Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supporting Information: Dipolar Relaxation in Thin Films of Supramolecular Stacks of Benzenecarboxamides: Insights to Enhance their Ferroelectric Characteristics

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## Details of MD simulations:

The molecules were considered in an all-atom representation and the interaction parameters were taken from the DREIDING force field.[1] The functional form of the force field is provided in Equations 1 and 2 below. The interaction parameters are provided in Tables S1- S6 for the sake of completeness. The atom notations are: $C_3$-$sp^3$, $C_2$-carbon atom of amide group, $C_R$-aromatic carbon, H-Hydrogen, $H_{hb}$-Hydrogen participating in hydrogen bond, $N_R$-Nitrogen, $O_R$-Oxygen and Cl-Chlorine of tetrachloromethane.

$$E = \sum^{\text{bond}} K_r(r-r_o)^2 + \sum^{\text{angle}} K_\theta(\theta-\theta_0)^2 + \sum^{\text{dihedral}} K_\phi[1+dcos(n\phi)] + \sum^{\text{improper}} (1/2)K_\omega\left[\frac{1+cos(\omega_0)}{sin(\omega_0)}\right]^2[cos(\omega)-cos(\omega_0)] + E_{nb} \tag{1}$$

$$E_{nb} = E_{vdW} + E_Q + E_{hb}$$

$$\text{where,} \quad E_{vdW} = Aexp(-Cr_{ij}) - \frac{B}{r_{ij}^6}$$

$$E_{hb} = \begin{cases} L(r) & r < r_{in} \\ S(r) * LJ(r) & r_{in} < r < r_{out} \\ 0 & r > r_{out} \end{cases} \tag{2}$$

$$\text{Where,} \quad LJ(r) = D_{hb}\left[5\left(\frac{R_{hb}}{R_{DA}}\right)^{12} - 6\left(\frac{R_{hb}}{R_{DA}}\right)^{10}\right]cos^4(\theta_{DHA})$$

$$S(r) = \frac{[r_{out}^2 - r^2]^2[r_{out}^2 + 2r^2 - 3r_{in}^2]}{[r_{out}^2 - r_{in}^2]^3}$$

