**Supplementary Information**

**Influence of Meta-Extended Rigid-Core, Complementary Hydrogen Bonding and Flexible Chain on Polymorphism in Schiff-based Liquid Crystals: (4)MeOBD(3)AmBA:nOBAs**

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References, Schemes and figure numbers refer to main text.

**Appendix-A**

NMR spectra analyzed [61,62] to determine the presence of H-atoms on the body of HBLC. Data for observed chemical shifts (δH) for all members of (4)MeOBD(3)AmBA:nOBA’s for n=3,4,5,6,7,8,9,10,11 and 12 is:

**1H NMR Study**

**(4)MeOBD(3)AmnBA:3OBA** is observed with chemical shift (δH); 1.05 (3H, t, *J* =7.5Hz,-C**H**3), 1.78-1.90 (2H, m,-OCH2C**H**2CH2-), 3.88 (3H, s, -O-C**H**3), 3.97-4.01 (2H, t, J = 6.6 Hz, -OC**H**2-CH2-), 6.92-8.07 (12H, m, Ar-**H**), 8.43 (1H, s, -C**H**=N), 9.89 (1H, s, -COO**H**).

**(4)MeOBD(3)AmnBA:4OBA** is observed with chemical shift (δH);0.99 (3H, t, *J* =6.9Hz,-C**H**3), 1.44-1.57 (2H, m,-[C**H**2]1- ), 1.75-1.82 (2H, m, -OCH2C**H**2CH2-), 3.88 (3H, s, -O-C**H**3), 4.01-4.05 (2H, t, J = 6.6 Hz, -OC**H**2-CH2-), 6.92-8.07 (12H, m, Ar-**H**), 8.43 (1H, s, -C**H**=N), 9.89 (1H, s, -COO**H**).

**(4)MeOBD(3)AmnBA:5OBA** is observed with chemical shift (δH); 0.91 (3H, t, *J* =6.9Hz,-C**H**3), 1.33-1.50 (4H, m,-[C**H**2]2- ), 1.77-1.86 (2H, m,-OCH2C**H**2CH2-), 3.88 (3H, s, -O-C**H**3), 4.00-4.04 (2H, t, J = 6.6 Hz, -OC**H**2-CH2-), 6.92-8.07 (12H, m, Ar-**H**), 8.43 (1H, s, -C**H**=N), 9.89 (1H, s, -COO**H**).

**(4)MeOBD(3)AmnBA:6OBA** is observed with chemical shift (δH); 0.91 (3H, t, *J* =6.9Hz,-C**H**3), 1.32-1.49 (6H, m,-[C**H**2]3- ), 1.76-1.85 (2H, m,-OCH2C**H**2CH2-), 3.88 (3H, s, -O-C**H**3), 4.00-4.04 (2H, t, J = 6.6 Hz, -OC**H**2-CH2-), 6.92-8.07 (12H, m, Ar-**H**), 8.43 (1H, s, -C**H**=N), 9.89 (1H, s, -COO**H**).

**(4)MeOBD(3)AmnBA:7OBA** is observed with chemical shift (δH); 0.90 (3H, t, *J* =6.9Hz,-C**H**3), 1.31-1.49 (8H, m,-[C**H**2]4- ), 1.76-1.85 (2H, m,-OCH2C**H**2CH2-), 3.89 (3H, s, -O-C**H**3), 4.00-4.04 (2H, t, J = 6.6 Hz, -OC**H**2-CH2-), 6.92-8.07 (12H, m, Ar-**H**), 8.43 (1H, s, -C**H**=N), 9.89 (1H, s, -COO**H**).

**(4)MeOBD(3)AmnBA:8OBA** is observed with chemical shift (δH); 0.89 (3H, t, *J* =6.9Hz,-C**H**3), 1.29-1.47 (10H, m,-[C**H**2]5- ), 1.76-1.85 (2H, m,-OCH2C**H**2CH2-), 3.89 (3H, s, -O-C**H**3), 4.00-4.04 (2H, t, J = 6.6 Hz, -OC**H**2-CH2-), 6.92-8.07 (12H, m, Ar-**H**), 8.43 (1H, s, -C**H**=N), 9.89 (1H, s, -COO**H**).

