma = 88.3180(10) deg.
Volume	2306.46(8) A^3
Z, Calculated density	4, 1.248 Mg/m^3
Absorption coefficient	0.086 mm^-1
F(000)	920
Crystal size	0.20 x 0.15 x 0.10 mm
Theta range for data collection	1.34 to 26.45 deg.
Limiting indices	-12<=h<=12, -18<=k<=19, -21<=l<=21
Reflections collected / unique	35532 / 9485 [R(int) = 0.0644]
Completeness to theta = 26.45	99.6 %
Absorption correction	Semi-empirical from equivalents
Max.and min. transmission	0.9914 and 0.9829
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9485 / 0 / 583
Goodness-of-fit on F^2	0.927
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1038
R indices (all data)	R1 = 0.1539, wR2 = 0.1445
Largest diff. peak and hole	0.206 and -0.174 e.A^-3
CCDC No.:	**1415623**

Table S_2. Atomic coordinates (Å x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for BPCPDB. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
C(26)	6275(5)	10150(3)	7129(3)	159(2)
C(1')	7885(4)	6641(3)	-1386(3)	119(1)
C(1)	6711(4)	803(2)	-948(2)	97(1)
C(2)	5773(3)	2298(2)	-1963(2)	90(1)
C(2')	10263(4)	6356(3)	-1075(3)	120(1)
C(3)	6269(3)	2117(2)	-512(2)	57(1)
C(3')	8813(3)	7288(2)	-460(2)	61(1)
C(4')	7577(3)	7737(2)	-385(2)	64(1)
C(4)	6532(3)	1534(2)	350(2)	64(1)
C(5')	7411(3)	8238(2)	121(2)	62(1)
C(5)	6483(3)	1888(2)	969(2)	62(1)
C(6')	8443(3)	8331(2)	567(2)	54(1)
C(6)	6179(2)	2833(2)	774(2)	50(1)
C(7)	5918(3)	3415(2)	-76(2)	59(1)
C(7')	9687(3)	7917(2)	474(2)	61(1)
C(8')	9875(3)	7405(2)	-24(2)	65(1)
C(8)	5953(3)	3071(2)	-702(2)	62(1)
C(9)	6199(3)	3174(2)	1450(2)	56(1)
C(9')	8156(3)	8844(2)	1119(2)	61(1)
C(10')	9037(3)	9361(2)	2084(2)	59(1)
C(10)	6026(3)	4570(2)	1704(2)	55(1)
C(11')	8165(3)	8965(2)	2844(2)	71(1)
C(11)	5209(3)	4354(2)	2480(2)	65(1)
C(12)	5392(3)	4863(2)	2963(2)	61(1)
C(12')	8001(3)	9436(2)	3381(2)	70(1)
C(13')	8703(3)	10279(2)	3168(2)	59(1)
C(13)	6379(3)	5585(2)	2666(2)	51(1)
C(14)	7180(3)	5797(2)	1876(2)	59(1)
C(14')	9603(3)	10646(2)	2409(2)	72(1)
C(15')	9767(3)	10185(2)	1863(2)	72(1)
C(15)	7012(3)	5288(2)	1397(2)	59(1)

C(16')	8443(3)	10759(2)	3763(2)	71(1)
C(16)	6616(3)	6162(2)	3145(2)	57(1)
C(17')	9073(3)	12050(2)	4043(2)	66(1)
C(17)	6007(3)	6368(2)	4436(2)	64(1)
C(18')	8426(3)	12892(2)	3741(2)	79(1)
C(18)	5078(3)	7020(2)	4475(2)	73(1)
C(19')	8317(3)	13422(2)	4229(2)	81(1)
C(19)	5251(3)	7500(2)	4990(2)	71(1)
C(20)	6374(3)	7308(2)	5456(2)	63(1)
C(20')	8836(3)	13095(2)	5015(2)	68(1)
C(21')	9482(3)	12235(2)	5321(2)	84(1)
C(21)	7287(3)	6627(2)	5420(2)	72(1)
C(22')	9609(3)	11707(2)	4824(2)	86(1)
C(22)	7110(3)	6155(2)	4909(2)	72(1)
C(23)	5815(3)	8501(2)	5987(2)	79(1)
C(23')	9152(3)	13361(2)	6278(2)	83(1)
C(24')	8871(4)	14156(2)	6573(2)	89(1)
C(24)	6414(4)	8895(2)	6555(2)	94(1)
C(25')	9183(4)	13890(3)	7476(2)	103(1)
C(25)	5701(5)	9733(3)	6564(2)	125(2)
C(26')	8960(4)	14704(3)	7761(2)	112(1)
N(1)	6328(3)	1770(2)	-1132(2)	75(1)
N(1')	8966(3)	6750(2)	-932(2)	82(1)
O(1')	7071(2)	9195(1)	1221(1)	79(1)
O(1)	6517(2)	2726(1)	2176(1)	78(1)
O(2')	9255(2)	8896(1)	1524(1)	69(1)
O(2)	5841(2)	4113(1)	1168(1)	66(1)
O(3)	7419(2)	6818(1)	2891(1)	77(1)
O(3')	7605(3)	10502(2)	4388(2)	116(1)
O(4)	5809(2)	5873(1)	3919(1)	76(1)
O(4')	9251(2)	11542(1)	3515(1)	76(1)
O(5)	6645(2)	7727(1)	5989(1)	79(1)
O(5')	8691(2)	13686(2)	5435(1)	87(1)

Table S3. Bond lengths [Å] and angles [deg] for BPCPDB

C(26)-C(25)	1.521(4)
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(1')-N(1')	1.432(4)
C(1')-H(1'1)	0.9600
C(1')-H(1'2)	0.9600
C(1')-H(1'3)	0.9600
C(1)-N(1)	1.436(3)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600

