Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary material for

Tuneable helices of plasmonic nanoparticles using liquid crystal templates: molecular dynamics investigation of an unusual odd-even effect in liquid crystalline dimers

Mateusz Pawlak, Maciej Bagiński, Pablo Llombart, Dominik Beutel, Guillermo González-Rubio, Ewa Górecka, Carsten Rockstuhl, Józef Mieczkowski, Damian Pociecha, and Wiktor Lewandowski

Supplementary note 1. Synthesis of Au NPs.

7.5 g of dodecylamine was dissolved in 250 ml of cyclohexane. Next, 37 % solution of formaldehyde was added, and the mixture was vigorously stirred for 10 min. After the phase separation, the aqueous phase was removed, and the organic phase was washed with distilled water twice. Subsequently, 100 ml of $HAuCl_4$ (4 mg/ml) aqueous solution was rapidly added to the vigorously stirred organic phase. The mixture was stirred for 40 min. In that time, the colour of the mixture changed from yellow to dark red. After the reaction, 5 ml of dodecanethiol was added and stirred for 12 h. The obtained solution of dodecanethiol-coated AuNPs was evaporated under reduced pressure, and the solid residue was dissolved in a small amount of toluene. To obtain a solution of nanoparticles with a narrow size distribution, portions of acetone were added, and the mixture was centrifugated after adding each portion. From fractions of nanoparticles precipitated after adding each portion of acetone, one with the narrowest size distribution was dissolved in a new portion of cyclohexane. To 10 mg of as-prepared AuNPs dissolved in cyclohexane, 20 mg of HOB-like ligand (Fig. S6) dissolved in dichloromethane was added. The mixture was stirred for 12 h at room temperature. Then, volume of the mixture was limited to ca. 3 ml by rotatory evaporation and 20 ml of ethanol was added. After centrifugation, supernatant was removed and precipitated final Au NPs covered with mixture of dodecanethiol and HOB-like ligand were dissolved in new portion of chloroform. The absence of an unbound ligand in final NPs was confirmed by thin-layer chromatography. Concentration of gold in obtained dispersion of NPs was 5 mg/ml and average diameter of NPs determined by TEM was (4.0 ± 0.5) nm.

Supplementary note 2. Outlook on increasing the PCD response dictated by helical pitch of helical nanofialments.

One of the future directions of research on composites presented in this work is maximizing the shift of plasmonic circular dichroism band by: (1) bringing nanoparticles closer together that would enable higher degree of plasmonic coupling, (2) using larger gold nanoparticles or nanoparticles made of e.g. silver, again translating to stronger plasmonic properties and thus stronger plasmonic coupling, (3) assembling anisotropic nanoparticles such as nanorods, having stronger and directional plasmonic properties, (4) influencing the geometry of helical nanofilaments e.g. by varying the molecular architecture.

Supplementary Figures.

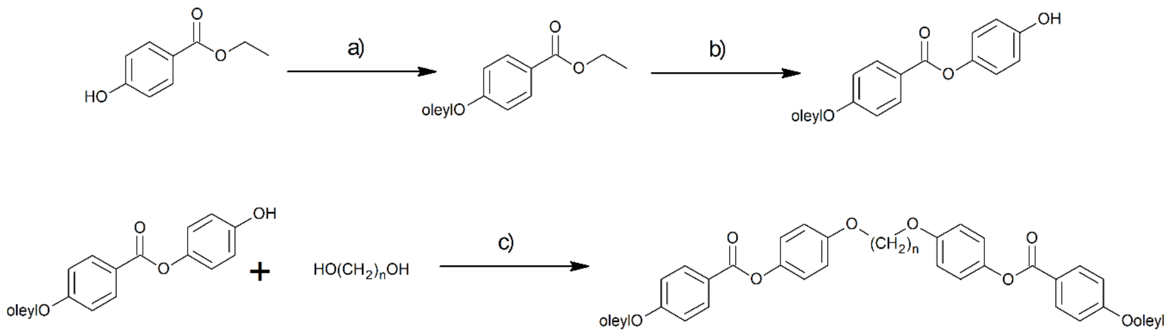

Fig. S1. Synthetic route of HOB-n-HOB dimers. Reagents and conditions: a) oleyl alcohol, PPh_3, DIAD, THF, ultrasounds, b) 1. KOH, ethanol, reflux, 2. $(COCl)_2$, toluene, reflux, 3. Hydroquinone, triethylamine, DMAP, THF, reflux, c) PPh_3, DIAD, THF, ultrasounds.

