Supplementary material

Long-range single domain array of a 5-nm pattern of supramolecules via solvent annealing in a double-sandwich cell

Kiok Kwon [1], *Kangho Park*[1] *and Hee-Tae Jung*[1*]

[1]Department of Chemical & Biomolecular Engineering (BK-21 plus) and KAIST Institute for Nanocentury, KAIST, Daejeon 34141, Korea

*Correspondence to: heetae@kaist.ac.kr

Figures S1-9:

Contact angle (°)	Carbon	Si	SiO_2	PVA89	PVA80	PVA40	PDMS	TAF
Dendrimer 1 solution (10 wt % in ODCB)	14.7	20.1	16.5	9.2	9.9	10.5	47.2	75.1
ODCB	20.6	10.2	14.6	-	-	-	44.5	81.5
Dendrimer 1 melt (100°C, isotropic melt)	39.8	24.0	20.3	22.2	24.6	25.4	50.8	74.1

Table S1. Contact angle of dendrimer 1 solution (10 wt% in ODCB), pure solvent (ODCB) and dendrimer melt on various solid surfaces. Contact angle of dendrimer solution and pure solvent is measured at 25 °C. Contact angle of dendrimer melt is at 100 °C above isotropic transition temperature (87 °C) by placing a solid surface on hot-stage.

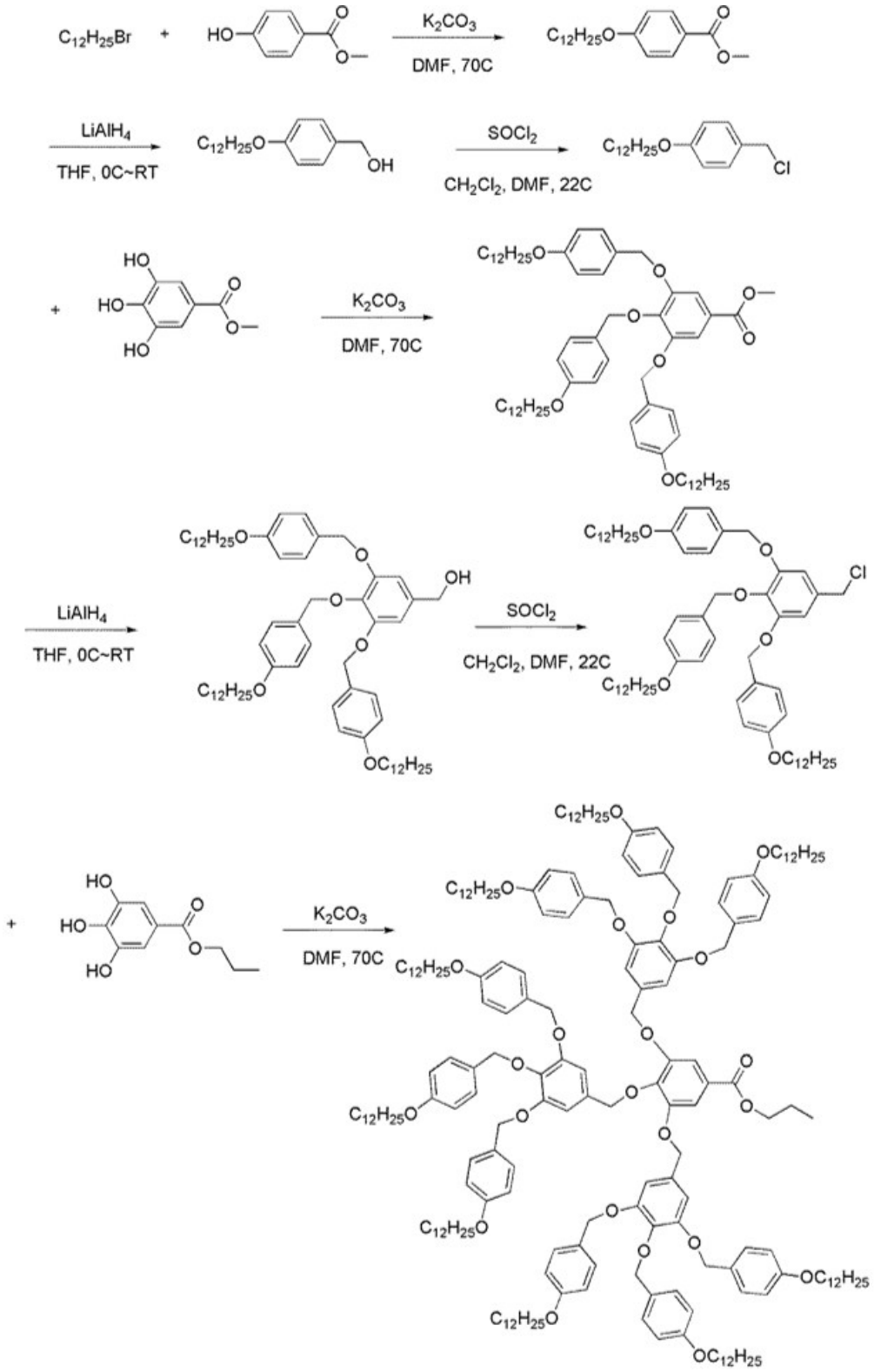


Figure S1. Supramolecular material **1** [1, 2, 3-tris [(3, 4, 5-tris [(4-(n-dodecan-1-yloxy) benzyl) oxy] benzyl) oxy] –benzene was prepared by alkylation of propyl gallate with 3, 4, 5- tris[(4-(n-dodecan-1-yloxy) benzyl) oxy] benzyl] alcohol in DMF at 70℃ with K_2CO_3.

