

SUPPLEMENTARY INFORMATION

Phase Behaviour of Liquid Crystalline Dendronized Fullerene Binary Mixtures

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1. Materials and Methods

Reagents

1-Bromoheptane (99 %), *p*-toluenesulfonic acid (PTSA, 99 %) (all from J&K Chemical), methyl 3,4,5-trihydroxybenzoate (98 %), 1,8-octanediol (98+ %), 4-(dimethylamino)pyridine (DMAP, 99 %), *N,N*-diisopropylcarbodiimide (DIPC, 99 %), 1,2-dichlorobenzene (99 %) (all from Alfa Aesar), trifluoroacetic acid (chemically pure), *N,N*-dimethylformamide (DMF, analytical reagent), (all from Sinopharm Chemical Reagent Co., Ltd, China) were used as received. Chloroform (analytical reagent, Sinopharm Chemical Reagent Co., Ltd, China) was purified by distillation before use. [60]Fullerene (99.9 %) was purchased from Yongxin Technology Co., Ltd (Henan, China). [60]Fullerenoacetic acid was synthesized as reference.^{1,2} All other chemicals were commercially available and were used as received.

Instruments and Methods

NMR spectra were obtained on an Agilent Direct-Drive II 400 MHz NMR spectrometer (400 MHz ¹H and 100 MHz ¹³C Larmor frequency). The chemical shifts (δ values) were measured in parts per million (ppm) down-field from tetramethylsilane (TMS) as an internal reference.

MALDI-TOF mass spectra were acquired on a GCT-Primier mass spectrometer. Dithranol was served as matrix and was prepared in tetrahydrofuran (THF) at a concentration of 10 mg/mL. Silver trifluoroacetate (AgTFA) was served as cationizing agent and was prepared in THF at a concentration of 10 mg/mL.

DSC measurements were carried out on a TA Q 200 instrument with nitrogen as the purge gas. Aluminum sample pans were used.

SAXS experiments were carried out on an X-ray scattering instrument (SAXSess mc², Anton Paar) equipped with line collimation and a 2200 W sealed-tube X-ray generator (Cu-K α , $\lambda = 0.154$ nm). Powder samples were wrapped in aluminum foil for SAXS experiments. The sample was kept under vacuum during irradiation. An imaging plate was used to record the scattering pattern. Silver behenate was used as the calibration standard.