$$E_Q = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

## Force-field parameters:

**Table S1: Non-bonded interaction parameters of atoms in system.**

| Atom pairs | pair style | A ($\frac{kcal}{mole}$) | C ($Å^{-1}$) | B ($\frac{Å^6 * kcal}{mole}$) |
|---|---|---|---|---|
| $C_2$,$C_2$ | $E_{vdW}$ | 88366.7126395 | 0.2777754 | 583.0176588 |
| $C_2$,$C_3$ | $E_{vdW}$ | 88366.7126395 | 0.2777754 | 583.0176588 |
| $C_2$,$C_R$ | $E_{vdW}$ | 88366.7126395 | 0.2777754 | 583.0176588 |
| $C_2$,H | $E_{vdW}$ | 17353.2373205 | 0.2675420 | 135.2359749 |
| $C_2$,$H_{hb}$ | $E_{vdW}$ | 1199.2541785 | 0.2718906 | 11.1370044 |
| $C_2$,$N_R$ | $E_{vdW}$ | 73336.2339858 | 0.2709990 | 438.3045053 |
| $C_2$,$O_R$ | $E_{vdW}$ | 69732.3531147 | 0.2645411 | 395.6858342 |
| $C_2$,Cl | $E_{vdW}$ | 141410.6995235 | 0.2813384 | 1051.9927862 |
| $C_3$,$C_3$ | $E_{vdW}$ | 88366.7126395 | 0.2777754 | 583.0176588 |
| $C_3$,$C_R$ | $E_{vdW}$ | 88366.7126395 | 0.2777754 | 583.0176588 |
| $C_3$,H | $E_{vdW}$ | 17353.2373205 | 0.2675420 | 135.2359749 |
| $C_3$,$H_{hb}$ | $E_{vdW}$ | 1199.2541785 | 0.2718906 | 11.1370044 |
| $C_3$,$N_R$ | $E_{vdW}$ | 73336.2339858 | 0.2709990 | 438.3045053 |
| $C_3$,$O_R$ | $E_{vdW}$ | 69732.3531147 | 0.2645411 | 395.6858342 |
| $C_3$,Cl | $E_{vdW}$ | 141410.6995235 | 0.2813384 | 1051.9927862 |
| $C_R$,$C_R$ | $E_{vdW}$ | 88366.7126395 | 0.2777754 | 583.0176588 |
| $C_R$,H | $E_{vdW}$ | 17353.2373205 | 0.2675420 | 135.2359749 |
| $C_R$,$H_{hb}$ | $E_{vdW}$ | 1199.2541785 | 0.2718906 | 11.1370044 |
| $C_R$,$N_R$ | $E_{vdW}$ | 73336.2339858 | 0.2709990 | 438.3045053 |
| $C_R$,$O_R$ | $E_{vdW}$ | 69732.3531147 | 0.2645411 | 395.6858342 |
| $C_R$,Cl | $E_{vdW}$ | 141410.6995235 | 0.2813384 | 1051.9927862 |
| H,H | $E_{vdW}$ | 3407.7859921 | 0.2580359 | 31.3691509 |
| H,$H_{hb}$ | $E_{vdW}$ | 235.5065810 | 0.2620786 | 2.5833242 |
| H,$N_R$ | $E_{vdW}$ | 14401.5889528 | 0.2612501 | 101.6685107 |
| H,$O_R$ | $E_{vdW}$ | 13693.8677062 | 0.2552434 | 91.7827423 |
| H,Cl | $E_{vdW}$ | 141410.6995235 | 0.2813384 | 1051.9927862 |
| $H_{hb}$,$H_{hb}$ | $E_{vdW}$ | 16.2754791 | 0.2662500 | 0.2127429 |
| $H_{hb}$,$N_R$ | $E_{vdW}$ | 995.2705314 | 0.2653949 | 8.3726438 |
| $H_{hb}$,$O_R$ | $E_{vdW}$ | 946.3610601 | 0.2591984 | 7.5585273 |
| $H_{hb}$,Cl | $E_{vdW}$ | 1919.1318453 | 0.2753033 | 20.0955291 |
| $N_R$,$N_R$ | $E_{vdW}$ | 60862.3208284 | 0.2645453 | 329.5111845 |
| $N_R$,$O_R$ | $E_{vdW}$ | 57871.4315792 | 0.2583879 | 297.4710649 |
| $N_R$,Cl | $E_{vdW}$ | 117357.8583902 | 0.2743891 | 790.8734337 |
| $O_R$,$O_R$ | $E_{vdW}$ | 55027.5202694 | 0.2525106 | 268.5463760 |
| $O_R$,Cl | $E_{vdW}$ | 111590.6718585 | 0.2677707 | 713.9726163 |
| Cl,Cl | $E_{vdW}$ | 226295.4606144 | 0.2849939 | 1898.2080654 |

**Table S2: Bond parameters**

| Bonded Atoms list | $K_r$ (kcal/mol/Å$^2$) | $r_0$ (Å) |
|---|---|---|
| $C_2$,$C_R$ | 525 | 1.39 |
| $C_2$,$N_R$ | 525 | 1.34 |
| $C_2$,$O_2$ | 525 | 1.35 |
| $C_3$,$C_3$ | 350 | 1.53 |
| $C_3$,H | 350 | 1.09 |
| $C_3$,$N_R$ | 350 | 1.41 |
| $C_R$,$C_R$ | 525 | 1.39 |
| $C_R$,H | 350 | 1.02 |
| $H_{hb}$,$N_R$ | 350 | 0.97 |
| $C_3$,Cl | 350 | 1.757 |

**Table S3: Angle parameters**

| Atoms forming angles | $K_\theta$ (kcal/mol/$rad^2$) | $\theta_0$ (°) |
|---|---|---|
| $C_3$,$C_3$,$C_3$ | 50 | 109.471 |
| $C_3$,$C_3$,$C_R$ | 50 | 109.471 |
| $C_3$,$C_3$,H | 50 | 109.471 |
| $C_3$,$C_3$,$N_R$ | 50 | 109.471 |
| $C_3$,$C_R$,$C_R$ | 50 | 120.0 |
| $C_3$,$N_R$,$C_R$ | 50 | 120.0 |
| $C_3$,$N_R$,$H_{hb}$ | 50 | 120.0 |
| $C_R$,$C_3$,H | 50 | 109.471 |
| $C_R$,$C_R$,$C_R$ | 50 | 120.0 |
| $C_R$,$C_R$,$C_2$ | 50 | 120.0 |
| $C_R$,$C_R$,H | 50 | 120.0 |
| $C_R$,$C_2$,$N_R$ | 50 | 120.0 |
| $C_R$,$C_2$,$O_R$ | 50 | 120.0 |
| $C_2$,$N_R$,$H_{hb}$ | 50 | 120.0 |
| H,$C_3$,H | 50 | 109.471 |
| H,$C_3$,$N_R$ | 50 | 109.471 |
| $N_R$,$C_2$,$O_R$ | 50 | 120.0 |
| Cl,$C_3$,Cl | 50 | 109.471 |