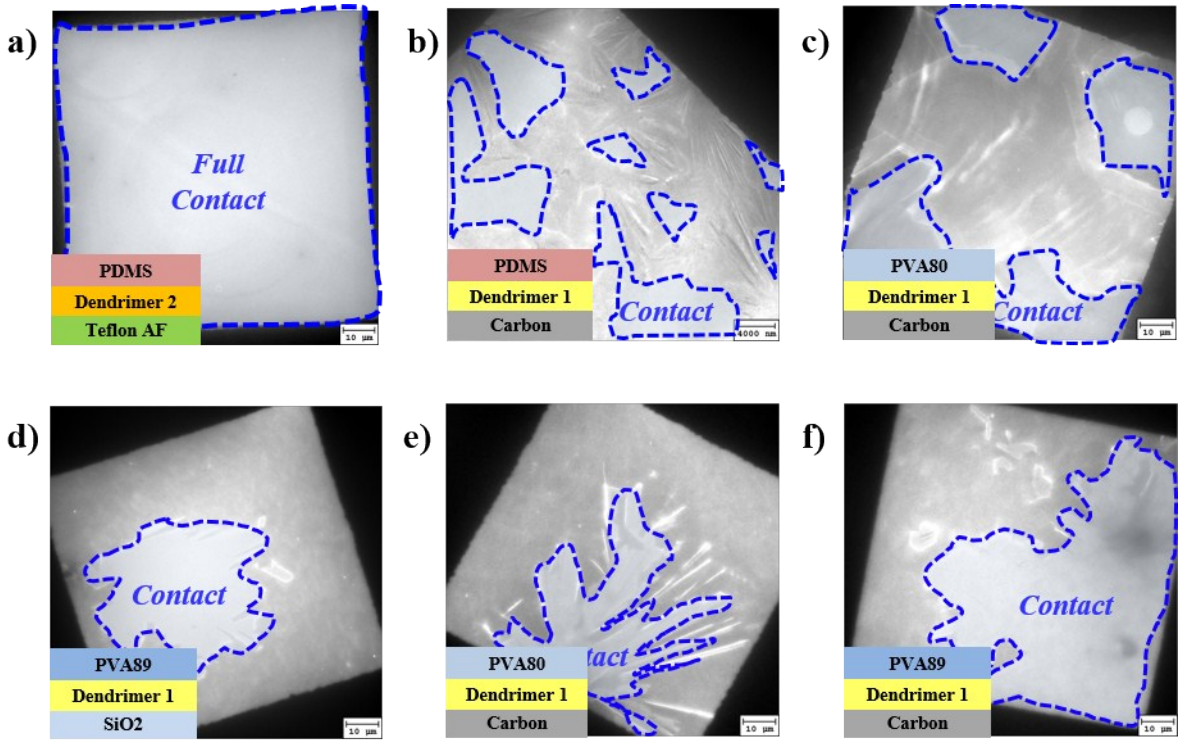


Figure S2. Low magnification TEM image of dendrimer film annealed via thermal annealing in double-sandwiched cell. Highly ordered vertical orientation of dendrimer column is only observed at marked region, which was driven by conformal contact of dendrimer melt and solid surfaces of double-sandwiched cell.