2. Synthetic Procedures and Characterization Data

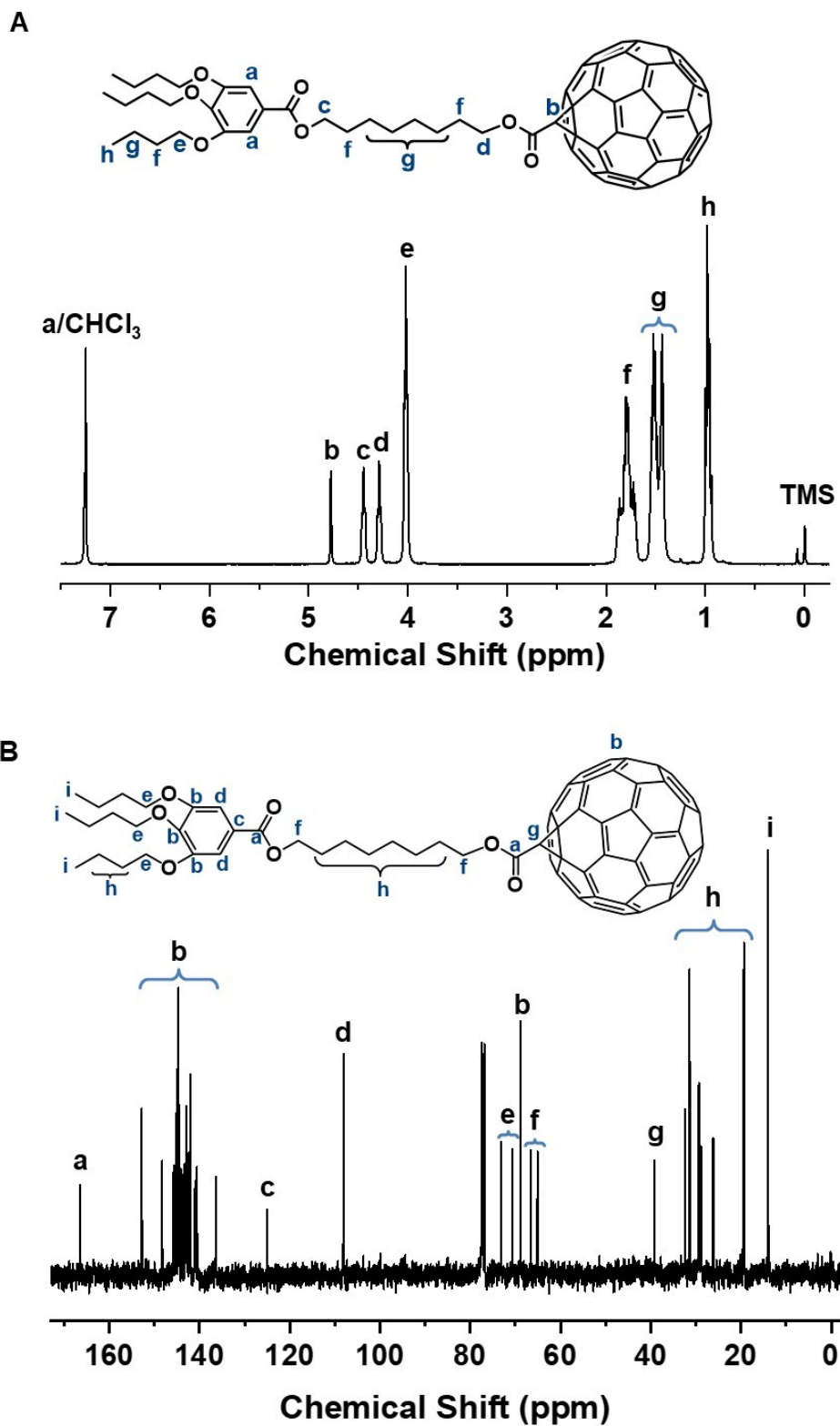
C₆₀-4 was synthesized as same as the procedure reported previously.³

¹H NMR (400 MHz, CDCl₃): δ 0.98 (q, 9H), 1.35-1.61 (m, 14H), 1.67-1.93 (m, 10H), 4.02 (t, 6H), 4.29 (t, 2H), 4.45 (t, 2H), 4.78 (s, 1H), 7.25 (s, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 13.82, 19.04, 19.19, 25.88, 25.98, 28.60, 28.68, 29.17, 31.22, 32.20, 38.96, 64.94, 66.42, 68.70, 70.49, 72.97, 107.91, 124.93, 136.23, 140.40, 140.75, 140.94, 141.91, 142.04, 142.18, 142.24, 142.65, 142.80, 143.10, 143.56, 143.79, 144.25, 144.91, 145.43, 145.64, 148.11, 152.65, 166.27, 166.30.

MALDI-TOF, Calc. for C₈₉H₄₆O₇Ag: (M•Ag)⁺ 1333.229. Found: 1333.410.

