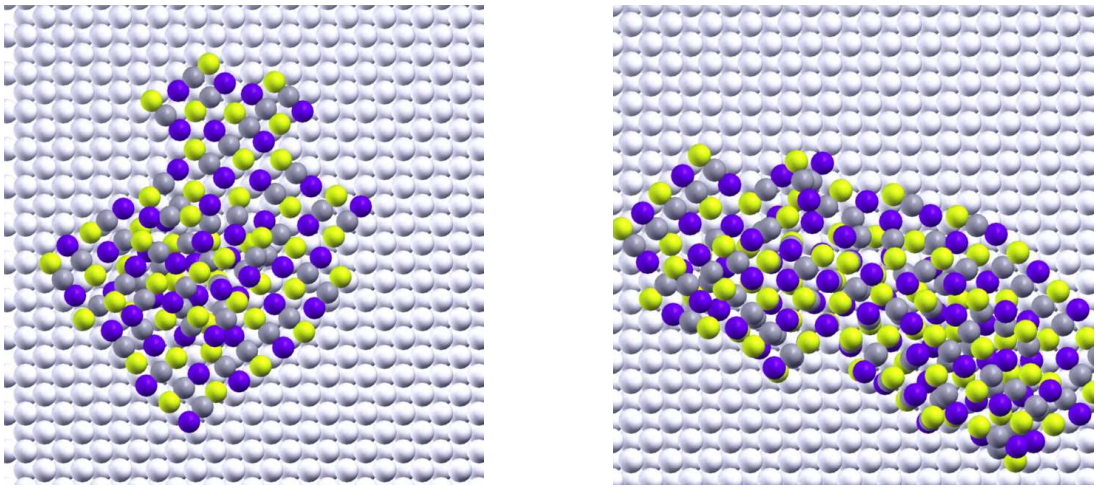
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for "Fundamental Aspects in Surface Self-Assembly: A Theoretical Study of Polarity and Shape"



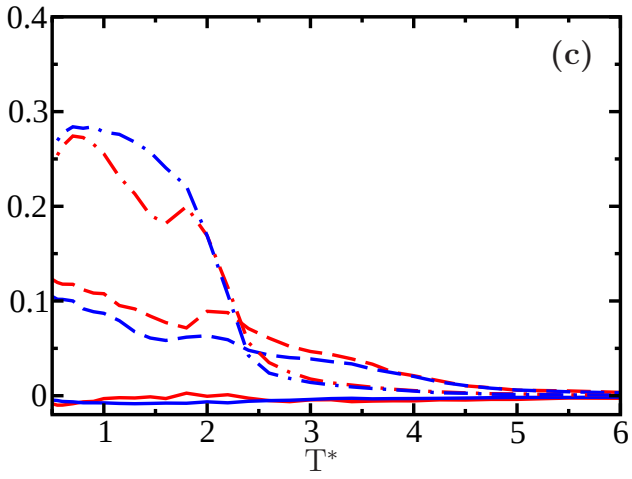


FIG. 1: Snapshots of system C2−l with different number of molecules: 50 (panel a) and 80 (panel b) reflecting similar SA behavior for varying system sizes. Both snapshots are at T* = 1.0. Regardless of size, the commensurate nature of phase and the antiparallel alignment of neighboring molecules are apparent. Panel c: values for the order parameters as a function of temperature (S_1 – continous line, S_2 – dashed line, S_4 – dashed-dotted line) for small (50 molecules, red curve) and large (80 molecules, blue curve) systems. The similarity between curves suggests no significant system size effects.