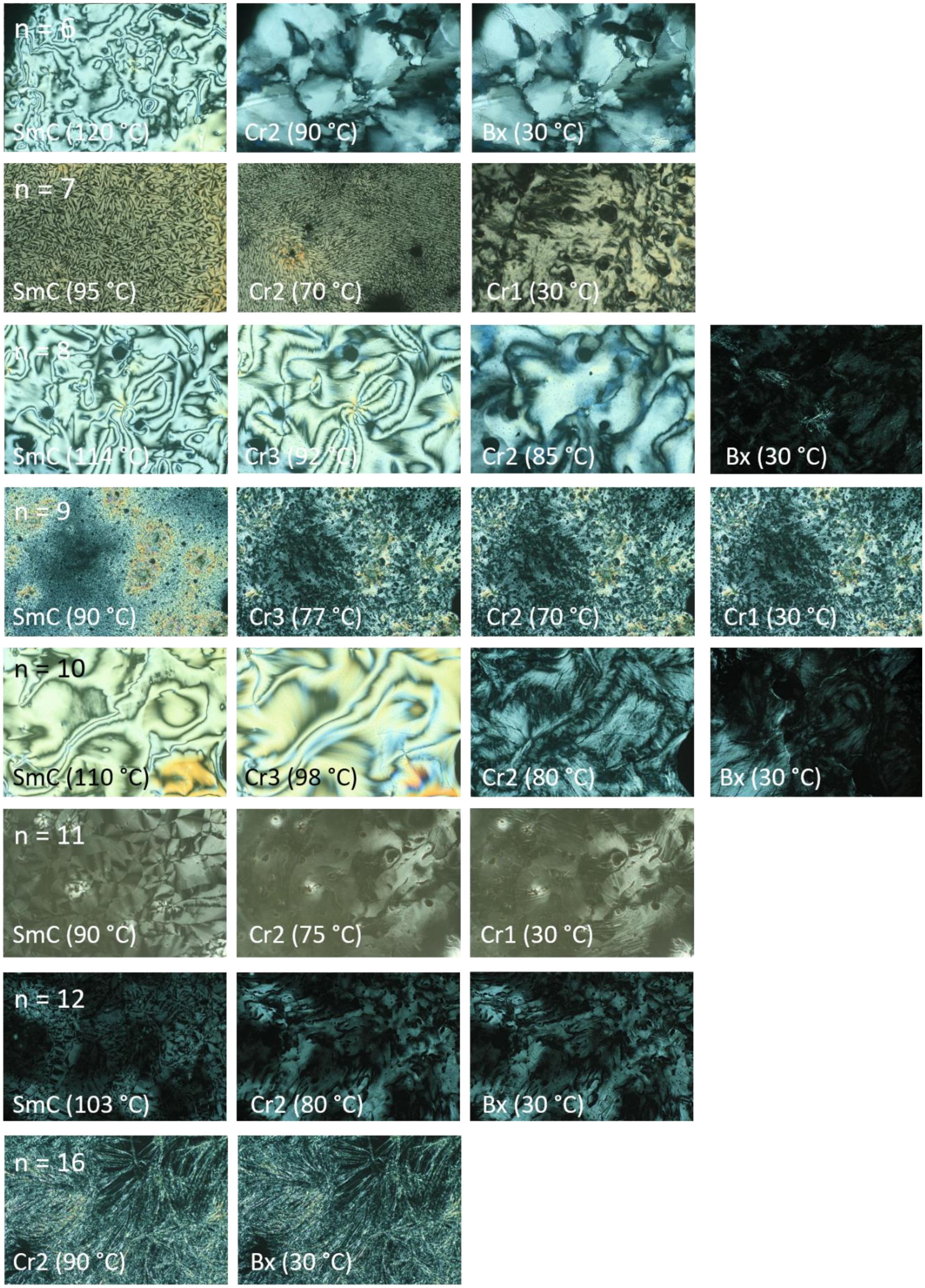

Fig. S2. POM images of phases formed by HOB-n-HOB dimers. Images were taken at temperatures given in brackets.

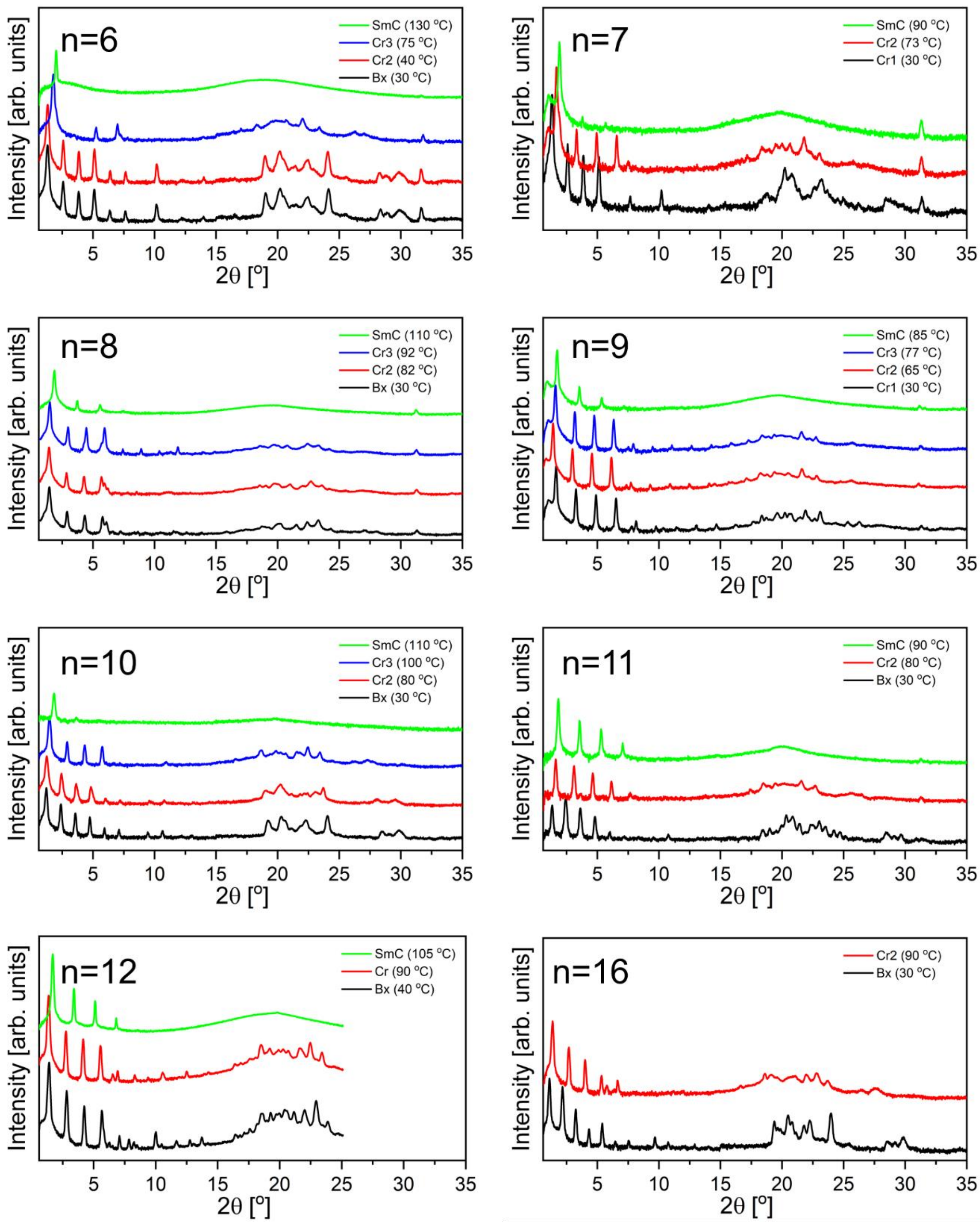

Fig. S3. XRD diffractograms collected at temperatures corresponding to different phases of HOB-n-HOB dimers. Note 1: In general, the layer thickness in the crystalline phases was considerably higher than in the smectic phase and comparable with the length of the HOB-n-HOB molecules. An increase in the layer thickness may be attributed to molecules adopting more linear conformations on cooling and/or lowering of the terminal chain interdigitation between neighbouring layers. Note2 : HOB-16-HOB dimer is not forming a SmC phase. Reasoning for this is given in the caption of Figure S6.