3. Supporting Figures



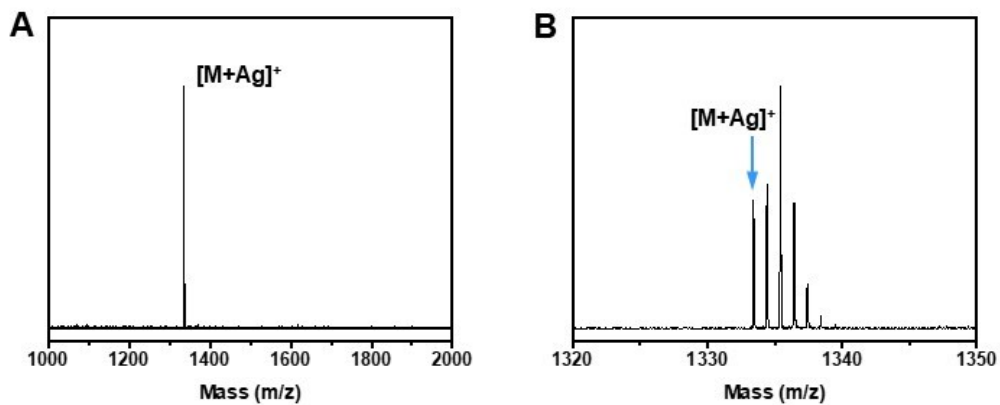


Figure S2. MALDI-TOF mass spectra of C_{60} -4. (A) The overview of the spectrum. (B) The zoom-in view of the spectrum.

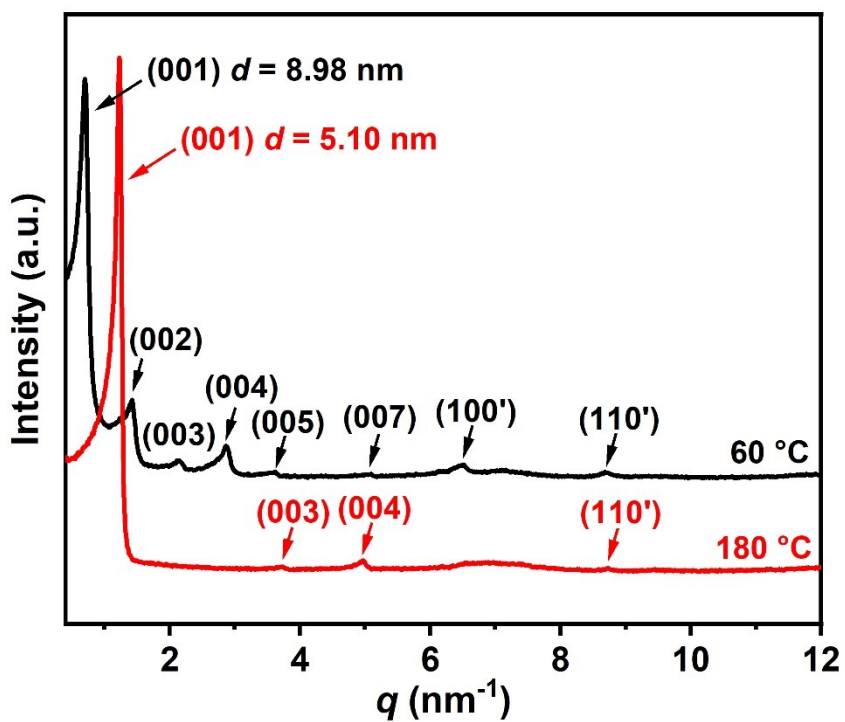


Figure S3. SAXS patterns of C_{60} -4 at 60 °C (L_x , black line) and 180 °C (L_Q , red line).