C(2)-N(1)	1.455(3)
C(2)-H(2A)	0.9600
C(2)-H(2B)	0.9600
C(2)-H(2C)	0.9600
C(2')-N(1')	1.434(4)
C(2')-H(2'1)	0.9600
C(2')-H(2'2)	0.9600
C(2')-H(2'3)	0.9600
C(3)-N(1)	1.363(3)
C(3)-C(8)	1.402(3)
C(3)-C(4)	1.403(4)
C(3')-N(1')	1.370(3)
C(3')-C(4')	1.399(3)
C(3')-C(8')	1.401(4)
C(4')-C(5')	1.372(3)
C(4')-H(4')	0.9300
C(4)-C(5)	1.368(3)
C(4)-H(4)	0.9300
C(5')-C(6')	1.374(3)
C(5')-H(5')	0.9300
C(5)-C(6)	1.383(3)
C(5)-H(5)	0.9300
C(6')-C(7')	1.385(3)
C(6')-C(9')	1.462(3)
C(6)-C(7)	1.385(3)
C(6)-C(9)	1.451(3)
C(7)-C(8)	1.370(3)
C(7)-H(7)	0.9300
C(7')-C(8')	1.375(3)
C(7')-H(7')	0.9300
C(8')-H(8')	0.9300
C(8)-H(8)	0.9300
C(9)-O(1)	1.202(3)
C(9)-O(2)	1.369(3)
C(9')-O(1')	1.207(3)
C(9')-O(2')	1.364(3)
C(10')-C(15')	1.363(3)
C(10')-C(11')	1.369(4)
C(10')-O(2')	1.407(3)
C(10)-C(11)	1.372(3)
C(10)-C(15)	1.375(3)
C(10)-O(2)	1.395(3)
C(11')-C(12')	1.379(3)
C(11')-H(11')	0.9300
C(11)-C(12)	1.381(3)
C(11)-H(11)	0.9300
C(12)-C(13)	1.382(3)
C(12)-H(12)	0.9300
C(12')-C(13')	1.377(3)

C(12')-H(12')	0.9300
C(13')-C(14')	1.379(4)
C(13')-C(16')	1.482(4)
C(13)-C(14)	1.385(3)
C(13)-C(16)	1.474(3)
C(14)-C(15)	1.371(3)
C(14)-H(14)	0.9300
C(14')-C(15')	1.379(3)
C(14')-H(14')	0.9300
C(15')-H(15')	0.9300
C(15)-H(15)	0.9300
C(16')-O(3')	1.190(3)
C(16')-O(4')	1.347(3)
C(16)-O(3)	1.196(3)
C(16)-O(4)	1.353(3)
C(17')-C(18')	1.347(4)
C(17')-C(22')	1.362(4)
C(17')-O(4')	1.412(3)
C(17)-C(18)	1.354(4)
C(17)-C(22)	1.369(4)
C(17)-O(4)	1.415(3)
C(18')-C(19')	1.382(4)
C(18')-H(18')	0.9300
C(18)-C(19)	1.390(4)
C(18)-H(18)	0.9300
C(19')-C(20')	1.362(4)
C(19')-H(19')	0.9300
C(19)-C(20)	1.380(4)
C(19)-H(19)	0.9300
C(20)-O(5)	1.366(3)
C(20)-C(21)	1.377(4)
C(20')-C(21')	1.369(4)
C(20')-O(5')	1.370(3)
C(21')-C(22')	1.393(4)
C(21')-H(21')	0.9300
C(21)-C(22)	1.373(4)
C(21)-H(21)	0.9300
C(22')-H(22')	0.9300
C(22)-H(22)	0.9300
C(23)-O(5)	1.425(3)
C(23)-C(24)	1.511(4)
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(23')-O(5')	1.422(3)
C(23')-C(24')	1.517(4)
C(23')-H(23C)	0.9700
C(23')-H(23D)	0.9700
C(24')-C(25')	1.472(4)
C(24')-H(24A)	0.9700

C(24')-H(24B)	0.9700
C(24)-C(25)	1.459(4)
C(24)-H(24C)	0.9700
C(24)-H(24D)	0.9700
C(25')-C(26')	1.528(4)
C(25')-H(25A)	0.9700
C(25')-H(25B)	0.9700
C(25)-H(25C)	0.9700
C(25)-H(25D)	0.9700
C(26')-H(26D)	0.9600
C(26')-H(26E)	0.9600
C(26')-H(26F)	0.9600

C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
N(1')-C(1')-H(1'1)	109.5
N(1')-C(1')-H(1'2)	109.5
H(1'1)-C(1')-H(1'2)	109.5
N(1')-C(1')-H(1'3)	109.5
H(1'1)-C(1')-H(1'3)	109.5
H(1'2)-C(1')-H(1'3)	109.5
N(1)-C(1)-H(1A)	109.5
N(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
N(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
N(1)-C(2)-H(2A)	109.5
N(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
N(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
N(1')-C(2')-H(2'1)	109.5
N(1')-C(2')-H(2'2)	109.5
H(2'1)-C(2')-H(2'2)	109.5
N(1')-C(2')-H(2'3)	109.5
H(2'1)-C(2')-H(2'3)	109.5
H(2'2)-C(2')-H(2'3)	109.5
N(1)-C(3)-C(8)	121.9(3)
N(1)-C(3)-C(4)	121.3(3)
C(8)-C(3)-C(4)	116.8(2)
N(1')-C(3')-C(4')	121.2(3)
N(1')-C(3')-C(8')	121.8(3)
C(4')-C(3')-C(8')	117.0(2)

C(5')-C(4')-C(3')	120.9(3)
C(5')-C(4')-H(4')	119.6
C(3')-C(4')-H(4')	119.6
C(5)-C(4)-C(3)	121.1(3)
C(5)-C(4)-H(4)	119.5
C(3)-C(4)-H(4)	119.5
C(6')-C(5')-C(4')	122.0(3)
C(6')-C(5')-H(5')	119.0
C(4')-C(5')-H(5')	119.0
C(4)-C(5)-C(6)	121.8(3)
C(4)-C(5)-H(5)	119.1
C(6)-C(5)-H(5)	119.1
C(5')-C(6')-C(7')	117.6(2)
C(5')-C(6')-C(9')	118.3(3)
C(7')-C(6')-C(9')	124.1(3)
C(7)-C(6)-C(5)	117.6(2)
C(7)-C(6)-C(9)	123.3(2)
C(5)-C(6)-C(9)	119.1(2)
C(8)-C(7)-C(6)	121.4(3)
C(8)-C(7)-H(7)	119.3
C(6)-C(7)-H(7)	119.3
C(8')-C(7')-C(6')	121.4(3)
C(8')-C(7')-H(7')	119.3
C(6')-C(7')-H(7')	119.3
C(7')-C(8')-C(3')	121.0(3)
C(7')-C(8')-H(8')	119.5
C(3')-C(8')-H(8')	119.5
C(7)-C(8)-C(3)	121.3(3)
C(7)-C(8)-H(8)	119.3
C(3)-C(8)-H(8)	119.3
O(1)-C(9)-O(2)	121.1(2)
O(1)-C(9)-C(6)	126.5(3)
O(2)-C(9)-C(6)	112.3(2)
O(1')-C(9')-O(2')	121.9(3)
O(1')-C(9')-C(6')	125.0(3)
O(2')-C(9')-C(6')	113.1(3)
C(15')-C(10')-C(11')	121.7(2)
C(15')-C(10')-O(2')	117.9(3)
C(11')-C(10')-O(2')	120.3(2)
C(11)-C(10)-C(15)	121.3(2)
C(11)-C(10)-O(2)	121.5(2)
C(15)-C(10)-O(2)	117.1(2)
C(10')-C(11')-C(12')	118.4(3)
C(10')-C(11')-H(11')	120.8
C(12')-C(11')-H(11')	120.8
C(10)-C(11)-C(12)	119.1(3)
C(10)-C(11)-H(11)	120.4
C(12)-C(11)-H(11)	120.4
C(13)-C(12)-C(11)	120.4(2)