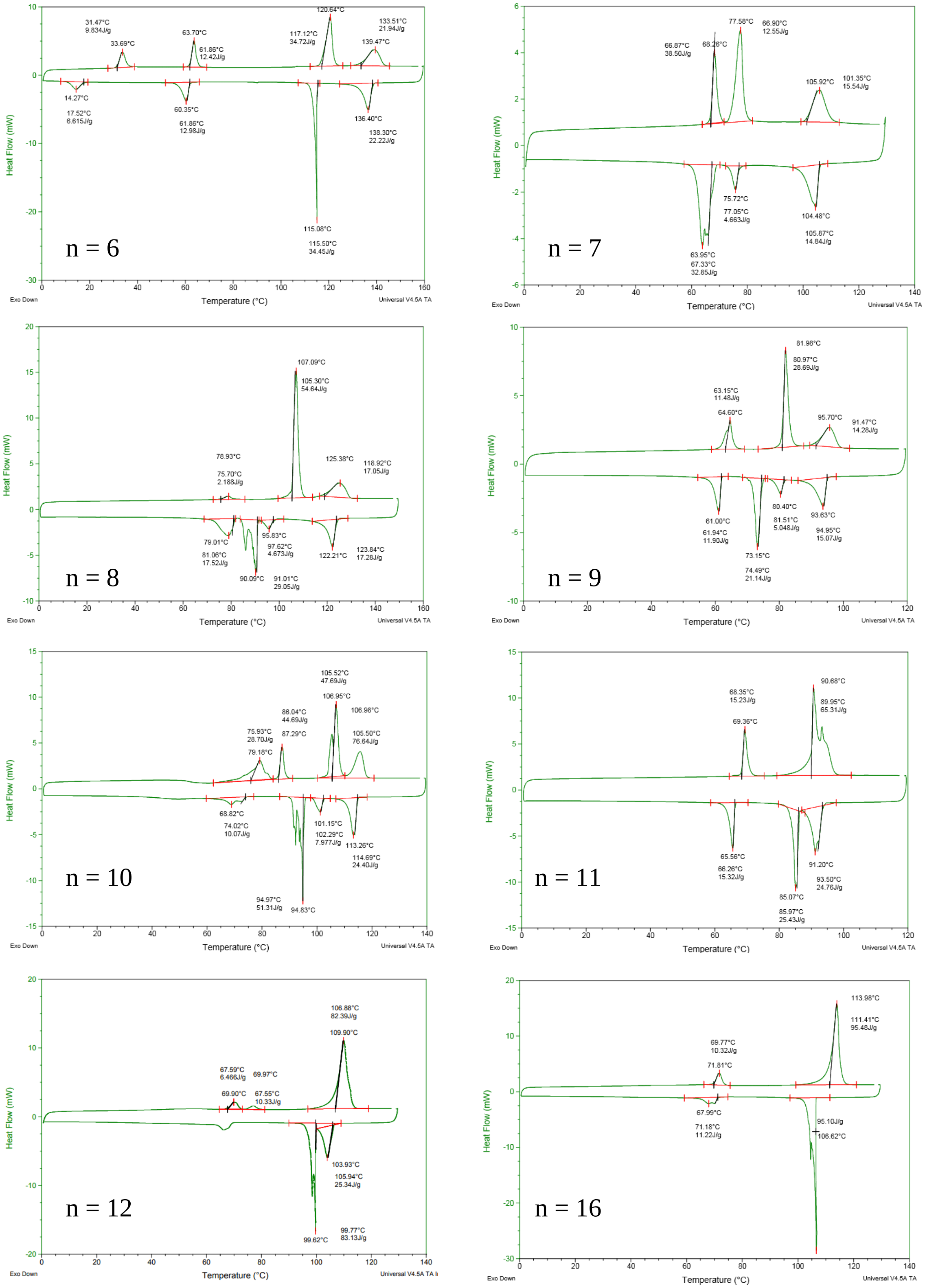

Fig S4. DSC curves of HOB-n-HOB dimers.

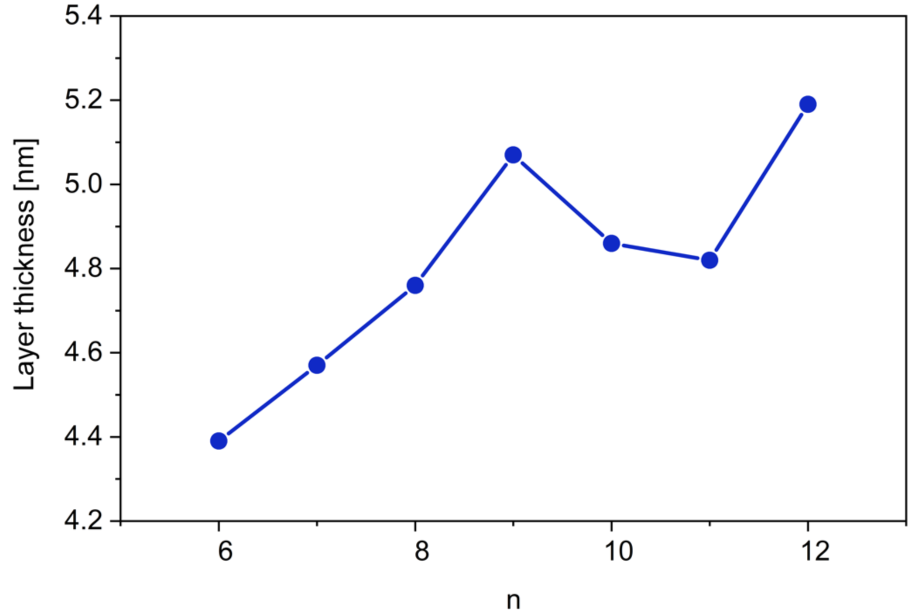

Fig. S5. Dependence of thickness of layers in SmC phase of HOB-n-HOB dimers on the length of the spacer.

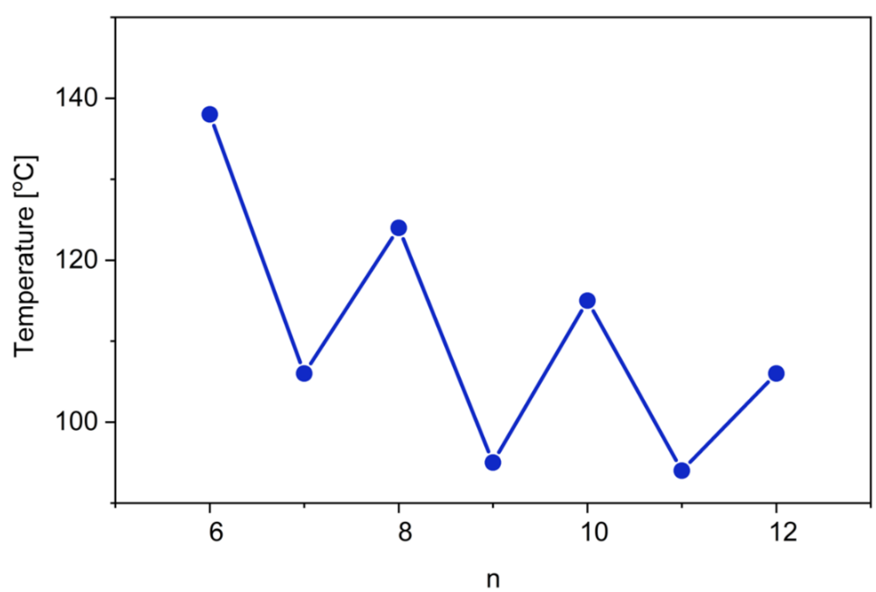

Fig. S6. Dependence of the temperature of the Iso-SmC transition on the spacer length in HOB-n-HOB dimers. It is worth highlighting a general trend: the elongation of alkyl chains in dimeric mesogens (both alkyl spacers and terminal chains) decreases the isotropisation temperatures in a series of homologues with the same parity of spacers lengths. Simultaneously, the elongation of alkyl chains has a much smaller effect on the SmC-Cr transitions temperatures. Thus, the temperature range in which the SmC phase is stable narrows with increasing n, e.g., for HOB-6-HOB the range is 23 °C (115-138 °C) while for

HOB-12-HOB it is only 6 °C (100-106 °C). Therefore, one can expect that the SmC phase will not be stable anymore in any temperature range for a long enough spacer. We hypothesise that it happens for n=16 and, therefore, the formation of the SmC phase is not observed; the crystalline phase melts directly into the isotropic phase. It is also worth noting that this observation illustrates a general rule that some kind of balance between the oily nature of alkyl chains and the rigid nature of aromatic rings is needed in organic molecules to endow them with a mesogenic character. When this balance is broken by an excess of alkyl chains, the compounds tend to lose their liquid-crystalline properties.