**Table S4: Dihedral parameters**

| Atoms List (order specific) | $K_\phi$ (kcal/mol) | d | n |
|---|---|---|---|
| $C_2$,$C_R$,$C_R$,$C_R$ | 3.125 | -1 | 2 |
| $C_2$,$C_R$,$C_R$,$C_2$ | 3.125 | -1 | 2 |
| $C_2$,$C_R$,$C_R$,H | 3.125 | -1 | 2 |
| $C_3$,$C_3$,$C_3$,$C_3$ | 0.111 | 1 | 3 |
| $C_3$,$C_3$,$C_3$,H | 0.111 | 1 | 3 |
| $C_3$,$C_3$,$C_3$,$N_R$ | 0.111 | 1 | 3 |
| $C_3$,$C_3$,$N_R$,$C_2$ | 0.166 | 1 | 3 |
| $C_3$,$C_3$,$N_R$,$H_{hb}$ | 0.166 | 1 | 3 |
| $C_R$,$C_2$,$N_R$,$C_3$ | 3.125 | -1 | 2 |
| $C_R$,$C_2$,$N_R$,$H_{hb}$ | 3.125 | -1 | 2 |
| $C_R$,$C_R$,$C_R$,$C_R$ | 3.125 | -1 | 2 |
| $C_R$,$C_R$,$C_R$,H | 3.125 | -1 | 2 |
| H,$C_3$,$C_3$,H | 0.111 | 1 | 3 |
| H,$C_3$,$C_3$,$N_R$ | 0.111 | 1 | 3 |
| H,$C_3$,$N_R$,$C_2$ | 0.166 | 1 | 3 |
| H,$C_3$,$N_R$,$H_{hb}$ | 0.166 | 1 | 3 |
| H,$C_R$,$C_R$,H | 0.111 | 1 | 3 |
| H,$C_R$,$C_R$,$C_R$ | 3.125 | -1 | 2 |
| $N_R$,$C_2$,$C_R$,$C_R$ | 0.625 | -1 | 2 |
| $O_R$,$C_2$,$C_R$,$C_R$ | 0.625 | -1 | 2 |
| $O_R$,$C_2$,$N_R$,$C_3$ | 3.125 | -1 | 2 |
| $O_R$,$C_2$,$N_R$,$H_{hb}$ | 3.125 | -1 | 2 |

**Table S5: Improper dihedral parameters**

| Atoms List (order specific) | $K_\omega$ (kcal/mol) | $\omega_0$ (°) |
|---|---|---|
| $C_3$,$C_2$,$N_R$,$H_{hb}$ | 40 | 0 |
| $C_R$,$C_R$,$C_R$,$C_2$ | 40 | 0 |
| $C_R$,$C_R$,$C_R$,H | 40 | 0 |
| $C_R$,$N_R$,$C_2$,$O_R$ | 40 | 0 |

**Table S6: Hydrogen bond parameters**

| System | $r_{in}$ (Å) | $r_{out}$ (Å) | $\theta_{DHA}$ (°) |
|---|---|---|---|
| 2BC | 2.5 | 3.5 | 120.0 |
| 3BC | 4.3 | 4.4 | 130.0 |
| 4BC | 2.5 | 3.5 | 120.0 |
| 5BC | 3.0 | 3.1 | 150.0 |
| 6BC | 2.5 | 3.5 | 120.0 |