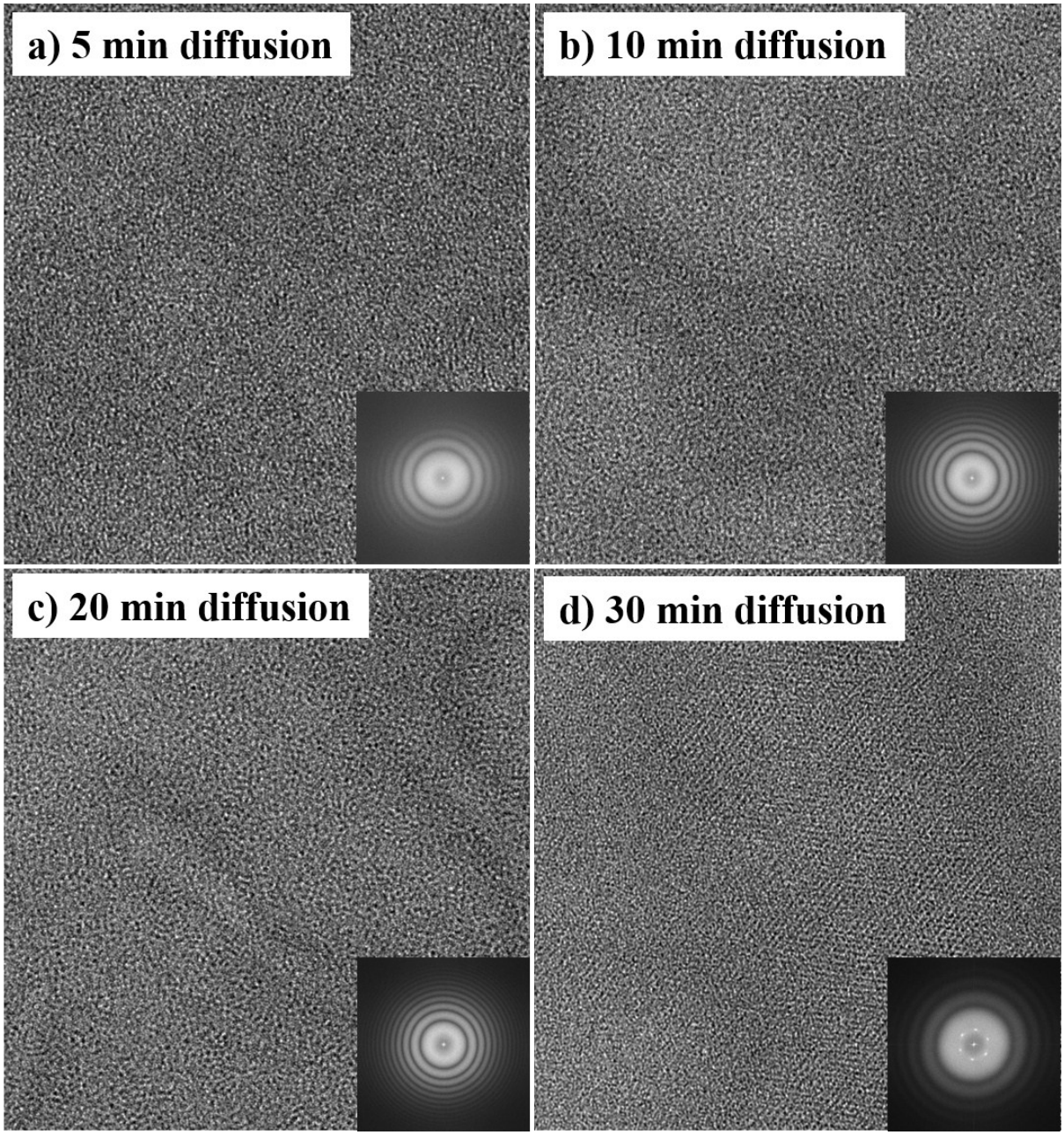


Figure S3. TEM image of suprmamolecular dendrimer material 1, confined between PVA 89 (400 nm) top-coat and Carbon supported TEM grid, treated with different (ODCB) solvent diffusion time (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min at 25 °C, and subsequent solvent evaporation for 60min at 50 °C.

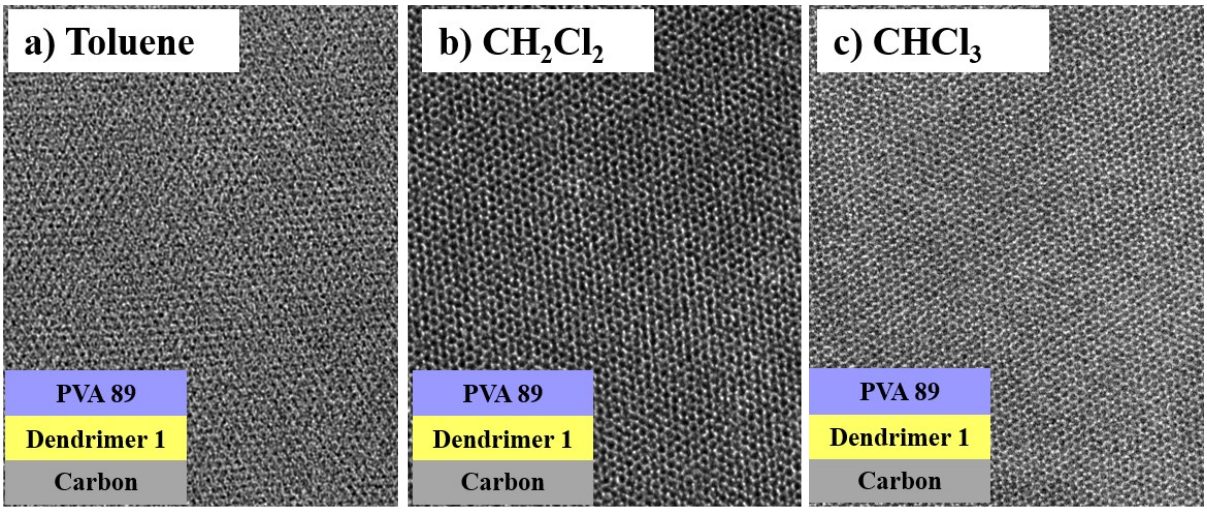


Figure S4. TEM image of suprmamolecular dendrimer material 1, confined between PVA 89 (400 nm) top-coat and Carbon supported TEM grid, treated with different solvent (a) toluene, (b) dichloromethane, (c) chloroform for 60 min at 25 °C, and subsequent solvent evaporation for 60 min at 50 °C.