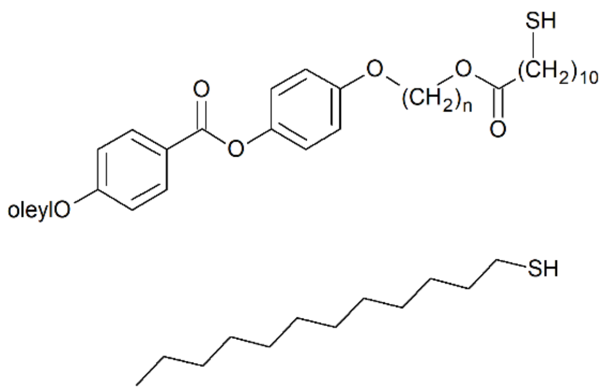

Fig. S7. Structures of HOB-like ligand (upper) and dodecanethiol (lower) introduced on the surface of AuNPs.

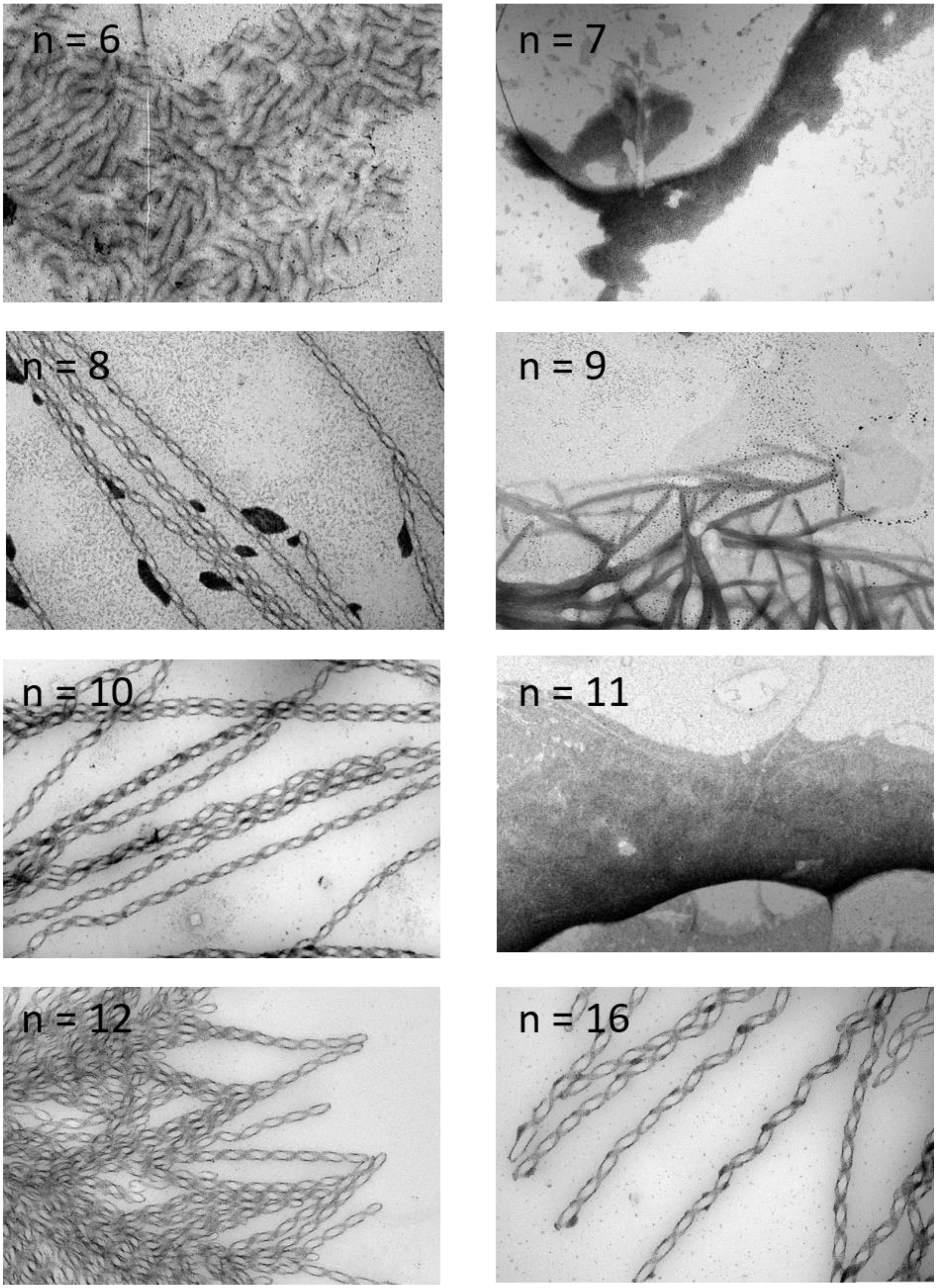

Fig. S8. Representative TEM images of composite materials made of HOB-n-HOB dimers with Au nanoparticles.

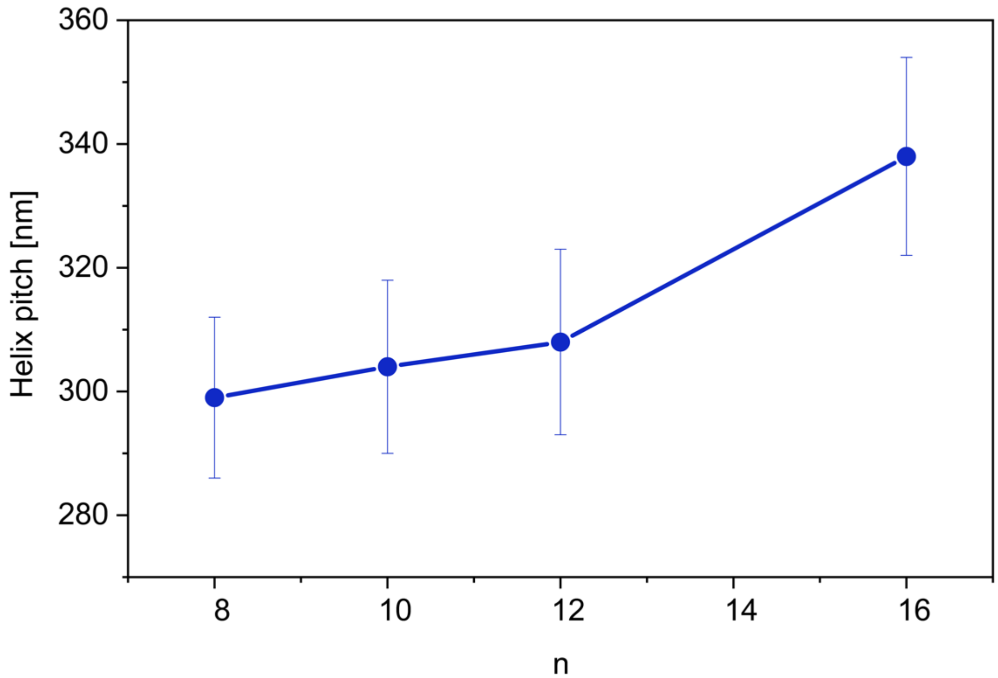

Fig. S9. Pitch of the helices formed by HOB-n-HOB dimers with Au NPs as a function of n.