**(4)MeOBD(3)AmnBA:9OBA** is observed with chemical shift (δH); 0.88 (3H, t, *J* =6.9Hz,-C**H**3), 1.28-1.48 (12H, m,-[C**H**2]6- ), 1.76-1.83 (2H, m,-OCH2C**H**2CH2-), 3.89 (3H, s, -O-C**H**3), 4.00-4.04 (2H, t, J = 6.6 Hz, -OC**H**2-CH2-), 6.92-8.07 (12H, m, Ar-**H**), 8.43 (1H, s, -C**H**=N), 9.89 (1H, s, -COO**H**).

**(4)MeOBD(3)AmnBA:10OBA** is observed with chemical shift (δH); 0.88 (3H, t, *J* =6.9Hz,-C**H**3), 1.28-1.46 (14H, m,-[C**H**2]7- ), 1.76-1.85 (2H, m,-OCH2C**H**2CH2-), 3.88 (3H, s, -O-C**H**3), 3.99-4.04 (2H, t, *J*= 6.6 Hz, -OC**H**2-CH2-), 6.91-8.07 (12H, m, Ar-**H**), 8.43 (1H, s, -C**H**=N), 9.89 (1H, s, -COO**H**).

**(4)MeOBD(3)AmnBA:11OBA** is observed with chemical shift (δH); 0.88 (3H, t, *J* =6.9Hz,-C**H**3), 1.27-1.46 (16H, m,-[C**H**2]8- ), 1.76-1.85 (2H, m,-OCH2C**H**2CH2-), 3.89 (3H, s, -O-C**H**3), 4.00-4.02 (2H, t, J = 6.6 Hz, -OC**H**2-CH2-), 6.91-8.07 (12H, m, Ar-**H**), 8.43 (1H, s, -C**H**=N), 9.90 (1H, s, -COO**H**).

**(4)MeOBD(3)AmnBA:12OBA** is observed with chemical shift (δH); 0.88(3H, t, *J*=6.9Hz,-C**H**3), 1.27-1.46 (18H, m,-[C**H**2]9- ), 1.76-1.85 (2H, m,-OCH2C**H**2CH2-), 3.88 (3H, s, -O-C**H**3), 3.99-4.02(2H, t, *J*=6.6 Hz,-O-C**H**2-CH2-), 6.91-8.07 (12H, m,Ar-**H**), 8.43 (1H, s,-C**H**=N), 9.89(1H, s,-COO**H**).

**1H NMR study for (4)MeOBD(3)AmBA:5OBA HBLC (**Fig-2**) as Representative:**

As per the molecular formula for n=5 in Scheme-1, the number of H-atoms expected to be on the molecular body of (4)MeOBD(3)AmBA:5OBA is TWENTY NINE.

Salient features of the observed 1H NMR spectra are;

a. A triplet at δ0.91ppm infers the presence of 3-H atoms relevant to end methyl group of 5OBA moiety.

b. A multiplet at δ1.33-1.86ppm infers the presence of 6-H atoms relevant to three methylene (-CH2-)units of 5OBA.

c. A singlet in the range of δ3.88ppm infers the presence of 3-H atoms pertaining to methoxy (-OCH3) group connected to Schiff base intermediate.

d. A triplet at δ4.00–4.04ppm infers the presence of 2-H atoms pertaining -OCH2 group of 5OBA.

e. A multiplet in the range of at δ6.92–8.07ppm infers the presence of 12-H atoms corresponding to three aromatic rings (Ar–H) of HBLC complex.

f. A singlet at δ8.43ppm infers the presence of 1-H atom pertaining to the Schiff base CH=N moiety.

g. Asignal (by integrated envelope) in the range of δ10.2-11.6ppm infers the presence of 2-H atoms pertaining to the two acid (-COOH)moieties that participate in HB.