# Solution Phase:

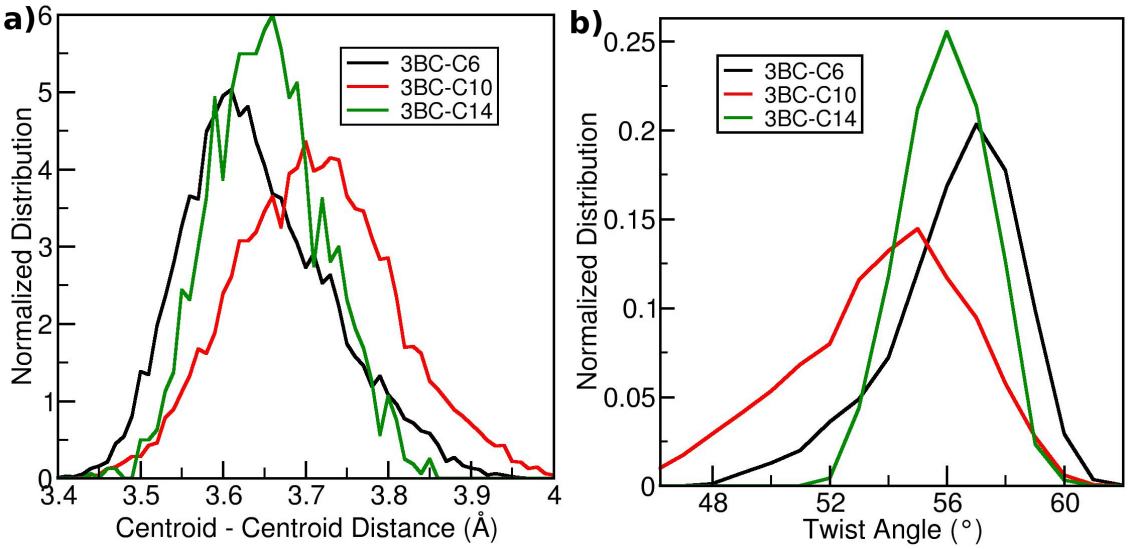


**Figure S1:** Results from MD simulations of preformed decamer of 3BC homologues in solution at 298.15 K (a) Normalized distribution of centroid-centroid distance and (b) Normalized distribution of twist angle.

# Liquid Crystalline Phase:

## System Details:

**Table S7: Details of LC phase simulations**

| System | Number of stacks | Number of molecules per stack | Total number of molecules | Total number of atoms |
|---|---|---|---|---|
| 3BC-C6 | 9 | 12 | 108 | 8424 |
| 3BC-C10 | 9 | 12 | 108 | 12312 |
| 3BC-C14 | 9 | 12 | 108 | 16200 |
| 5BC-C14 | 9 | 16 | 144 | 34848 |