C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8
C(13')-C(12')-C(11')	121.2(3)
C(13')-C(12')-H(12')	119.4
C(11')-C(12')-H(12')	119.4
C(14')-C(13')-C(12')	119.0(2)
C(14')-C(13')-C(16')	122.8(3)
C(12')-C(13')-C(16')	118.2(3)
C(12)-C(13)-C(14)	119.3(2)
C(12)-C(13)-C(16)	123.1(2)
C(14)-C(13)-C(16)	117.6(2)
C(15)-C(14)-C(13)	120.6(2)
C(15)-C(14)-H(14)	119.7
C(13)-C(14)-H(14)	119.7
C(13')-C(14')-C(15')	120.3(3)
C(13')-C(14')-H(14')	119.9
C(15')-C(14')-H(14')	119.9
C(10')-C(15')-C(14')	119.4(3)
C(10')-C(15')-H(15')	120.3
C(14')-C(15')-H(15')	120.3
C(14)-C(15)-C(10)	119.3(2)
C(14)-C(15)-H(15)	120.4
C(10)-C(15)-H(15)	120.4
O(3')-C(16')-O(4')	122.7(3)
O(3')-C(16')-C(13')	124.7(3)
O(4')-C(16')-C(13')	112.6(3)
O(3)-C(16)-O(4)	122.6(2)
O(3)-C(16)-C(13)	125.0(3)
O(4)-C(16)-C(13)	112.4(2)
C(18')-C(17')-C(22')	121.3(3)
C(18')-C(17')-O(4')	118.9(3)
C(22')-C(17')-O(4')	119.8(3)
C(18)-C(17)-C(22)	121.4(3)
C(18)-C(17)-O(4)	119.3(3)
C(22)-C(17)-O(4)	119.2(3)
C(17')-C(18')-C(19')	119.4(3)
C(17')-C(18')-H(18')	120.3
C(19')-C(18')-H(18')	120.3
C(17)-C(18)-C(19)	119.9(3)
C(17)-C(18)-H(18)	120.1
C(19)-C(18)-H(18)	120.1
C(20')-C(19')-C(18')	120.7(3)
C(20')-C(19')-H(19')	119.6
C(18')-C(19')-H(19')	119.6
C(20)-C(19)-C(18)	119.4(3)
C(20)-C(19)-H(19)	120.3
C(18)-C(19)-H(19)	120.3
O(5)-C(20)-C(21)	115.7(3)
O(5)-C(20)-C(19)	124.7(3)

C(21)-C(20)-C(19)	119.6(3)
C(19')-C(20')-C(21')	119.5(3)
C(19')-C(20')-O(5')	115.8(3)
C(21')-C(20')-O(5')	124.7(3)
C(20')-C(21')-C(22')	119.8(3)
C(20')-C(21')-H(21')	120.1
C(22')-C(21')-H(21')	120.1
C(20)-C(21)-C(22)	120.7(3)
C(20)-C(21)-H(21)	119.7
C(22)-C(21)-H(21)	119.7
C(17')-C(22')-C(21')	119.3(3)
C(17')-C(22')-H(22')	120.3
C(21')-C(22')-H(22')	120.3
C(17)-C(22)-C(21)	119.0(3)
C(17)-C(22)-H(22)	120.5
C(21)-C(22)-H(22)	120.5
O(5)-C(23)-C(24)	107.5(3)
O(5)-C(23)-H(23A)	110.2
C(24)-C(23)-H(23A)	110.2
O(5)-C(23)-H(23B)	110.2
C(24)-C(23)-H(23B)	110.2
H(23A)-C(23)-H(23B)	108.5
O(5')-C(23')-C(24')	106.4(3)
O(5')-C(23')-H(23C)	110.4
C(24')-C(23')-H(23C)	110.4
O(5')-C(23')-H(23D)	110.4
C(24')-C(23')-H(23D)	110.4
H(23C)-C(23')-H(23D)	108.6
C(25')-C(24')-C(23')	112.8(3)
C(25')-C(24')-H(24A)	109.0
C(23')-C(24')-H(24A)	109.0
C(25')-C(24')-H(24B)	109.0
C(23')-C(24')-H(24B)	109.0
H(24A)-C(24')-H(24B)	107.8
C(25)-C(24)-C(23)	112.9(3)
C(25)-C(24)-H(24C)	109.0
C(23)-C(24)-H(24C)	109.0
C(25)-C(24)-H(24D)	109.0
C(23)-C(24)-H(24D)	109.0
H(24C)-C(24)-H(24D)	107.8
C(24')-C(25')-C(26')	112.9(3)
C(24')-C(25')-H(25A)	109.0
C(26')-C(25')-H(25A)	109.0
C(24')-C(25')-H(25B)	109.0
C(26')-C(25')-H(25B)	109.0
H(25A)-C(25')-H(25B)	107.8
C(24)-C(25)-C(26)	114.4(3)
C(24)-C(25)-H(25C)	108.7
C(26)-C(25)-H(25C)	108.7

C(24)-C(25)-H(25D)	108.7
C(26)-C(25)-H(25D)	108.7
H(25C)-C(25)-H(25D)	107.6
C(25')-C(26')-H(26D)	109.5
C(25')-C(26')-H(26E)	109.5
H(26D)-C(26')-H(26E)	109.5
C(25')-C(26')-H(26F)	109.5
H(26D)-C(26')-H(26F)	109.5
H(26E)-C(26')-H(26F)	109.5
C(3)-N(1)-C(1)	121.9(3)
C(3)-N(1)-C(2)	121.3(2)
C(1)-N(1)-C(2)	115.8(2)
C(3')-N(1')-C(1')	121.7(3)
C(3')-N(1')-C(2')	121.5(3)
C(1')-N(1')-C(2')	116.5(3)
C(9')-O(2')-C(10')	116.0(2)
C(9)-O(2)-C(10)	118.0(2)
C(16)-O(4)-C(17)	116.0(2)
C(16')-O(4')-C(17')	116.7(2)
C(20)-O(5)-C(23)	118.2(2)
C(20')-O(5')-C(23')	118.2(2)

Symmetry transformations used to generate equivalent atoms:

Table S_4. Anisotropic displacement parameters ($Å^2$ x 10^3) for BPCPDB. The anisotropic displacement factor exponent takes the form:-2 pi^2 [h^2a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(26)	244(6)	138(4)	160(4)	-118(4)	-60(4)	16(4)
C(1')	120(3)	151(4)	151(4)	-121(3)	-46(3)	22(3)
C(1)	136(3)	85(2)	103(3)	-67(2)	-31(2)	27(2)
C(2)	120(3)	96(2)	72(2)	-51(2)	-31(2)	20(2)
C(2')	99(3)	161(4)	158(4)	-128(3)	1(3)	13(3)
C(3)	62(2)	61(2)	62(2)	-40(2)	-11(1)	4(1)
C(3')	67(2)	65(2)	61(2)	-38(2)	4(2)	-9(2)
C(4')	64(2)	70(2)	69(2)	-39(2)	-9(2)	-5(2)
C(4)	77(2)	53(2)	75(2)	-36(2)	-19(2)	10(2)
C(5')	67(2)	59(2)	70(2)	-37(2)	-7(2)	3(2)
C(5)	75(2)	57(2)	61(2)	-30(2)	-17(2)	5(2)
C(6')	65(2)	48(2)	53(2)	-25(1)	-2(1)	-5(1)
C(6)	54(2)	51(2)	53(2)	-29(1)	-10(1)	1(1)
C(7)	68(2)	53(2)	63(2)	-32(2)	-11(2)	5(1)
C(7')	63(2)	67(2)	62(2)	-36(2)	-4(2)	-10(2)
C(8')	61(2)	73(2)	73(2)	-44(2)	0(2)	-3(2)
C(8)	80(2)	58(2)	55(2)	-30(2)	-15(2)	9(2)

C(9)	64(2)	51(2)	59(2)	-28(2)	-8(2)	-1(1)
C(9')	74(2)	53(2)	61(2)	-28(2)	-8(2)	0(2)
C(10')	73(2)	57(2)	62(2)	-38(2)	-9(2)	-1(2)
C(10)	76(2)	48(2)	51(2)	-30(1)	-14(2)	7(2)
C(11')	94(2)	57(2)	70(2)	-34(2)	-2(2)	-15(2)
C(11)	81(2)	55(2)	62(2)	-30(2)	2(2)	-16(2)
C(12)	76(2)	54(2)	55(2)	-28(1)	4(2)	-7(2)
C(12')	90(2)	63(2)	57(2)	-28(2)	5(2)	-14(2)
C(13')	75(2)	56(2)	52(2)	-28(2)	-5(2)	-6(2)
C(13)	65(2)	43(2)	50(2)	-24(1)	-7(1)	0(1)
C(14)	72(2)	53(2)	56(2)	-27(2)	-2(2)	-6(1)
C(14')	93(2)	61(2)	69(2)	-37(2)	5(2)	-20(2)
C(15')	89(2)	68(2)	67(2)	-40(2)	10(2)	-21(2)
C(15)	75(2)	55(2)	50(2)	-27(1)	1(1)	-1(2)
C(16')	93(2)	68(2)	62(2)	-38(2)	-2(2)	-11(2)
C(16)	72(2)	50(2)	51(2)	-25(1)	-2(2)	0(2)
C(17')	82(2)	68(2)	65(2)	-43(2)	-7(2)	-7(2)
C(17)	88(2)	60(2)	52(2)	-35(2)	8(2)	-16(2)
C(18')	103(3)	78(2)	70(2)	-41(2)	-26(2)	8(2)
C(18)	86(2)	79(2)	67(2)	-43(2)	-8(2)	-2(2)
C(19')	107(3)	76(2)	80(2)	-48(2)	-33(2)	21(2)
C(19)	91(2)	66(2)	68(2)	-41(2)	-2(2)	1(2)
C(20)	86(2)	57(2)	53(2)	-30(2)	2(2)	-12(2)
C(20')	73(2)	74(2)	79(2)	-53(2)	-14(2)	3(2)
C(21')	106(3)	84(2)	87(2)	-56(2)	-37(2)	18(2)
C(21)	88(2)	72(2)	66(2)	-38(2)	-5(2)	2(2)
C(22')	114(3)	79(2)	92(3)	-56(2)	-39(2)	26(2)
C(22)	90(2)	68(2)	67(2)	-39(2)	1(2)	-1(2)
C(23)	122(3)	61(2)	64(2)	-36(2)	-7(2)	2(2)
C(23')	93(2)	97(2)	83(2)	-61(2)	-15(2)	4(2)
C(24')	112(3)	98(3)	81(2)	-59(2)	-16(2)	9(2)
C(24)	140(3)	83(2)	79(2)	-53(2)	-20(2)	12(2)
C(25')	109(3)	128(3)	107(3)	-81(3)	-26(2)	15(2)
C(25)	198(4)	102(3)	108(3)	-73(3)	-39(3)	27(3)
C(26')	137(3)	124(3)	116(3)	-89(3)	-14(3)	0(3)
N(1)	105(2)	69(2)	74(2)	-50(2)	-30(2)	22(1)
N(1')	76(2)	106(2)	101(2)	-79(2)	-4(2)	-1(2)
O(1')	88(2)	81(2)	90(2)	-55(1)	-22(1)	24(1)
O(1)	115(2)	66(1)	61(1)	-33(1)	-24(1)	14(1)
O(2')	77(1)	73(1)	77(1)	-51(1)	-10(1)	0(1)
O(2)	98(2)	52(1)	62(1)	-35(1)	-22(1)	9(1)
O(3)	101(2)	67(1)	69(1)	-40(1)	12(1)	-28(1)
O(3')	158(2)	116(2)	93(2)	-71(2)	44(2)	-57(2)
O(4)	103(2)	73(1)	63(1)	-45(1)	17(1)	-26(1)
O(4')	98(2)	76(1)	75(1)	-52(1)	4(1)	-20(1)
O(5)	106(2)	72(1)	78(1)	-49(1)	-13(1)	-1(1)
O(5')	114(2)	93(2)	89(2)	-66(1)	-32(1)	21(1)