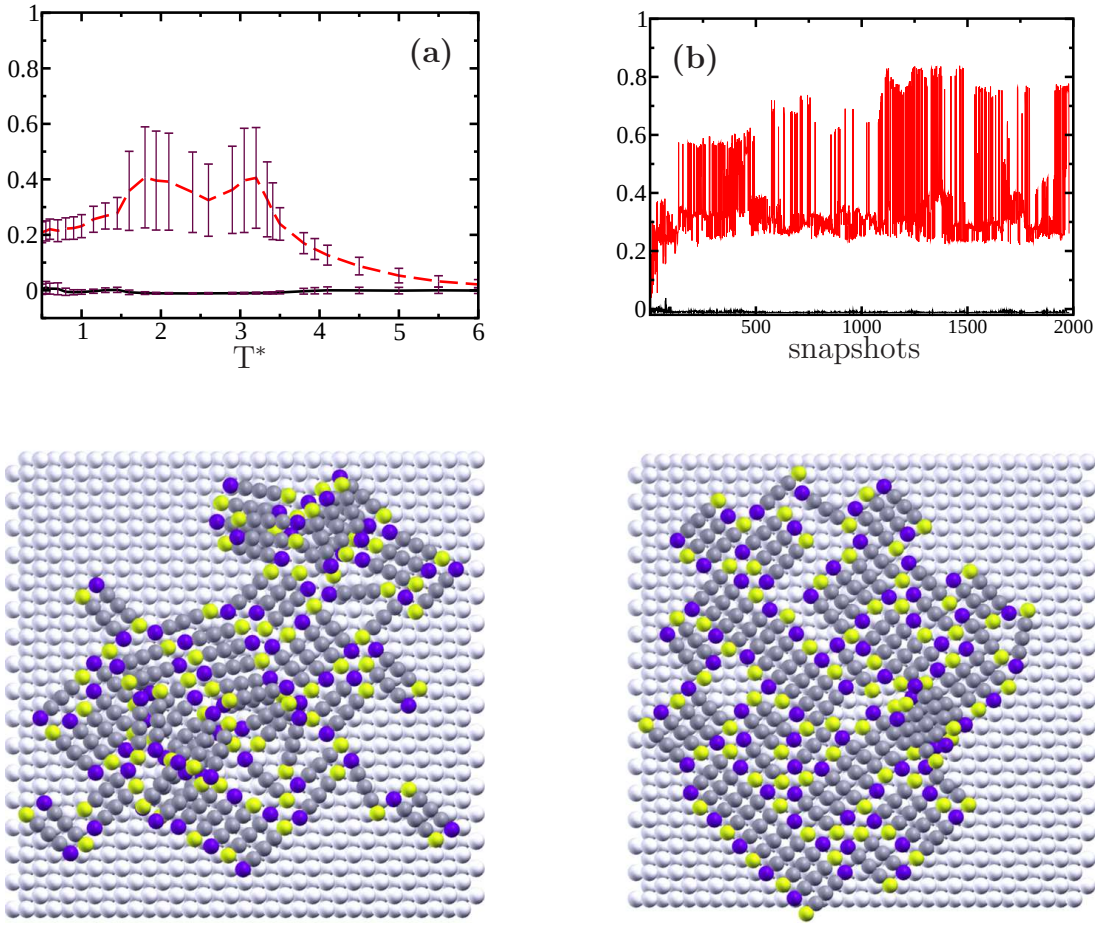


FIG. 2: Order parameters for the fully converged C4−l/D4 system. Panel a: averages for S_1 (black line) and S_2 (red dashed line) with associated standard deviations. S_1 is characterized by values close to zero and a low standard deviation, signifying the lack of nematic phase. In contrast, S_2 has a high variation among snapshots in the region T* = 0.5 - 3.5. Panel b: variation of S_1 (black) and S_2 (red) between a series of microstates for D4 at T* = 2.9. S_2 fluctuates randomly between low (0.2) and high (0.8) values, signaling some variation in order among neighbors, compounded by a large variation in the range within which molecules adopt an antiparallel alignment. Panel c and panel d: snapshots of D4 system reflecting weaker (panel c) and stronger (panel d) antiparallel alignment. Both snapshots share a common local antiparallel alignment with variable length theme, with a strong entropic effect in the region of temperature T* = 0.5 - 3.5.