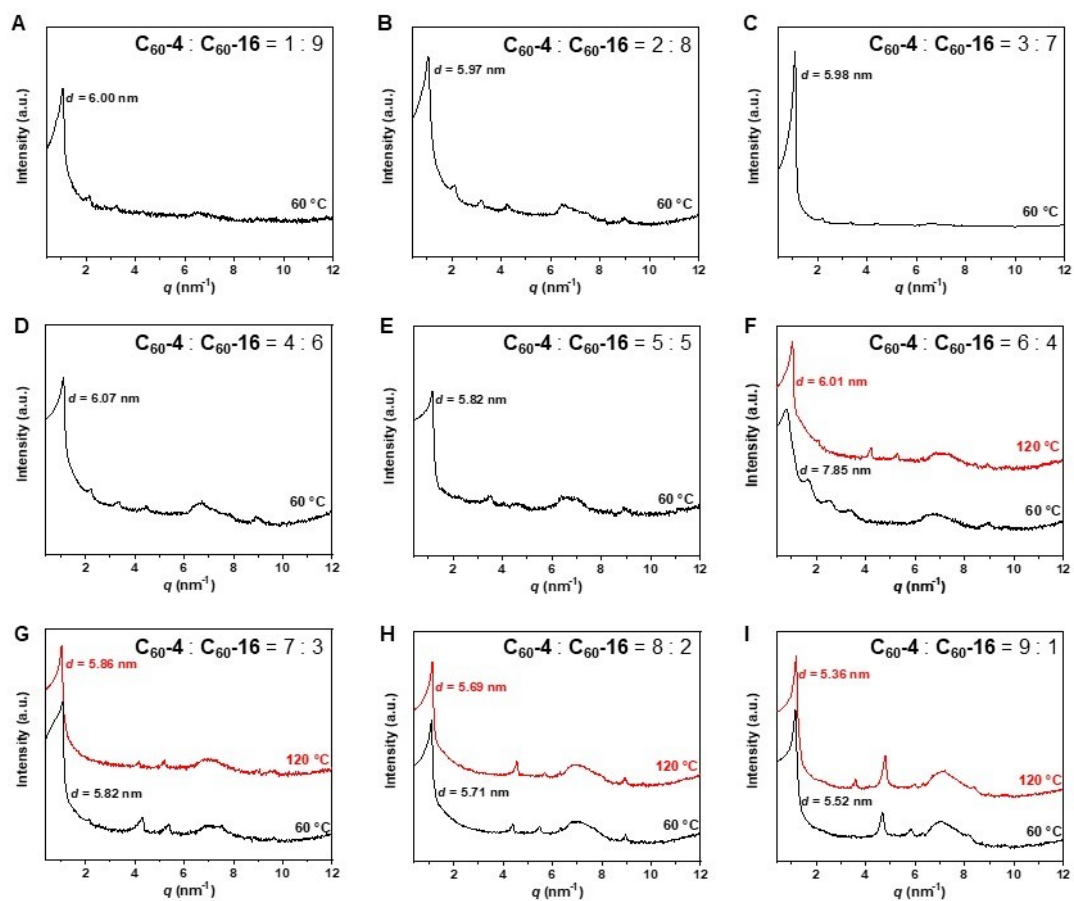


Figure S4. SAXS patterns of the C_{60-4} and C_{60-16} blends with molar ratio 1 : 9 (A), 2 : 8 (B), 3 : 7 (C), 4 : 6 (D), 5 : 5 (E), 6 : 4 (F), 7 : 3 (G), 8 : 2 (H), 9 : 1 (I).

4. References

- (1) T. Tada, Y. Ishida and K. Saigo, Synthesis and reactions of 2,2-[60]fullerenoalkanoyl chlorides, *J. Org. Chem.*, 2006, **71**, 1633-1639.
- (2) B. Ma, C. E. Bunker, R. Guduru, X.-F. Zhang and Y.-P. Sun, Quantitative spectroscopic studies of the photoexcited state properties of methano- and pyrrolidino-[60]fullerene derivatives, *J. Phys. Chem. A*, 1997, **101**, 5626-5632.
- (3) X. Zhang, C.-H. Hsu, X. Ren, Y. Gu, B. Song, H.-J. Sun, S. Yang, E. Chen, Y. Tu, X. Li, Y. Li and X. Zhu, Supramolecular [60]fullerene liquid crystals formed by self-organized two-dimensional crystals, *Angew. Chem. Inter. Ed.*, 2015, **54**, 114-117.