Table S_5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for BPCPDB

	x	y	z	U(eq)
H(26A)	6230	9672	7724	238
H(26B)	5744	10689	7111	238
H(26C)	7213	10351	6910	238
H(1'1)	7076	6386	-978	178
H(1'2)	8164	6211	-1647	178
H(1'3)	7689	7252	-1835	178
H(1A)	7464	634	-598	146
H(1B)	6982	751	-1489	146
H(1C)	5943	379	-633	146
H(2A)	4811	2394	-1854	135
H(2B)	5901	1942	-2312	135
H(2C)	6242	2907	-2272	135
H(2'1)	10910	6865	-1428	180
H(2'2)	10152	5957	-1371	180
H(2'3)	10597	5981	-520	180
H(4')	6858	7695	-681	77
H(4)	6742	895	504	77
H(5')	6574	8523	164	74
H(5)	6660	1484	1535	74
H(7)	5716	4054	-224	70
H(7')	10410	7986	754	74
H(8')	10721	7132	-73	78
H(8)	5763	3479	-1265	74
H(11')	7695	8393	2994	85
H(11)	4541	3871	2677	78
H(12)	4847	4719	3492	73
H(12')	7405	9179	3897	84
H(14)	7837	6288	1668	71
H(14')	10101	11206	2265	86
H(15')	10369	10434	1350	86
H(15)	7559	5427	869	71
H(18')	8056	13114	3210	95
H(18)	4326	7145	4157	88
H(19')	7885	14008	4018	97
H(19)	4615	7947	5021	86
H(21')	9835	12005	5858	101
H(21)	8031	6486	5746	87
H(22')	10054	11125	5024	103
H(22)	7730	5697	4885	86
H(23A)	4877	8279	6219	95
H(23B)	5817	8994	5393	95
H(23C)	10125	13231	6246	99

H(23D)	8659	12779	6687	99
H(24A)	9420	14717	6178	107
H(24B)	7912	14324	6536	107
H(24C)	6369	8400	7150	112
H(24D)	7373	9064	6341	112
H(25A)	10131	13695	7519	124
H(25B)	8606	13346	7874	124
H(25C)	4741	9561	6775	150
H(25D)	5745	10224	5967	150
H(26D)	9502	15253	7356	168
H(26E)	9232	14506	8338	168
H(26F)	8007	14865	7767	168

Table S_6. Torsion angles [deg] for BPCPDB

N(1')-C(3')-C(4')-C(5')	177.0(3)
C(8')-C(3')-C(4')-C(5')	-2.3(4)
N(1)-C(3)-C(4)-C(5)	179.4(3)
C(8)-C(3)-C(4)-C(5)	-0.2(4)
C(3')-C(4')-C(5')-C(6')	0.7(4)
C(3)-C(4)-C(5)-C(6)	-0.2(4)
C(4')-C(5')-C(6')-C(7')	1.4(4)
C(4')-C(5')-C(6')-C(9')	-177.5(2)
C(4)-C(5)-C(6)-C(7)	0.2(4)
C(4)-C(5)-C(6)-C(9)	-177.5(2)
C(5)-C(6)-C(7)-C(8)	0.3(4)
C(9)-C(6)-C(7)-C(8)	177.9(2)
C(5')-C(6')-C(7')-C(8')	-1.9(4)
C(9')-C(6')-C(7')-C(8')	177.0(2)
C(6')-C(7')-C(8')-C(3')	0.3(4)
N(1')-C(3')-C(8')-C(7')	-177.5(3)
C(4')-C(3')-C(8')-C(7')	1.8(4)
C(6)-C(7)-C(8)-C(3)	-0.7(4)
N(1)-C(3)-C(8)-C(7)	-178.9(3)
C(4)-C(3)-C(8)-C(7)	0.7(4)
C(7)-C(6)-C(9)-O(1)	-174.0(3)
C(5)-C(6)-C(9)-O(1)	3.5(4)
C(7)-C(6)-C(9)-O(2)	4.2(4)
C(5)-C(6)-C(9)-O(2)	-178.3(2)
C(5')-C(6')-C(9')-O(1')	0.3(4)
C(7')-C(6')-C(9')-O(1')	-178.6(3)
C(5')-C(6')-C(9')-O(2')	-179.7(2)
C(7')-C(6')-C(9')-O(2')	1.4(4)
C(15')-C(10')-C(11')-C(12')	1.9(4)
O(2')-C(10')-C(11')-C(12')	178.8(3)
C(15)-C(10)-C(11)-C(12)	-0.6(4)
O(2)-C(10)-C(11)-C(12)	-176.7(2)
C(10)-C(11)-C(12)-C(13)	0.4(4)

C(10')-C(11')-C(12')-C(13')	-0.6(4)
C(11')-C(12')-C(13')-C(14')	-1.1(4)
C(11')-C(12')-C(13')-C(16')	178.2(3)
C(11)-C(12)-C(13)-C(14)	0.3(4)
C(11)-C(12)-C(13)-C(16)	179.3(3)
C(12)-C(13)-C(14)-C(15)	-0.9(4)
C(16)-C(13)-C(14)-C(15)	-179.9(2)
C(12')-C(13')-C(14')-C(15')	1.6(4)
C(16')-C(13')-C(14')-C(15')	-177.7(3)
C(11')-C(10')-C(15')-C(14')	-1.4(5)
O(2')-C(10')-C(15')-C(14')	-178.4(3)
C(13')-C(14')-C(15')-C(10')	-0.4(5)
C(13)-C(14)-C(15)-C(10)	0.8(4)
C(11)-C(10)-C(15)-C(14)	0.0(4)
O(2)-C(10)-C(15)-C(14)	176.3(2)
C(14')-C(13')-C(16')-O(3')	174.3(3)
C(12')-C(13')-C(16')-O(3')	-5.0(5)
C(14')-C(13')-C(16')-O(4')	-4.7(4)
C(12')-C(13')-C(16')-O(4')	176.0(3)
C(12)-C(13)-C(16)-O(3)	-176.7(3)
C(14)-C(13)-C(16)-O(3)	2.3(4)
C(12)-C(13)-C(16)-O(4)	3.0(4)
C(14)-C(13)-C(16)-O(4)	-178.0(2)
C(22')-C(17')-C(18')-C(19')	0.7(5)
O(4')-C(17')-C(18')-C(19')	-176.2(3)
C(22)-C(17)-C(18)-C(19)	1.3(4)
O(4)-C(17)-C(18)-C(19)	179.0(2)
C(17')-C(18')-C(19')-C(20')	-1.1(5)
C(17)-C(18)-C(19)-C(20)	0.2(4)
C(18)-C(19)-C(20)-O(5)	-179.4(3)
C(18)-C(19)-C(20)-C(21)	-1.6(4)
C(18')-C(19')-C(20')-C(21')	0.6(5)
C(18')-C(19')-C(20')-O(5')	178.9(3)
C(19')-C(20')-C(21')-C(22')	0.3(5)
O(5')-C(20')-C(21')-C(22')	-177.9(3)
O(5)-C(20)-C(21)-C(22)	179.6(2)
C(19)-C(20)-C(21)-C(22)	1.7(4)
C(18')-C(17')-C(22')-C(21')	0.1(5)
O(4')-C(17')-C(22')-C(21')	177.1(3)
C(20')-C(21')-C(22')-C(17')	-0.7(5)
C(18)-C(17)-C(22)-C(21)	-1.3(4)
O(4)-C(17)-C(22)-C(21)	-179.0(2)
C(20)-C(21)-C(22)-C(17)	-0.2(4)
O(5')-C(23')-C(24')-C(25')	174.9(3)
O(5)-C(23)-C(24)-C(25)	176.5(3)
C(23')-C(24')-C(25')-C(26')	177.5(3)
C(23)-C(24)-C(25)-C(26)	180.0(3)
C(8)-C(3)-N(1)-C(1)	177.2(3)
C(4)-C(3)-N(1)-C(1)	-2.4(4)