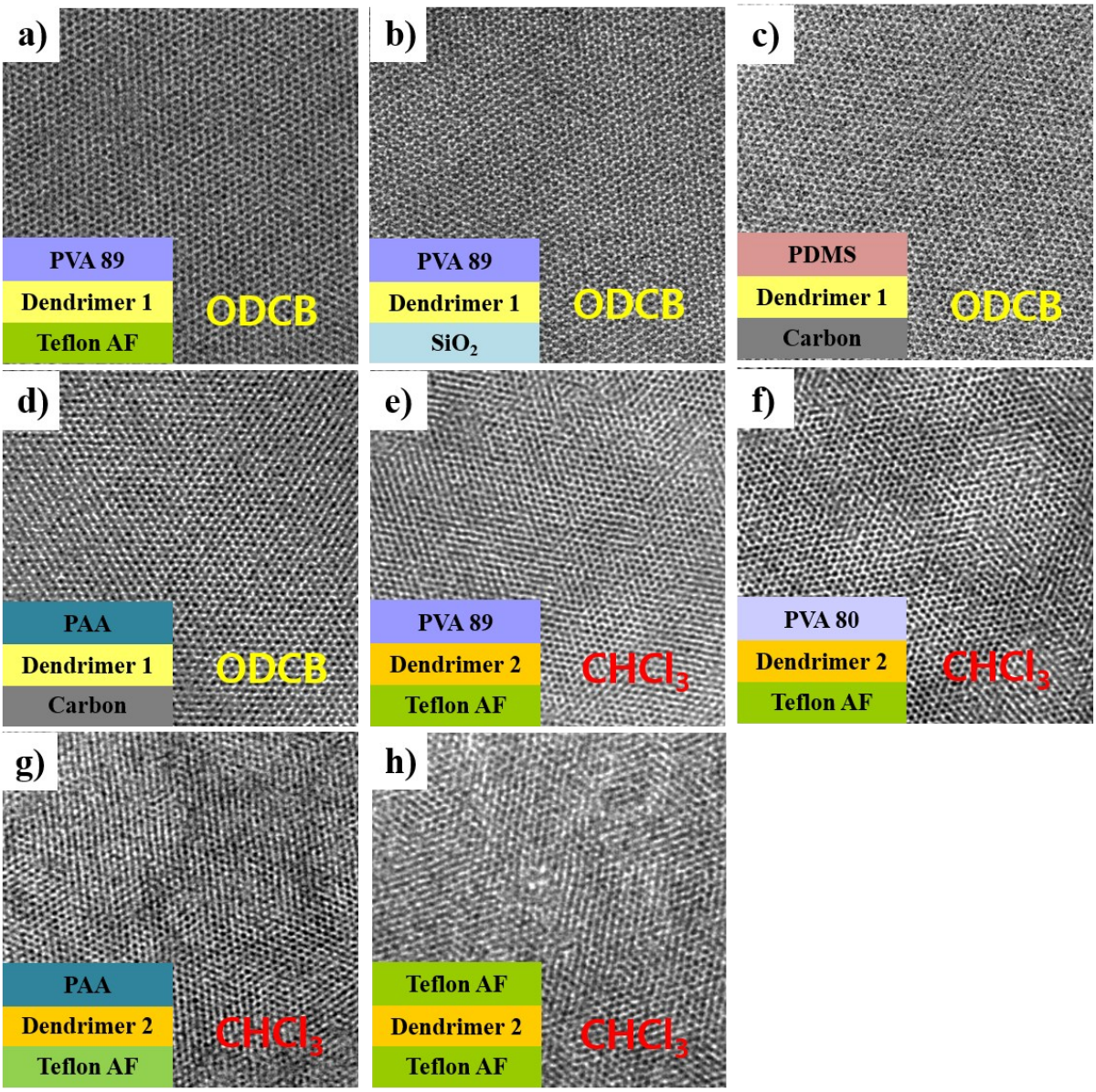


Figure S5. TEM images of supramolecular column created by solvent annealing a film of dendrimer 1 film (a-d) with ODCB and dendrimer film 2 (e-h) with chloroform between different solid surface pairs. (a) Teflon AF bottom - Dendrimer 1 - PVA 89 top with ODCB, (b) SiO2 bottom - Dendrimer 1 - PVA 89 top with ODCB, (c) Carbon bottom - Dendrimer 1 – PDMS top with ODCB, (d) Carbon bottom – Dendrimer 1 - PAA (Polyacrylic acid) top with ODCB, (e) Teflon AF bottom - Dendrimer 2 - PVA 89 top with chloroform, (f) Teflon AF bottom - Dendrimer 2 – PVA 80 top with chloroform, (g) Teflon AF bottom- Dendrimer 2 - PAA top with