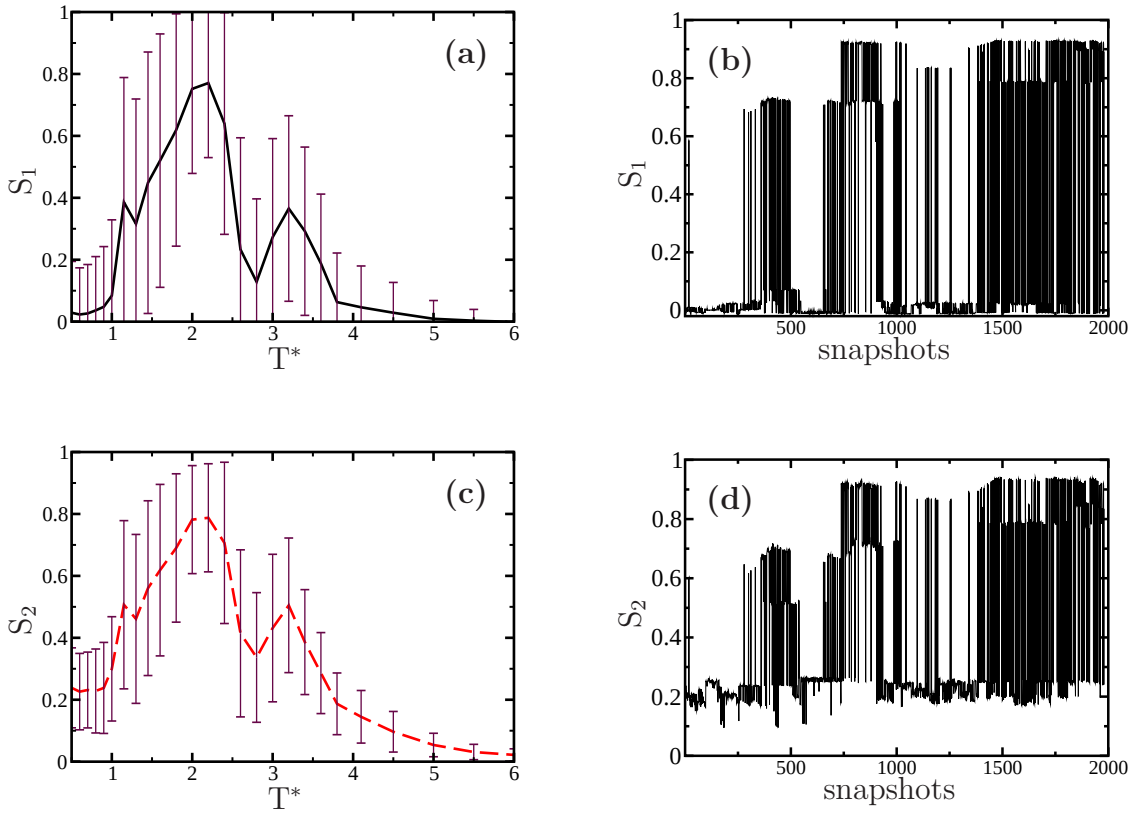


FIG. 3: Variation of order parameters between polymorphic states in early runs of D4/C4−l system. The averages for both S_1 (panel a) and S_2 (panel c) exhibit high standard deviations at all temperatures, suggesting the adoption of more than one strategy for self-assembly. Panels b and d: S_1 and S_2 for individual snapshots at T* = 1.45, as a function of simulation time. Both S_1 and S_2 fluctuate between high and low values. This indicates an initial coexistence of phases, including nematic (panel b). The long-run behavior is that described in Figure 2.