An overview of 1H NMR spectra (points a−g) infers the presence of TWENTY NINE H-atoms on the molecular body of the HBLC. Since, observed number of H-atoms is found to agree with THE expected number of H-atoms, the targeted synthesis is argued to be successful. The HBLC product is considered to be pure at spectroscopic level.

It is also noticed (Fig-2) that chemical shift relevant to the H-atom pertaining to hydroxyl (-OH) moieties (i.e., Schiff based intermediate and nOBA) of acid groups (–COOH) is found (δ~10-12) to vouch [61,62] for the de-shielding effect due to their vicinity of HB interaction.

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**Appendix-B**

**13C NMR Study**

The presence of C-atoms on the body of HBLC complexes is estimated [61,62] from the13C-NMR spectra. Data for chemical shift are presented here for all the ten resulting HBLCs (n=3-12).

**(4)MeOBD(3)AmnBA:3OBA**

δC:10.42, 22.41, 55.42, 55.55, 69.72, 114.18, 114.26, 116.27, 120.27, 120.45, 121.36, 121.86, 127.00, 127.20, 128.87, 129.23, 129.35, 130.46, 130.77, 132.00, 132.33, 152.51, 160.86, 162.55, 163.70, 172.04, 190.90.

**(4)MeOBD(3)AmnBA:4OBA**

δC:13.78, 19.16, 31.10, 55.42, 55.55, 67.95, 114.17, 114.26, 116.27, 120.27, 120.45, 121.34, 121.86, 127.01, 127.20, 128.86, 129.23, 129.34, 130.45, 130.77, 132.00, 132.32, 152.51, 160.86, 162.54, 163.71, 172.05, 190.89.

**(4)MeOBD(3)AmnBA:5OBA**

δC:13.97, 22.40,28.17, 28.76, 55.42, 55.55, 68.27, 114.19, 114.27, 116.28, 120.28, 120.46, 121.35, 121.87,127.01,127.21, 128.88, 129.24,129.35, 130.46, 130.78, 132.01, 132.33, 146.42, 152.52, 160.86, 162.56, 163.71, 172.05, 172.36, 190.89.

**(4)MeOBD(3)AmnBA:6OBA**

δC:13.98, 22.54, 25.62, 29.02, 31.50, 55.40, 55.53, 68.27, 114.17, 114.25, 116.27, 120.27, 120.45, 121.34, 121.86, 127.00, 127.20, 128.86, 129.22, 129.33, 130.46, 130.77, 132.00, 132.32, 146.40, 152.49, 160.86, 162.54, 163.70, 172.08, 172.39, 190.89.

**(4)MeOBD(3)AmnBA:7OBA**

δC:14.05, 22.58, 25.92, 29.00, 29.07, 31.73, 55.42, 55.55, 68.28,114.19, 114.26, 116.27,120.27,120.46, 121.35, 121.87, 127.01, 127.20, 128.88, 129.24, 129.35, 130.37, 130.46, 130.78, 132.01, 132.33, 146.42, 152.52, 160.86, 162.55, 163.71, 172.05, 190.89.

**(4)MeOBD(3)AmnBA:8OBA**

δC:14.08, 22.64, 25.98, 29.09, 29.20, 29.31, 31.79, 55.45, 55.58, 69.31, 114.21, 114.28, 116.24, 120.23, 120.44, 121.33, 121.87, 127.00, 127.19, 128.93, 129.25, 129.38, 130.34, 130.43, 130.77, 132.01, 132.34, 146.47, 152.59, 160.82, 162.56, 163.72, 171.78, 172.07, 190.86.