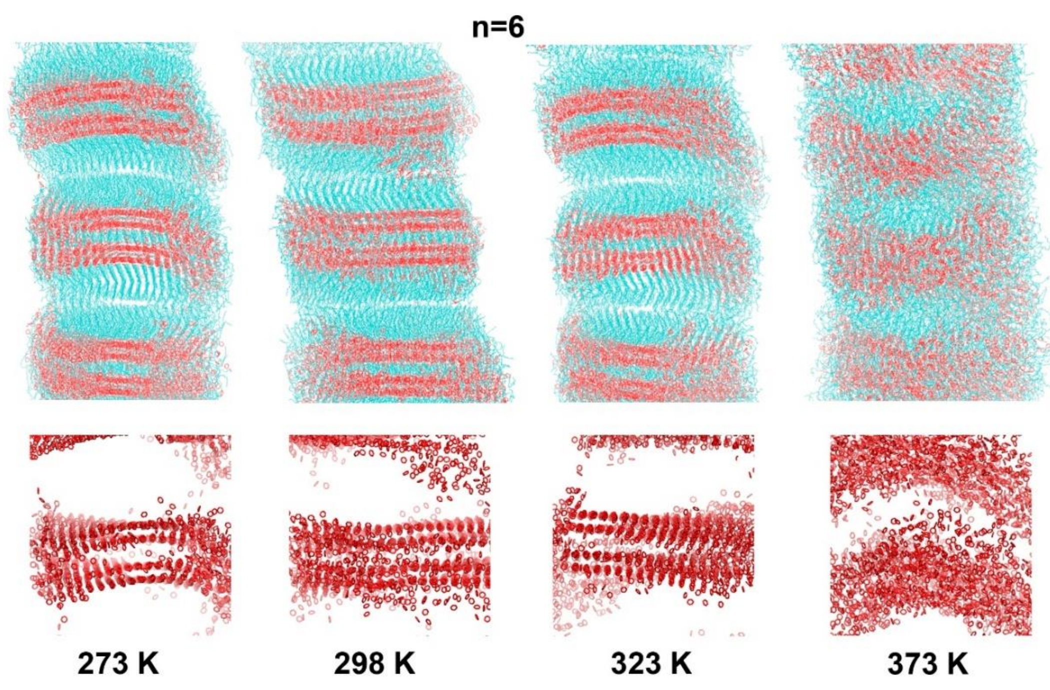

Fig. S10. MD snapshot of the lamellar structure formed by the HOB-6-HOB compound (top) and the configuration adopted by the aromatic moieties in the assembled structure at different temperatures (bottom). Cyan, red and blue sticks represent the oleyl chains, aromatic rings, and linkers.

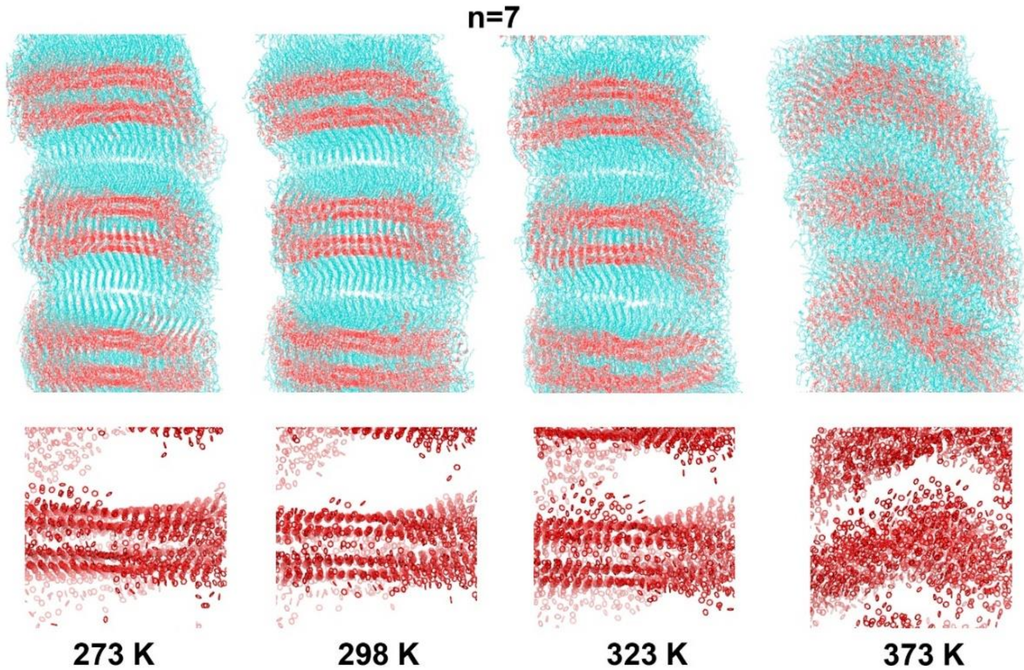

Fig. S11. MD snapshot of the lamellar structure formed by the HOB-7-HOB compound (top) and the configuration adopted by the aromatic moieties in the assembled structure at different temperatures (bottom). Cyan, red and blue sticks represent the oleyl chains, aromatic rings, and linkers.

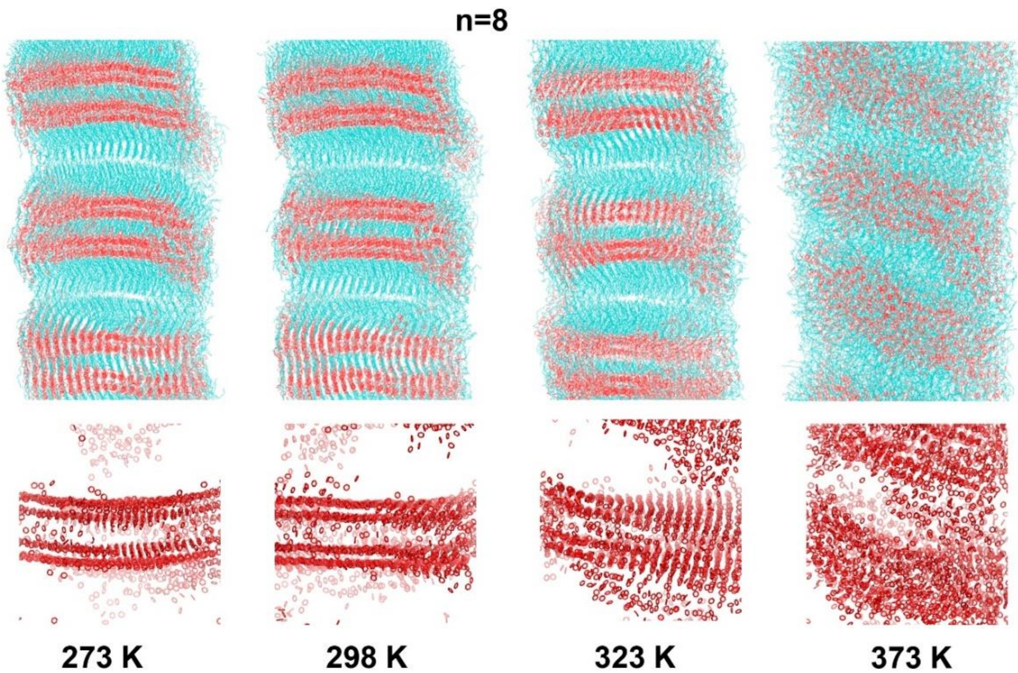

Fig. S12. MD snapshot of the lamellar structure formed by the HOB-8-HOB compound (top) and the configuration adopted by the aromatic moieties in the assembled structure at different temperatures (bottom). Cyan, red and blue sticks represent the oleyl chains, aromatic rings, and linkers.