C(8)-C(3)-N(1)-C(2)	-14.0(4)
C(4)-C(3)-N(1)-C(2)	166.4(3)
C(4')-C(3')-N(1')-C(1')	1.5(5)
C(8')-C(3')-N(1')-C(1')	-179.2(3)
C(4')-C(3')-N(1')-C(2')	174.6(3)
C(8')-C(3')-N(1')-C(2')	-6.1(5)
O(1')-C(9')-O(2')-C(10')	1.5(4)
C(6')-C(9')-O(2')-C(10')	-178.5(2)
C(15')-C(10')-O(2')-C(9')	-115.8(3)
C(11')-C(10')-O(2')-C(9')	67.1(3)
O(1)-C(9)-O(2)-C(10)	8.2(4)
C(6)-C(9)-O(2)-C(10)	-170.1(2)
C(11)-C(10)-O(2)-C(9)	-71.2(3)
C(15)-C(10)-O(2)-C(9)	112.5(3)
O(3)-C(16)-O(4)-C(17)	-2.5(4)
C(13)-C(16)-O(4)-C(17)	177.8(2)
C(18)-C(17)-O(4)-C(16)	104.4(3)
C(22)-C(17)-O(4)-C(16)	-77.8(3)
O(3')-C(16')-O(4')-C(17')	0.7(5)
C(13')-C(16')-O(4')-C(17')	179.8(2)
C(18')-C(17')-O(4')-C(16')	-105.8(3)
C(22')-C(17')-O(4')-C(16')	77.2(4)
C(21)-C(20)-O(5)-C(23)	174.0(2)
C(19)-C(20)-O(5)-C(23)	-8.2(4)
C(24)-C(23)-O(5)-C(20)	-174.4(2)
C(19')-C(20')-O(5')-C(23')	176.9(3)
C(21')-C(20')-O(5')-C(23')	-4.8(4)
C(24')-C(23')-O(5')-C(20')	179.7(2)

Symmetry transformations used to generate equivalent atoms:

Table S_7. Hydrogen bonds for BPCPDB [Å and deg.]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: fin

```
Bond precision:  C-C = 0.0044 A          Wavelength=0.71073

Cell:          a=9.8058(2)       b=15.4400(3)     c=16.9339(3)
               alpha=64.933(1)   beta=83.409(1)   gamma=88.318(1)
Temperature:   293 K

                Calculated                Reported
Volume          2306.46(8)                2306.46(8)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C26 H27 N O5              C26 H27 N O5
Sum formula     C26 H27 N O5              C26 H27 N O5
Mr              433.49                    433.49
Dx,g cm-3       1.248                     1.248
Z               4                         4
Mu (mm-1)       0.086                     0.086
F000            920.0                     920.0
F000'           920.46
h,k,lmax        12,19,21                  12,19,21
Nref            9523                      9485
Tmin,Tmax       0.985,0.991               0.983,0.991
Tmin'           0.983

Correction method= # Reported T Limits: Tmin=0.983 Tmax=0.991
AbsCorr = MULTI-SCAN

Data completeness= 0.996          Theta(max)= 26.450

R(reflections)= 0.0510( 3907)     wR2(reflections)= 0.1445( 9485)

S = 0.927                 Npar= 583
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

```
DIFF003_ALERT_1_A  _diffrn_measurement_device_type is missing
           Diffractometer make and type. Replaces _diffrn_measurement_type.
```

Alert level C

```
PLAT026_ALERT_3_C Ratio Observed / Unique Reflections too Low ....        41 %
PLAT220_ALERT_2_C Large Non-Solvent  C     Ueq(max)/Ueq(min) Range      3.2 Ratio
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....      N1' Check
PLAT242_ALERT_2_C Low       Ueq as Compared to Neighbors for .....     C20' Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....      2.1 Note
PLAT334_ALERT_2_C Small Average Benzene  C-C Dist. C10'   -C15'        1.37 Ang.
PLAT334_ALERT_2_C Small Average Benzene  C-C Dist. C17'   -C22'        1.37 Ang.
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............   0.0044 Ang.
```

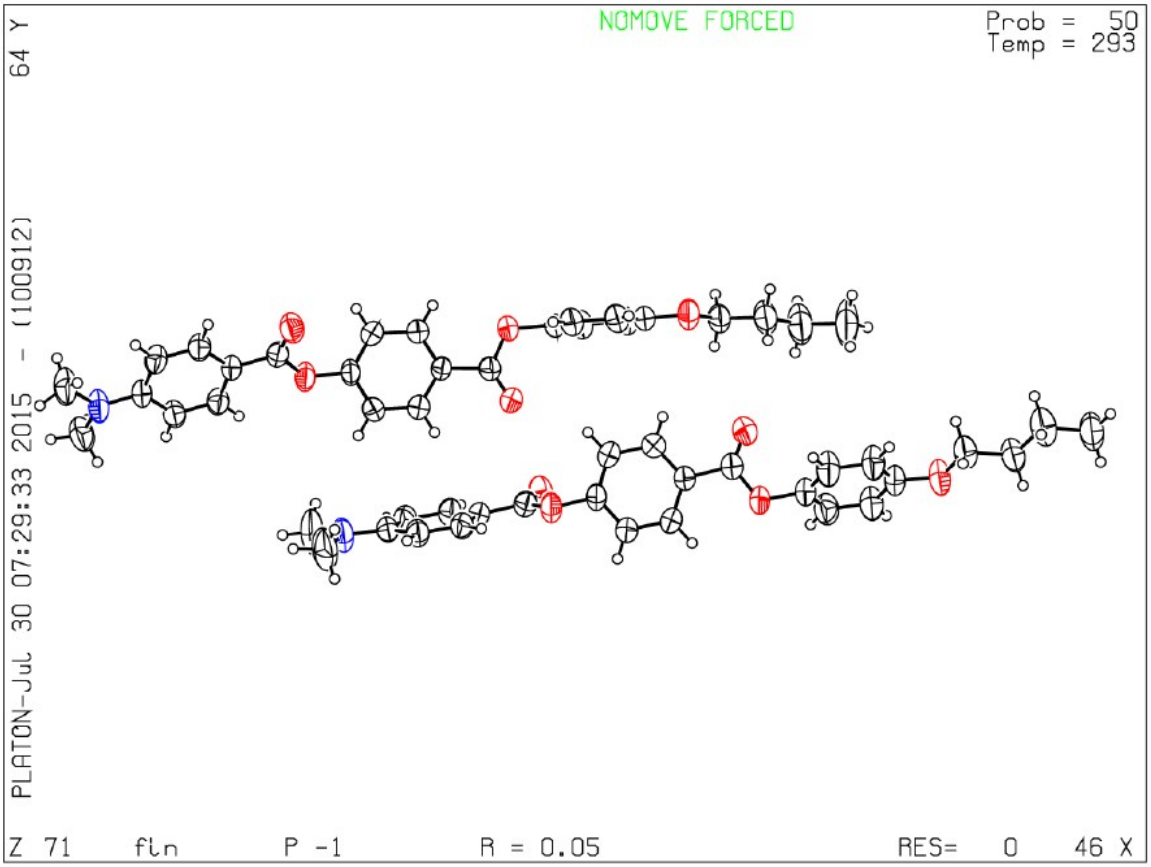
Alert level G