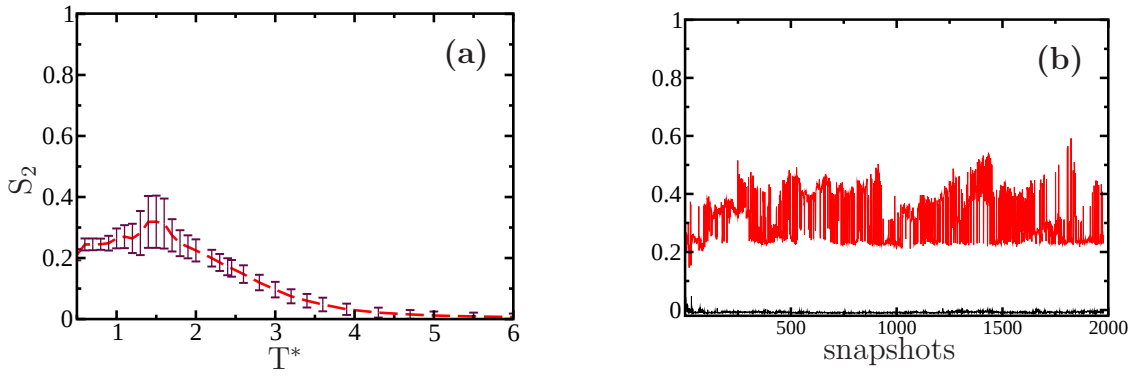


FIG. 4: Order parameters for $G1_2 - l$ system. Panel a: average S_2 and associated standard deviation as a function of temperature. The maximum of variation is around $T^* = 1.4$, with lower temperature range and magnitude relative to D4/C4$-l$ (see Figure 2). Panel b: variation of S_1 (black) and S_2 (red) between a series of microstates for D4 at $T^* = 1.4$. S_1 is close the zero and has a universally low variation, indicating the absence of nematic. S_2 fluctuates randomly between a minimum and a maximum, indicating a family of configurations with a continous variation in the long-range order.