chloroform, (h) Teflon AF bottom - Dendrimer 2 – Teflon AF top with chloroform. Schematic illustration of two solid surface (right bottom inset). Thickness of all top-coats are adjusted to 400 nm. All bottom substrate is carbon supporated TEM grid and polymer (20 nm) coated TEM grid. Solvent annealing conditions are fixed to 60 min diffusion (25°C) and 60 min evaporation (50 °C)

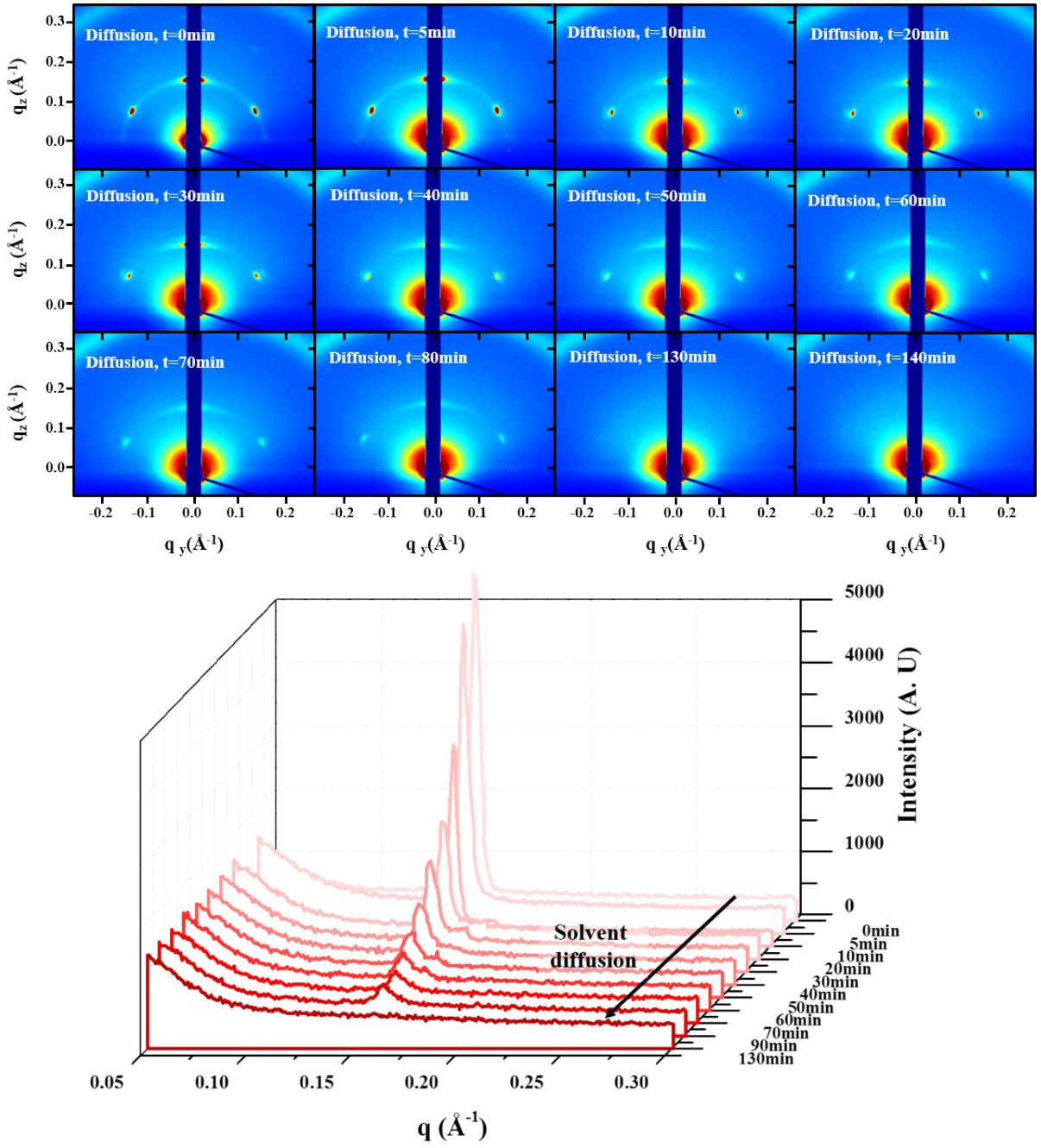


Figure S6. In-situ GISAXS analysis during solvent diffusion process. a) GISAXS images during solvent diffusion step for 140 min. b) The intensity of [-1-20] reflection pattern at out of plane was plotted as a function of diffusion time.