```
PLAT005_ALERT_5_G No _iucr_refine_instructions_details  in the CIF    Please Do !
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical         ? Check
PLAT093_ALERT_1_G No su's on H-positions, refinement reported as .     mixed Check
PLAT154_ALERT_1_G The su's on the Cell Angles are Equal .........   0.00100 Degree
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)       293 Check
PLAT200_ALERT_1_G Reported   _diffrn_ambient_temperature ..... (K)       293 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....        C2 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........         6 Note
PLAT899_ALERT_4_G SHELXL97   is Deprecated and Succeeded by SHELXL      2014 Note
```

```
   1 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   8 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   9 ALERT level G = General information/check it is not something unexpected

   6 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   6 ALERT type 2 Indicator that the structure model may be wrong or deficient
   2 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

Datablock fin - ellipsoid plot



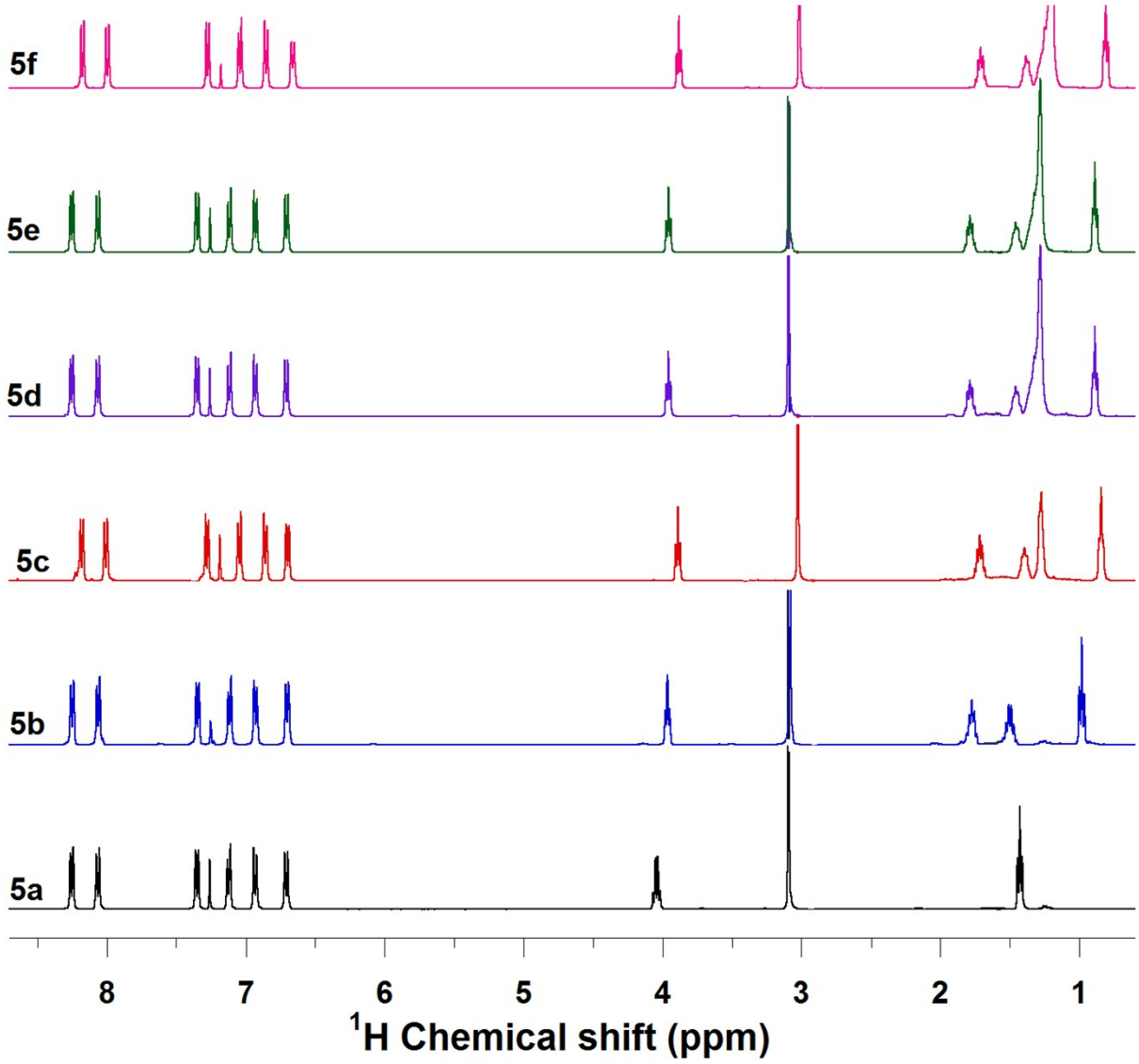


Figure S_1: Solution ^{1}H NMR spectra of synthesized mesogens {5(a-f)}

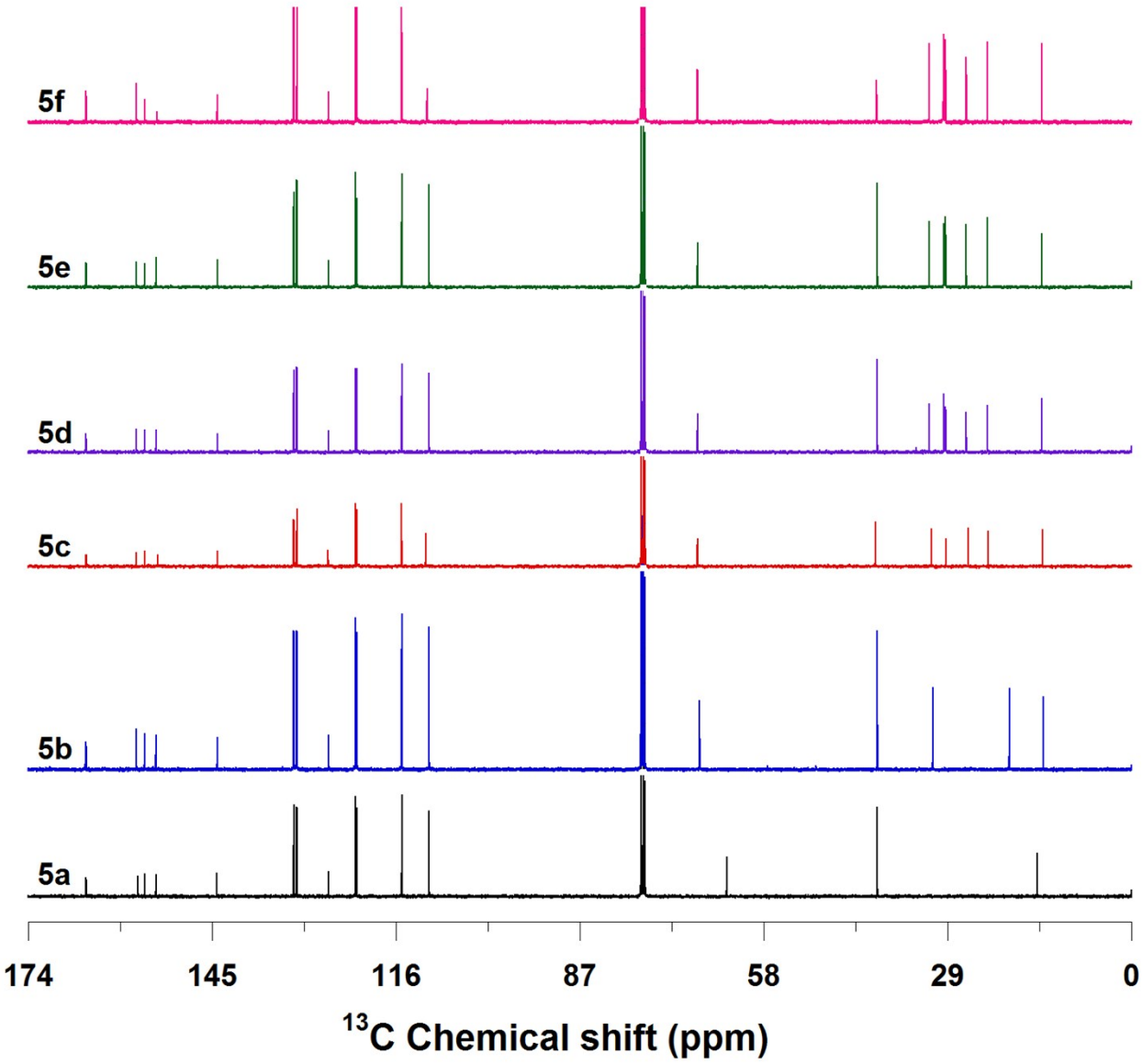


Figure S_2: Solution proton decoupled ^{13}C NMR spectra of synthesized mesogens {5(a-f)}

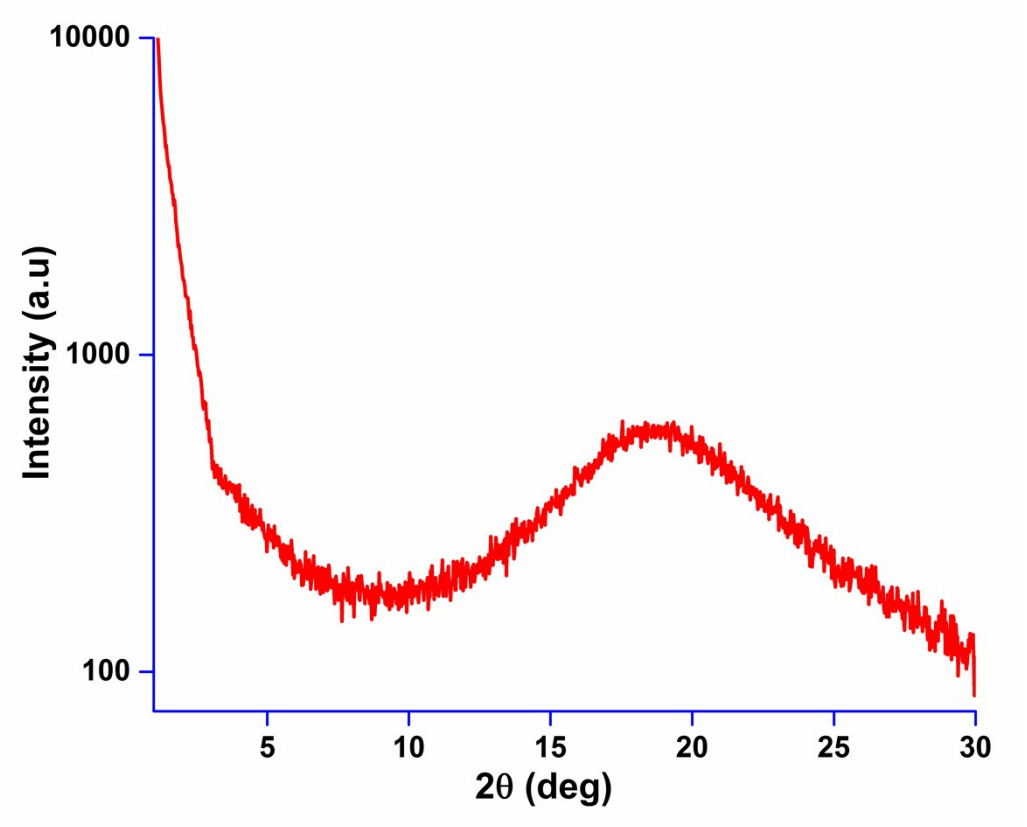


Figure S_3: Powder X-ray diffraction profile for DdPCPDB in nematic phase at 180 °C

Notes and References

1. M. E. Neubert, Jr. S. J. Laskos, L. J, Maurer, L. T. Carlino and J. P. Ferrato, *Mol. Cryst. Liq. Cryst.* 1978, **44**, 197-210.
2. G. S. Lee, Y. J. Lee, S. Y. Choi, Y. S. Park and K. B. Yoon, *J. Am. Chem. Soc.* 2000, **122**, 12151-12157.
3. B. Kosata, G. M. Tamba, U. Baumeister, K. Pelz, S. Diele, G. Pelzl, G. Galli, S. Samaritani, E.V. Agina, N. I. Boiko, V. P. Shibaev, and W. Weissflog, *Chem. Mater.* 2006, **18**, 691-701.