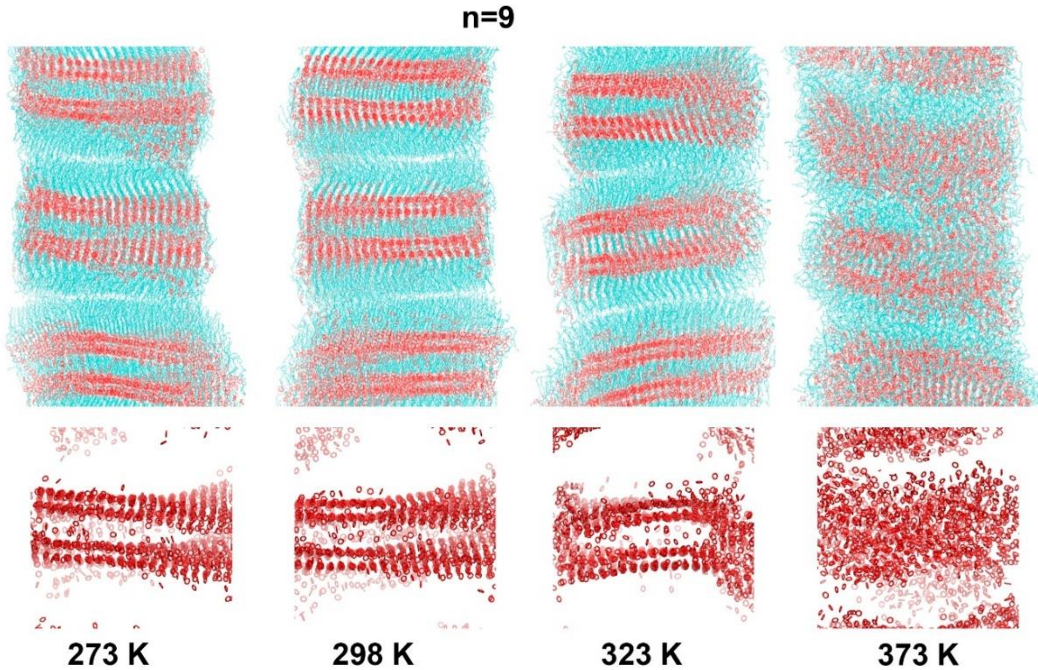

Fig. S13. MD snapshot of the lamellar structure formed by the HOB-9-HOB compound (top) and the configuration adopted by the aromatic moieties in the assembled structure at different temperatures (bottom). Cyan, red and blue sticks represent the oleyl chains, aromatic rings, and linkers.

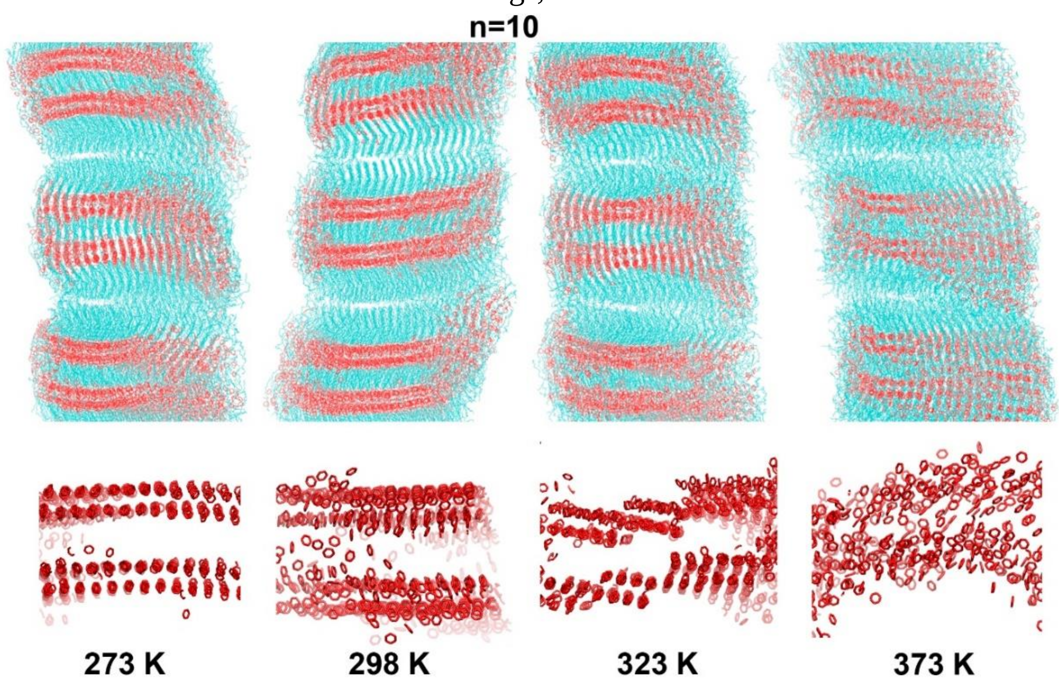

Fig. S14. MD snapshot of the lamellar structure formed by the HOB-10-HOB compound (top) and the configuration adopted by the aromatic moieties in the assembled structure at different temperatures (bottom). Cyan, red and blue sticks represent the oleyl chains, aromatic rings, and linkers.