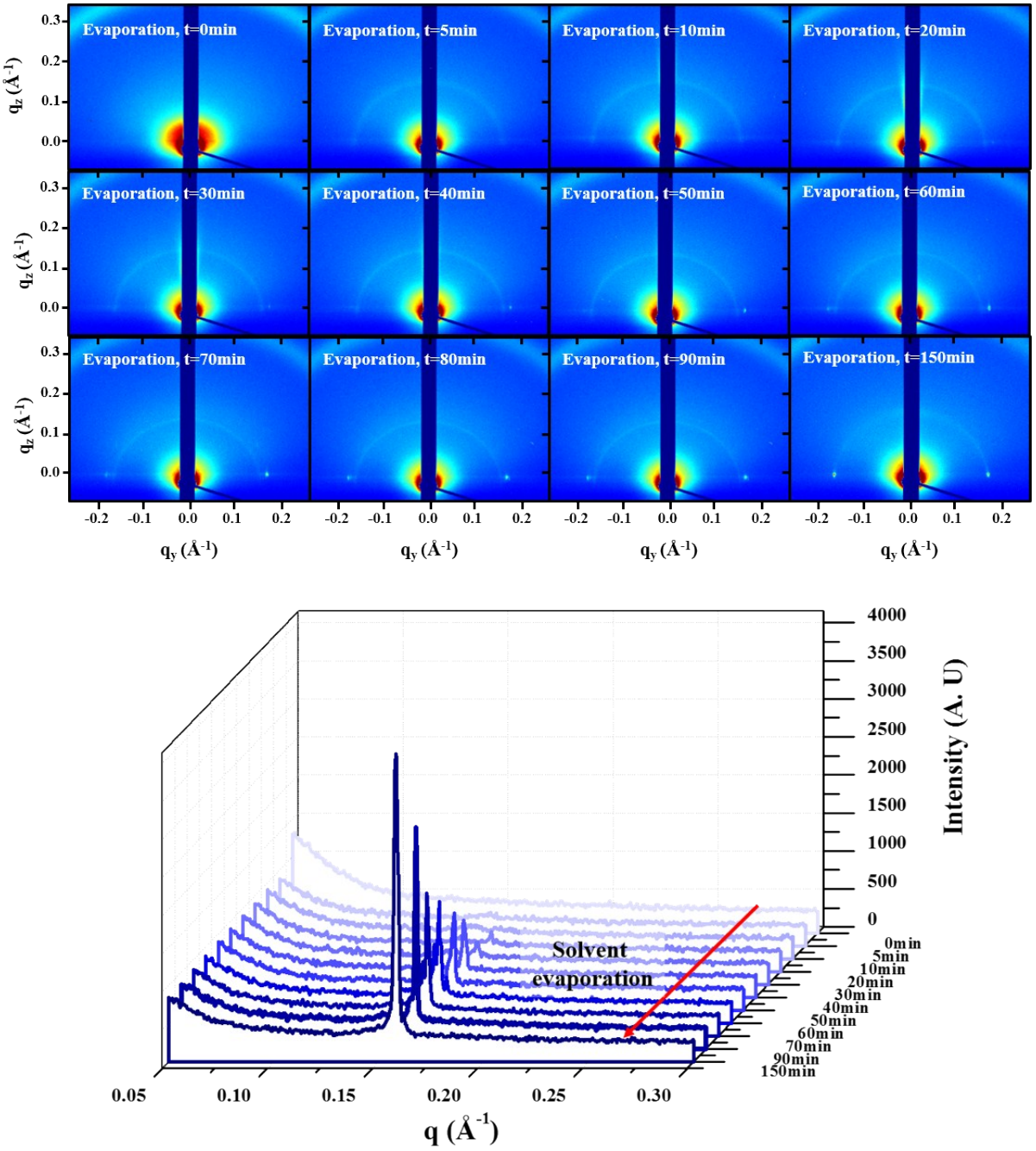
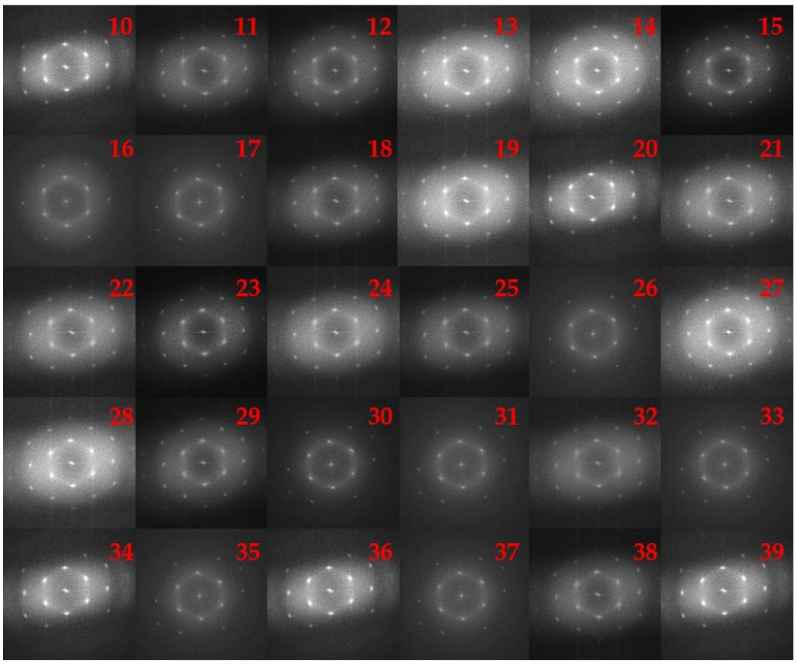