**(4)MeOBD(3)AmnBA:9OBA**

δC:14.05, 22.62, 25.93, 29.05, 29.20, 29.32, 29.47, 31.83, 55.40, 55.53, 68.26, 114.17, 114.24, 116.25, 120.24, 120.44, 121.33, 121.85, 126.99, 127.18, 128.87, 129.21, 129.33, 130.44, 130.75, 131.99, 132.31, 146.40, 152.50, 160.83, 162.53, 163.69, 164.61, 172.02, 172.33, 190.86.

**(4)MeOBD(3)AmnBA:10OBA**

δC:14.07, 22.64, 25.94, 29.06, 29.28, 29.32, 29.51, 31.86, 55.40, 55.53, 68.27, 114.17, 114.24, 116.27, 120.23, 120.44, 121.35, 121.84, 126.98, 127.19, 128.87, 129.21, 129.32, 130.50, 130.76, 131.99, 132.31, 146.39, 152.49, 160.82, 162.53, 163.69, 172.02, 172.34, 190.86.

**(4)MeOBD(3)AmnBA:11OBA**

δC:14.08, 22.65, 25.94, 29.06, 29.31, 29.56, 31.88, 55.42, 55.55, 68.28, 114.18, 114.25, 116.24, 120.24, 120.44, 121.31, 121.86, 127.00, 127.19, 128.89, 129.23, 129.35, 130.42, 130.76, 131.99, 132.33, 146.42, 152.54, 160.83, 162.54, 163.71, 171.95, 172.26, 190.86.

**(4)MeOBD(3)AmnBA:12OBA**

δC:14.07, 22.65, 25.94, 29.05, 29.31, 29.54, 29.60, 31.88, 55.40, 55.53, 68.26, 114.16, 114.24, 116.25, 120.21, 120.43, 121.37, 121.83, 126.95, 127.18, 128.88, 129.20, 129.32, 130.41, 130.54, 130.75, 131.99, 132.30, 146.40, 152.50, 160.80, 162.52, 163.67, 171.96, 172.28, 190.86.

The number of C-atoms in (4)MeOBD(3)AmBA:nOBA’s (for n=3 to 12) are estimated from the observed 13C NMR chemical shifts (δC).13C-NMR spectra for (4)MeOBD(3)AmnBA:5OBA is presented in Figure-3 (as representative). As per the proposed (Scheme-1) molecular formula, (4)MeOBD(3)AmnBA:5OBA is expected to possess TWENTY SEVEN Carbon atoms on its molecular body.

Salient features of 13C NMR spectrum are;

i)A peak at δ3.97 ppm infers the presence one C-atom of end methyl carbon of

5OBA.

ii)Peaks in the range of δ22.4–28.8ppm infer the presence of three C-atoms relevant

to the three methylene (-CH2-) groups of 5OBA.

iii)Peak at δ55.9ppm infers the presence of one C-atom corresponding to the

methoxy (-OCH3) group of schiff base moiety connected at para position of

aromatic ring .

iv)Peak at δ68.27ppm infers the presence of one C-atom adjacent to O-atom of

5OBA moiety.

v)Peaks in the range of δ114.19 - 152.52ppm infer the presence of eighteen C-atoms

of three aromatic rings in HBLC.

vi)Peak at δ160.86 ppm infers the presence of one carbon atom in the Schiff base

(CH=N-) moiety.

vii)Peaks in range of δ172.05 - 172.36ppm infer the presence of two C-atoms

pertaining to the two acid (–COOH) moieties.

An overview of the NMR (from i to vii) spectrum infers that TWENTY SEVEN Carbon atoms are present on the body of (4)MeOBD(3)AmnBA:5OBA. Since, observed number of C-atoms agrees with the expected, the targeted synthesis of HBLC complex is argued to be successful. Further, HBLC is considered to be pure at spectroscopic level.

It is also noticed (Fig-3) that the NMR signals (for C-atom) pertaining to the para-positioned (to nOBA) and meta-positioned (Schiff based intermediate) acid (–COOH) moieties are found to be witnessed (δ 10.2 – 11.6) to imply [61,62] a shift due to their vicinity to HB interaction.