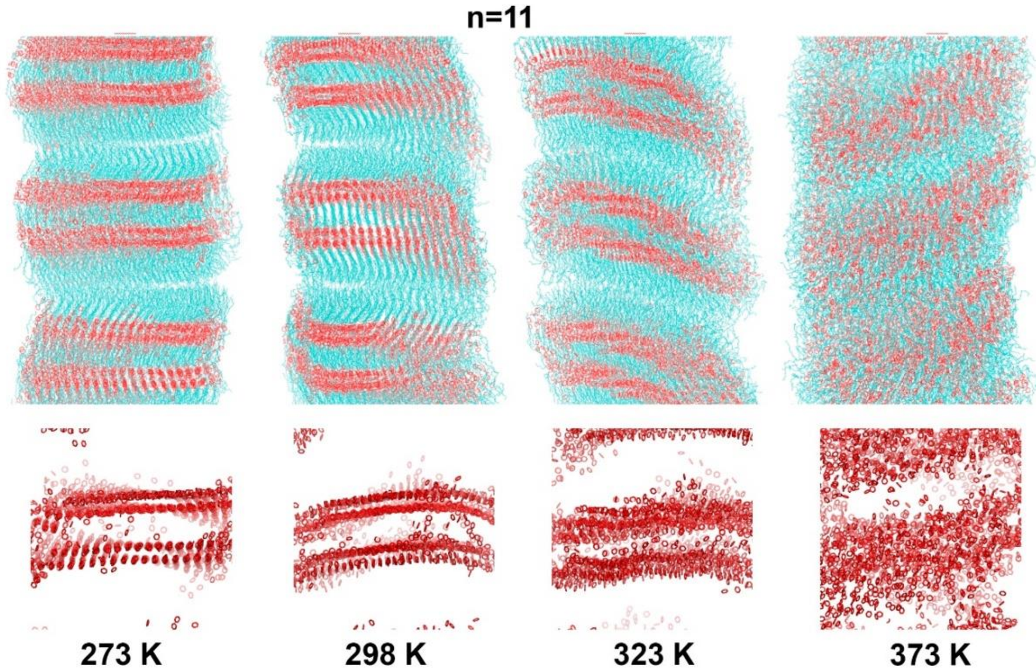

Fig. S15. MD snapshot of the lamellar structure formed by the HOB-11-HOB compound (top) and the configuration adopted by the aromatic moieties in the assembled structure at different temperatures (bottom). Cyan, red and blue sticks represent the oleyl chains, aromatic rings, and linkers.

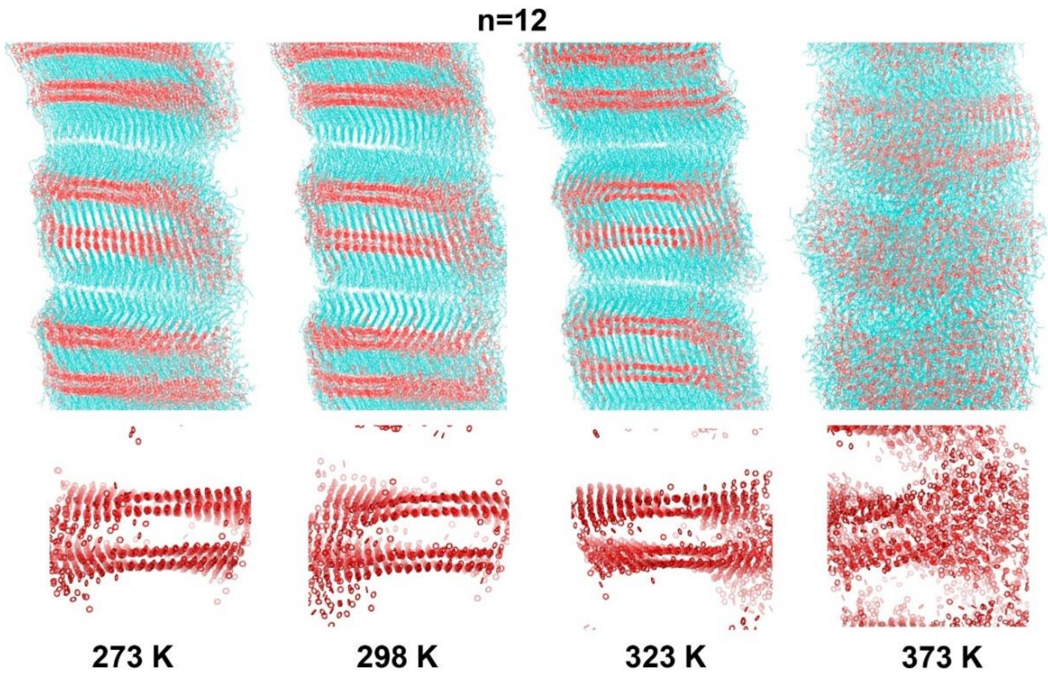

Fig. S16. MD snapshot of the lamellar structure formed by the HOB-12-HOB compound (top) and the configuration adopted by the aromatic moieties in the assembled structure at different temperatures (bottom). Cyan, red and blue sticks represent the oleyl chains, aromatic rings, and linkers.

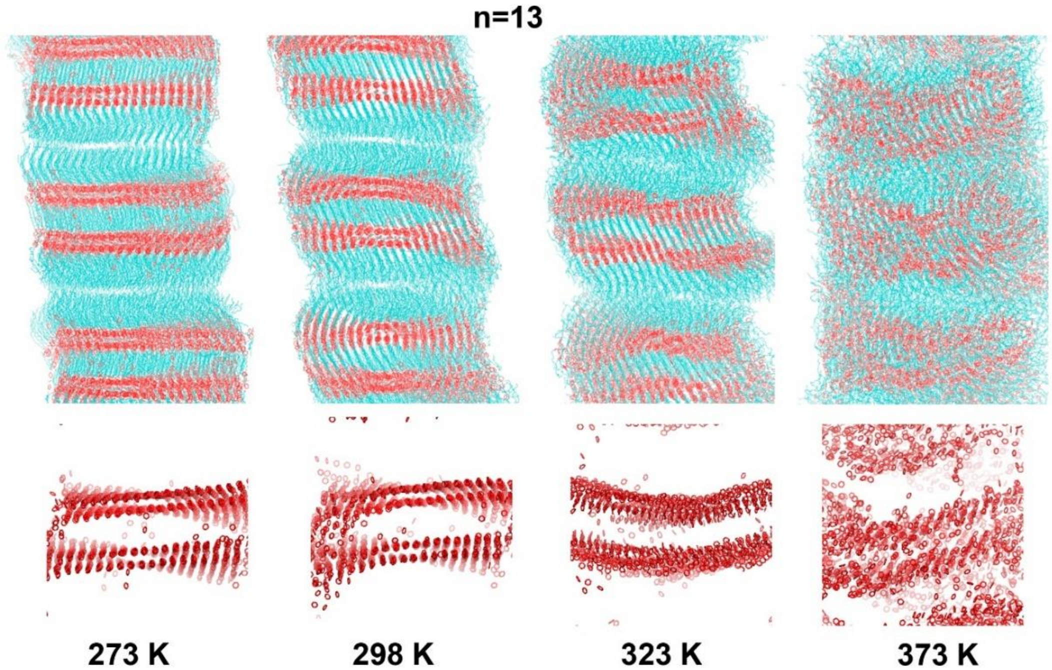

Fig. S17. MD snapshot of the lamellar structure formed by the HOB-13-HOB compound (top) and the configuration adopted by the aromatic moieties in the assembled structure at different temperatures (bottom). Cyan, red and blue sticks represent the oleyl chains, aromatic rings, and linkers.