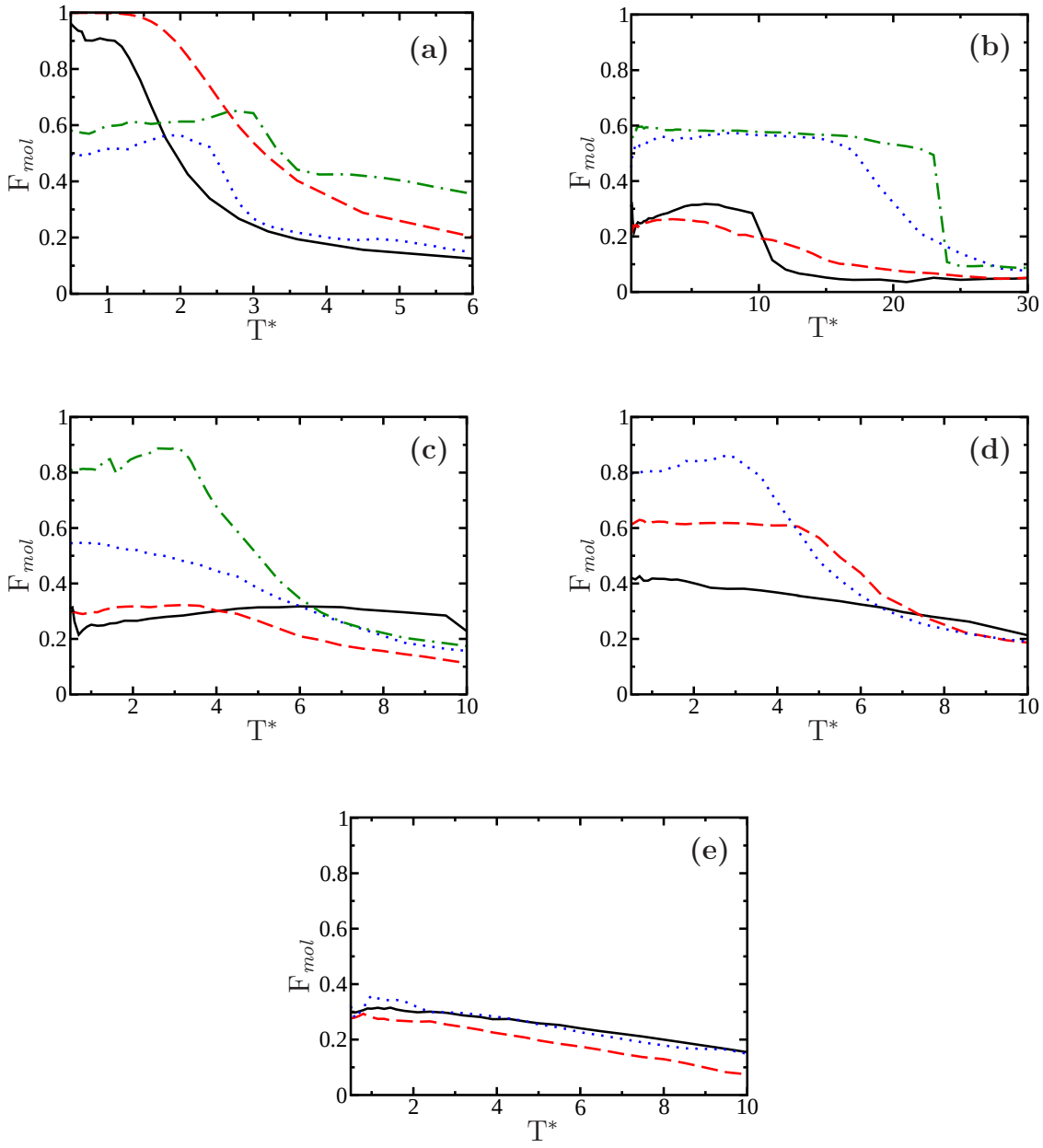


FIG. 5: Fraction of molecules touching the suface as a function of temperature. Panel a – series A: black line – A1($\varepsilon^*_{ss} = 1$), red dashes – A1($\varepsilon^*_{ss} = 3$), blue dots – A2($\varepsilon^*_{ss} = 1$), green dot-dashed line – A2($\varepsilon^*_{ss} = 3$); higher surface potential leads to higher values; stronger charges lead to lower values, characteristic of three-dimentional crystalline state. Panel b – series C$-h$: black line – C1$-h$, red dashes – C2$-h$, blue dots – C3$-h$, green dot-dashed line – C4$-h$; fraction increases with charge separation, up to 0.6, characteristic of the crystalline state (charge-driven assembly). Panel c – series D: black line – D1, red dashes – D2, blue dots – D3, green dot-dashed line – D4; fraction increases with molecular length, tending towards unity (surface-driven assembly). Panel d – series L: black line – L1, red dashes – L2, blue dots – L3; transition from charge-driven to surface-driven assembly. Panel e – series G$-h$: black line – G1$-h$, red dashes – G2$-h$, blue dots – G3$-h$; charge-driven assembly; fraction unaffected by geometry for short tail length.