Figure S7. In-situ GISAXS analysis during solvent evaporation process. a) GISAXS images during solvent evaporation step for 1450 min. b) The intensity of [110] reflection pattern at in-plane was plotted as a function of evaporation time.

a)



b)

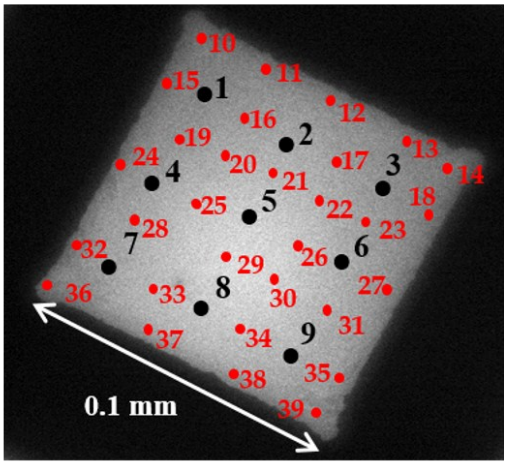


Figure S8. (a) FFT patterns of hexagonal columnar structure of dendrimer 1 on carbon supported TEM grid from (b) 30 different positions on the one square of TEM grid (0.1 mm x 0.1 mm).

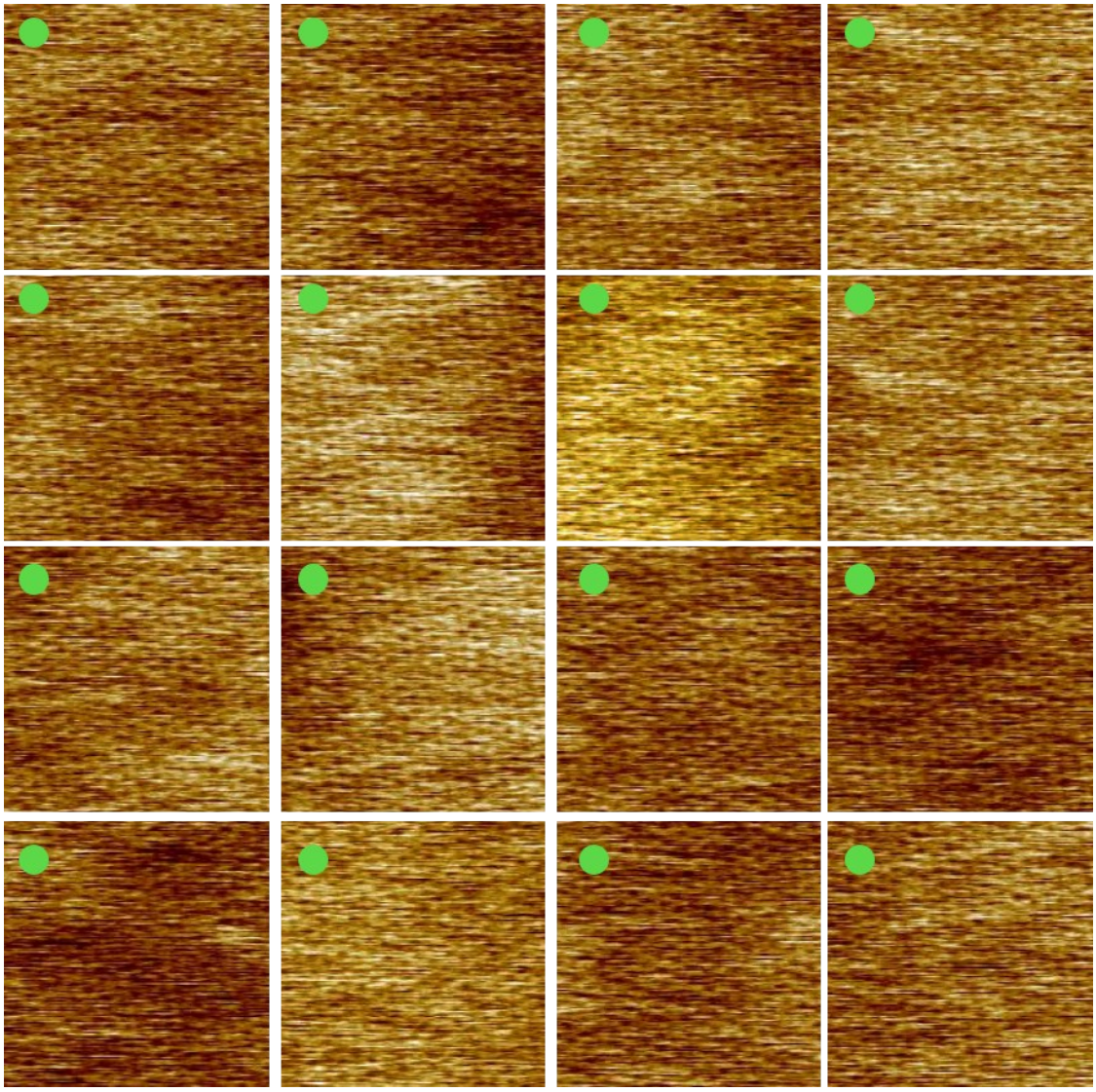


Figure S9. Original AFM image of 16 FFT patterns, marked green dots, inside of the dashed line of Figure 6d.