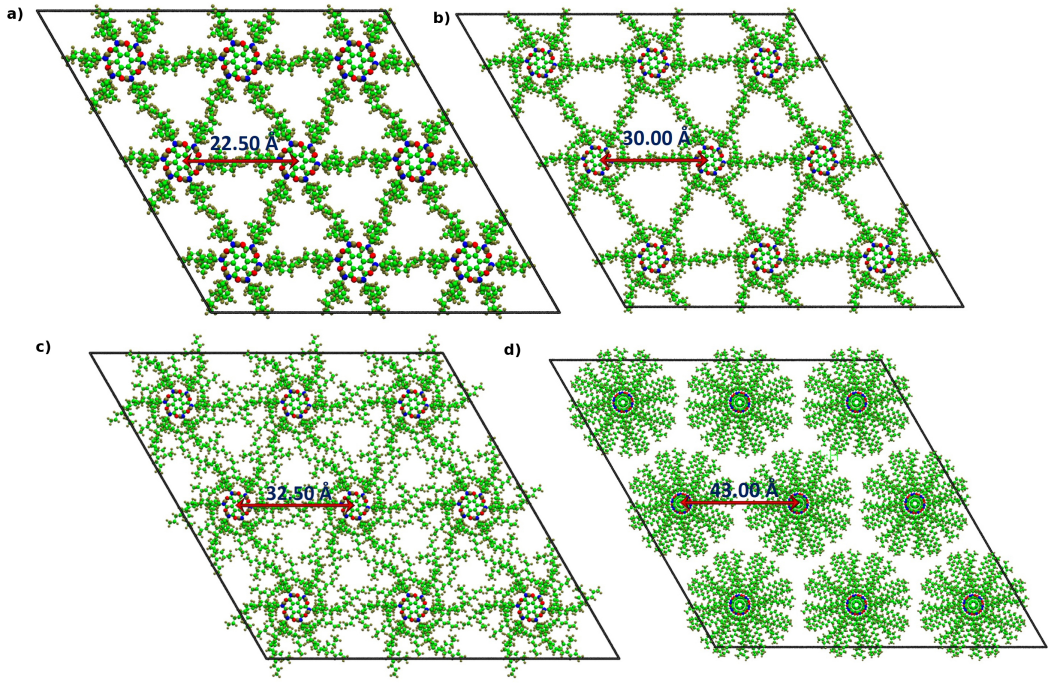


**Figure S2:** Initial structures of the systems in liquid crystalline (LC) phase. All amide dipoles are oriented in the same direction. (a) N,N′,N″-tri(hexyl)-1,3,5-benzenetricarboxamide (3BC-C6), (b) N,N′,-N″-tri(decyl)-1,3,5-benzenetricarboxamide (3BC-C10), (c) N,N′,N″-tri(tetradecyl)-1,3,5-benzenetricarboxamide (3BC-C14), and (d) N,N′,N″,N‴,N⁗-penta(tetradecyl)benzenepentacarboxamide (5BC-C14). Color Scheme: Green - Carbon, Tan - hydrogen, Red - Oxygen, Blue - Nitrogen.

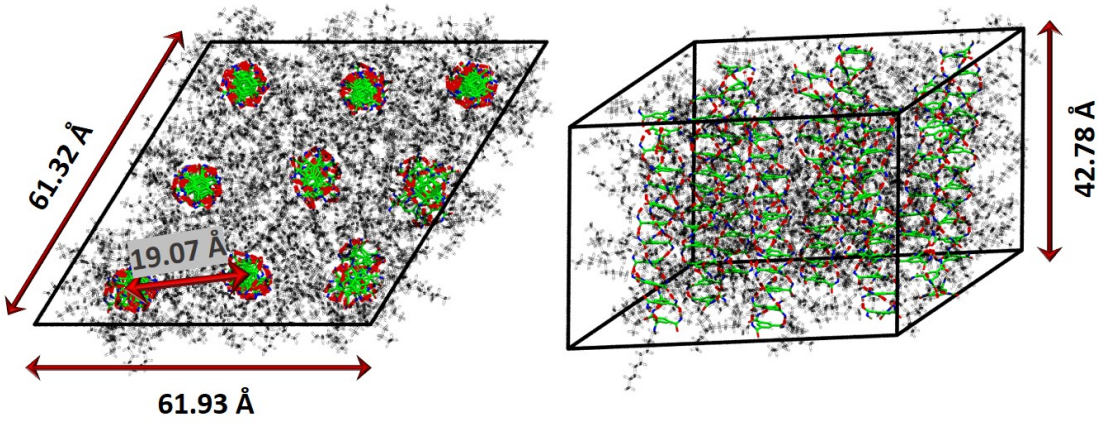


**Figure S3:** The final structure of 3BC-C10 from equilibrium simulations at 460 K. (a) top view and (b) side view. The colour scheme is same as in Figure S2.

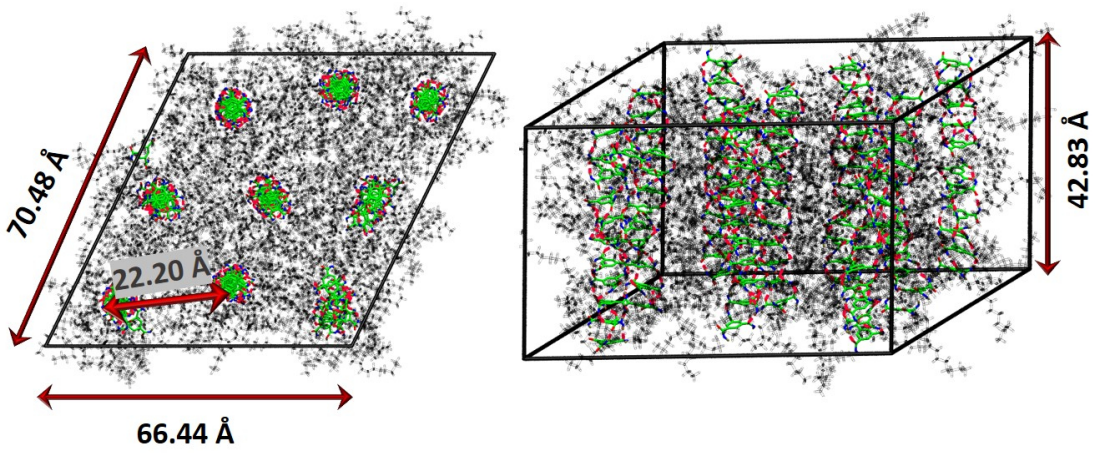


**Figure S4:** The final structure of 3BC-C14 from equilibrium simulations at 460 K. (a) top view and (b) side view. The colour scheme is same as in Figure S2.