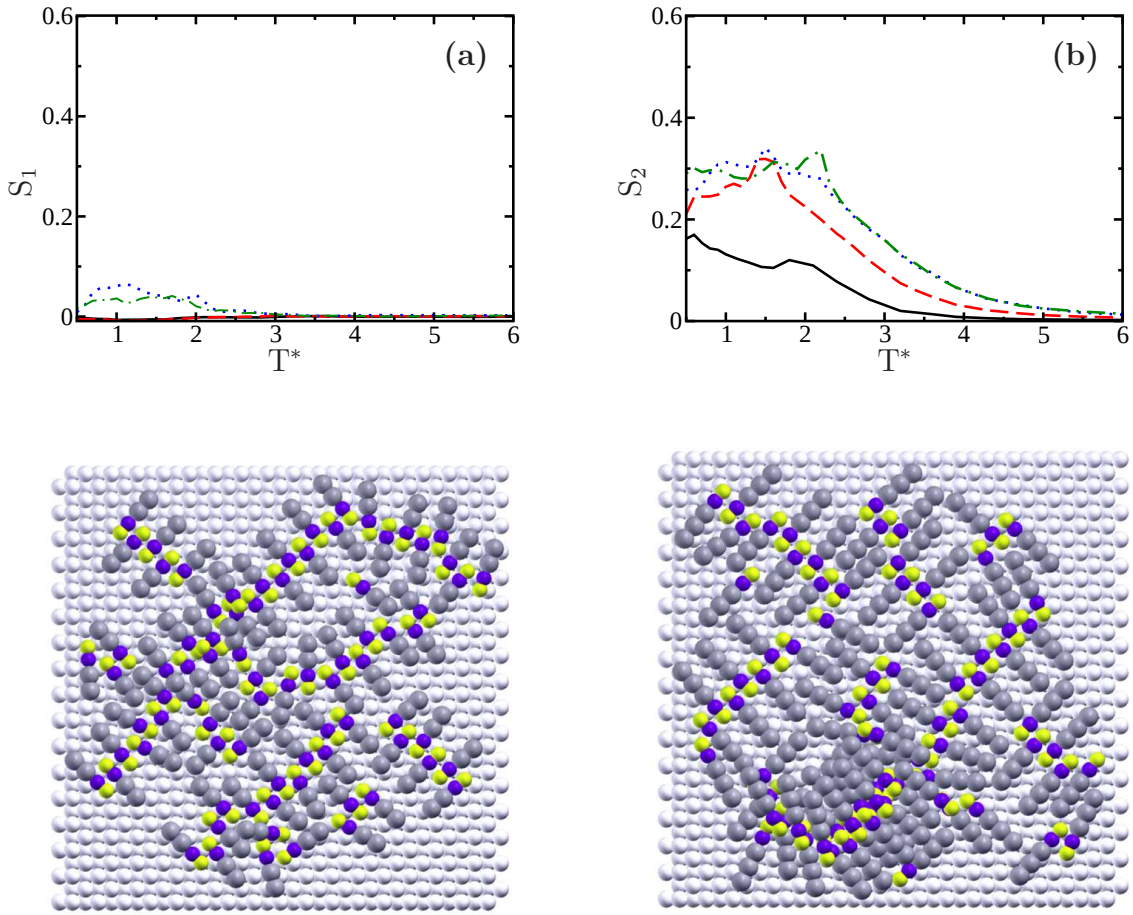


FIG. 6: Effects of tail length for the SA of molecules G1$-l$: Panels a and b: averages S_1 and S_2 respectively, as a function of temperature, when the tail is one (black line), two (red dashes), three (blue dots) and four (green dot-dashed lines) atoms long. Increasing tail length has no influence over S_1 (panel a) and has a slight influence on S_2 (pannel b) by stabilizing the head-group driven antiparallel monolayer over longer distances, as can be observed in panel c for $\mathrm{G1}_2 - l$. Further tail increase causes layers to stack due to a high surface density. The head-group driven antiparallel assembly is preserved across layers (panel d - $\mathrm{G1}_3 - l$)