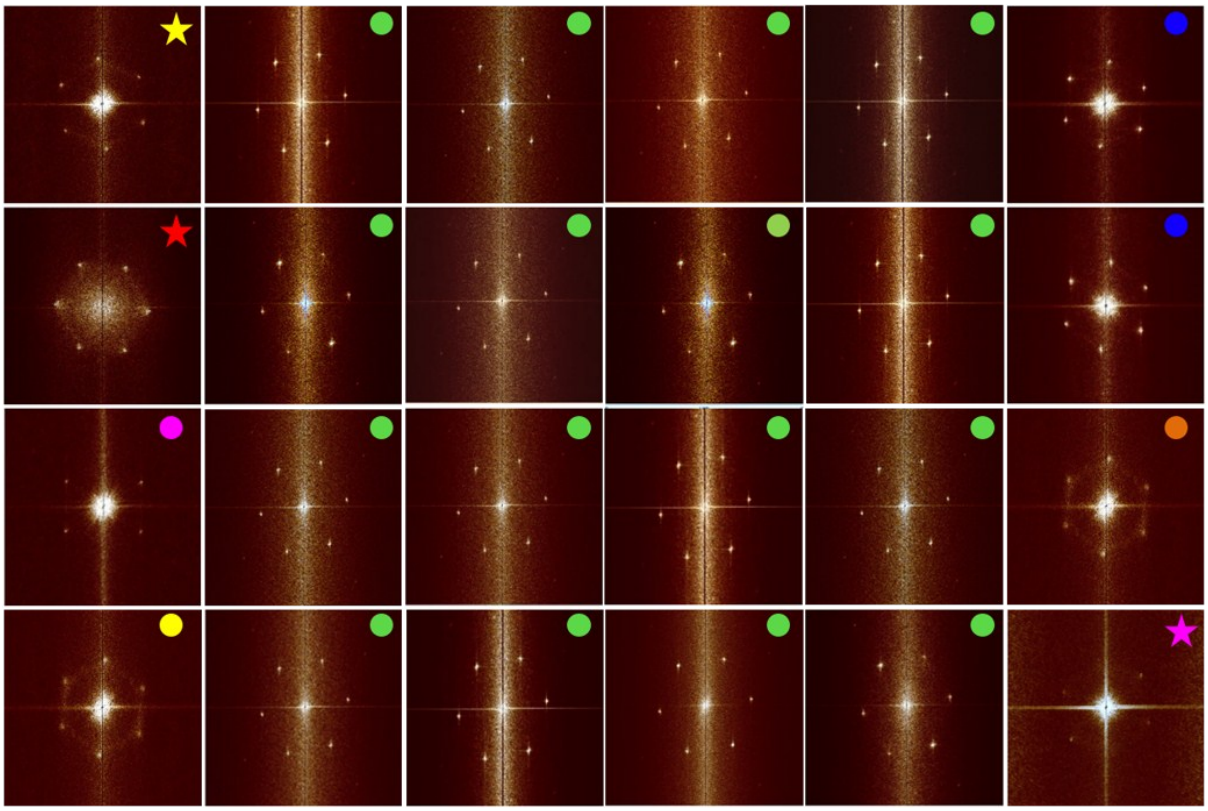


Figure S10. FFT pattern of 24 different marked regions in Figure 6d. A two-dimensional (2D) FFT pattern of the AFM image from 16 positions within the dashed line (denoted as green circles) exhibits a clear six-spot diffraction in the same array direction. The direction of a hexagonally packed cylindrical array changed to the dashed line boundary. This observation revealed that the entire region within the dashed line comprises a single domain and that other domains are present outside the dashed line.