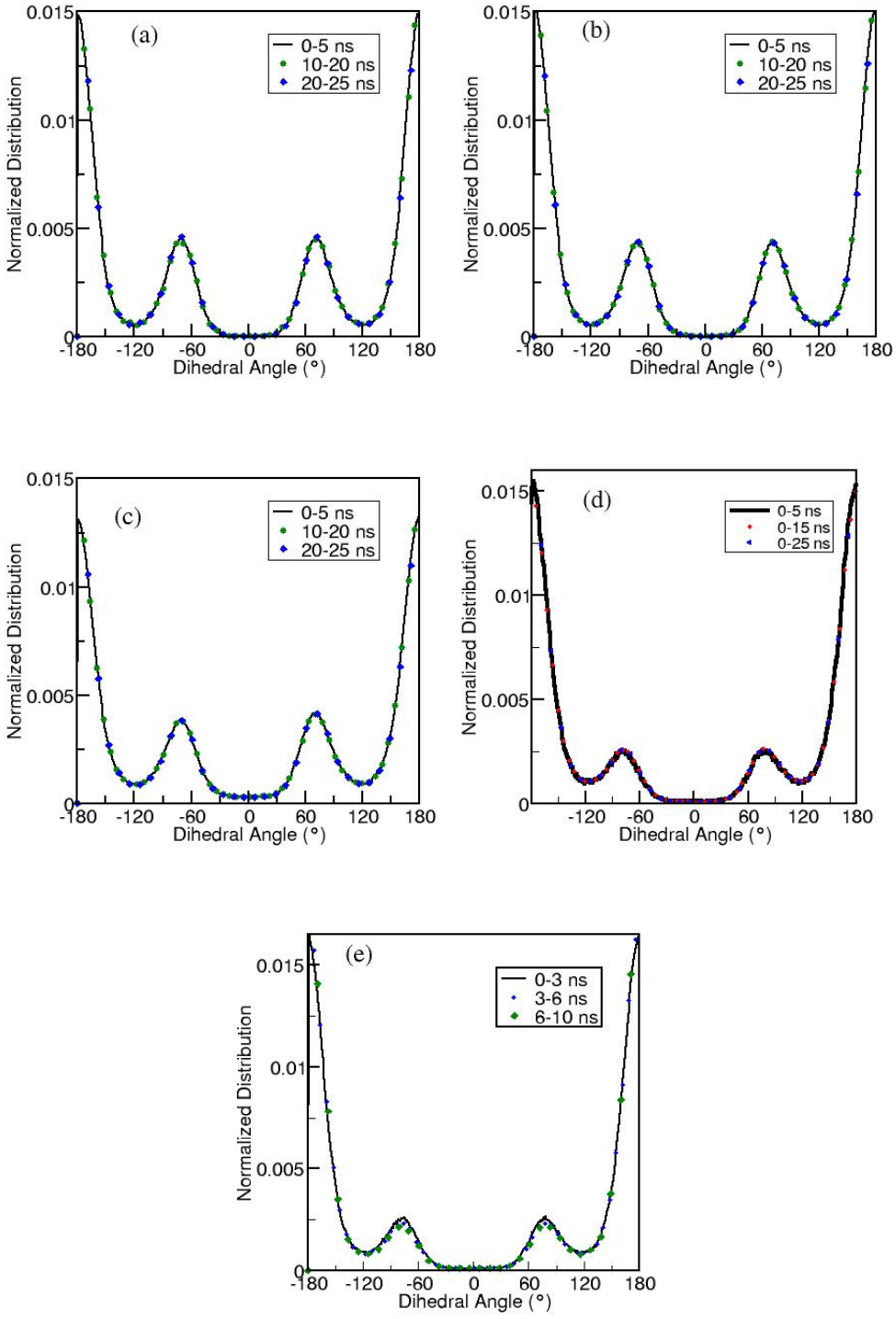


**Figure S5:** C-C-C-C dihedral angle distribution of the alkyl tails in various systems of the LC phase at various time points of corresponding MD trajectories: (a) 3BC-C6 related to Figure 7 of main MS (b) 3BC-C10 related to Figure 7 of main MS (c) 3BC-C14 related to Figure 7 of main MS (d) 5BC-C14 related to Figure 11 of main MS (e) 5BC-C14 related to Figure 12 of main MS.

# References

(1) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. DREIDING: A Generic Force Field for Molecular Simulations. *J. Phys. Chem.* **1990**, *94*, 8897–8909.