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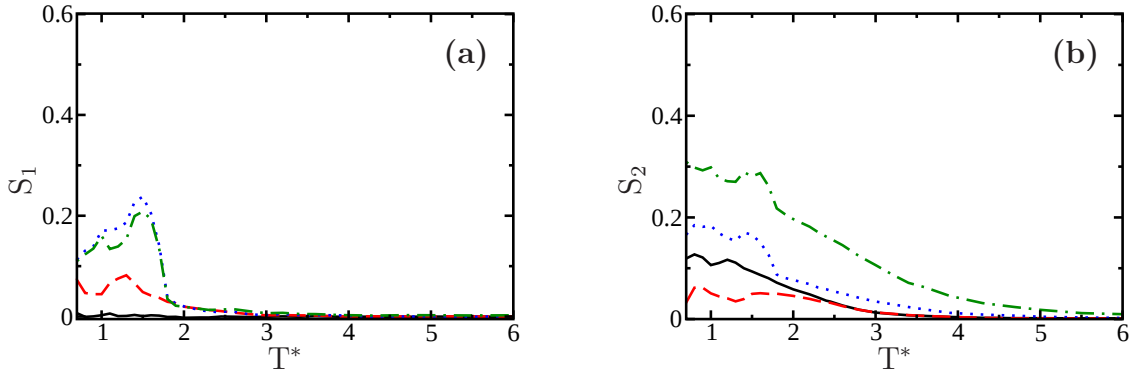

FIG. 7: Comparison of S_1 (panel a) and S_2 (panel b) between $G2_1 - l$ and $G2_3 - l$. G2 geometry is biaxial, leading to two versions of each parameter, one relative to the head group and one relative to the tail group: $G2_1 - l$ head - black line, $G2_1 - l$ tail - red dashes, $G2_3 - l$ head - blue dots, $G2_3 - l$ tail - green dot-dashed line. G2$-l$ series is characterized by low order parameters in general. A longer tail size facilitates a stronger alignment among molecules, particularly along the tail axis.

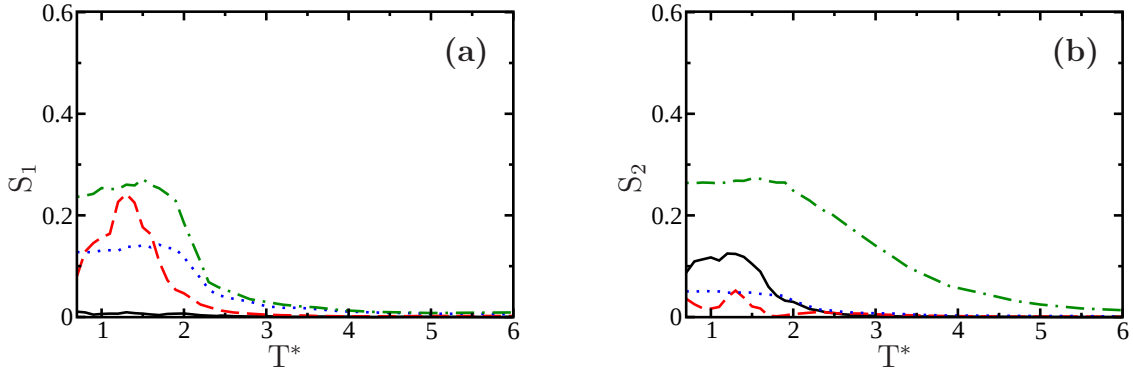

FIG. 8: Comparison of S_1 (panel a) and S_2 (panel b) between $G3_1 - l$ and $G3_4 - l$. G3 geometry is biaxial, leading to two versions of each parameter, one relative to the head group and one relative to the tail group, with the two axes being perpendicular to each other: $G3_1 - l$ head - black line, $G3_1 - l$ tail - red dashes, $G3_4 - l$ head - blue dots, $G3_4 - l$ tail - green dot-dashed line. S_1 and S_2 for G3$-l$ behave similar to those for G2$-l$.

TABLE I: Order parameters for series G relative to the *tail* axis for temperatures around $T^* = 1$.

Molecule	S_1	S_2	S_4
G2$-l$			
G2$_1 - l$	0.04	0.06	0.02
G2$_2 - l$	0.00	0.22	0.10
G2$_3 - l$	0.15	0.03	0.23
G3$-l$			
G3$_1 - l$	0.24	0.05	0.01
G3$_2 - l$	0.04	0.07	0.02
G3$_3 - l$	0.10	0.22	0.25
G3$_4 - l$	0.25	0.26	0.25