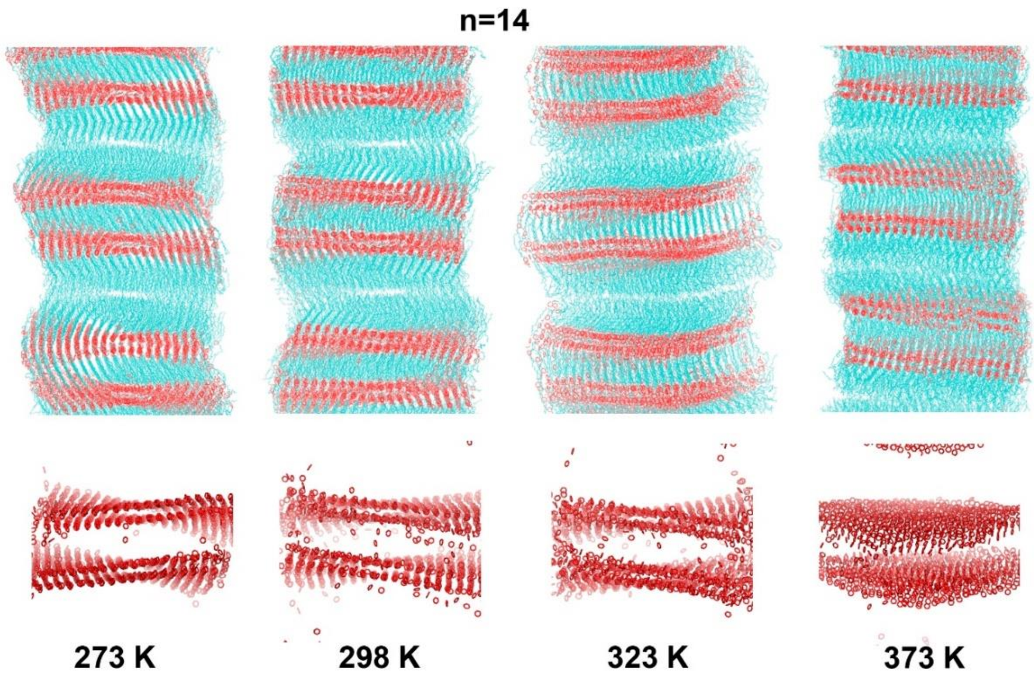

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Fig. S18. MD snapshot of the lamellar structure formed by the HOB-14-HOB compound (top) and the configuration adopted by the aromatic moieties in the assembled structure at different temperatures (bottom). Cyan, red and blue sticks represent the oleyl chains, aromatic rings, and linkers.

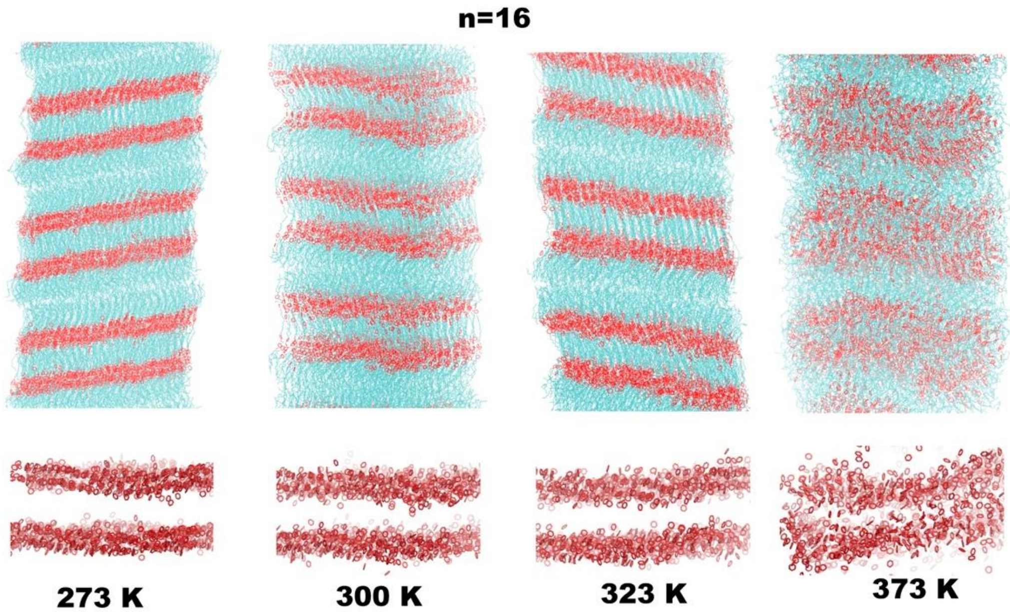

Fig. S19. MD snapshot of the lamellar structure formed by the HOB-16-HOB compound (top) and the configuration adopted by the aromatic moieties in the assembled structure at different temperatures (bottom). Cyan, red and blue sticks represent the oleyl chains, aromatic rings, and linkers.

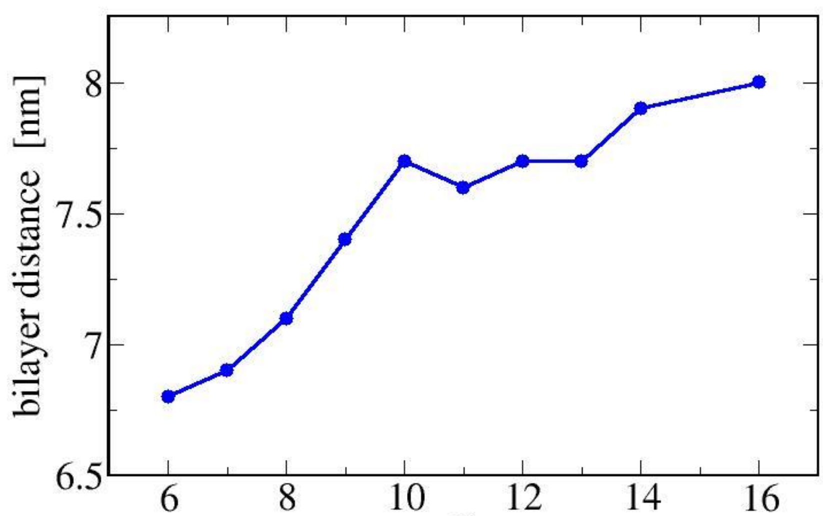

Fig. S20. Distance between two layers of molecules in the lamellar assembly a function of n at 298 K

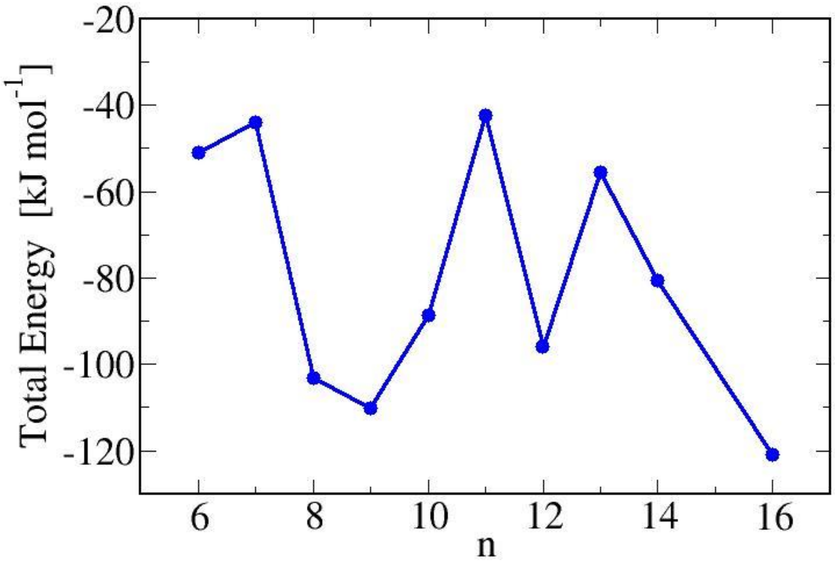

Fig. S21. The total energy of the assembled HOB-n-HOB system as a function of n at 298 K