Supplementary Information

Apex Hydrogen Bonds in Dendron Assembly Modulate Close-packed Mesocrystal Structures

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Supporting Figures

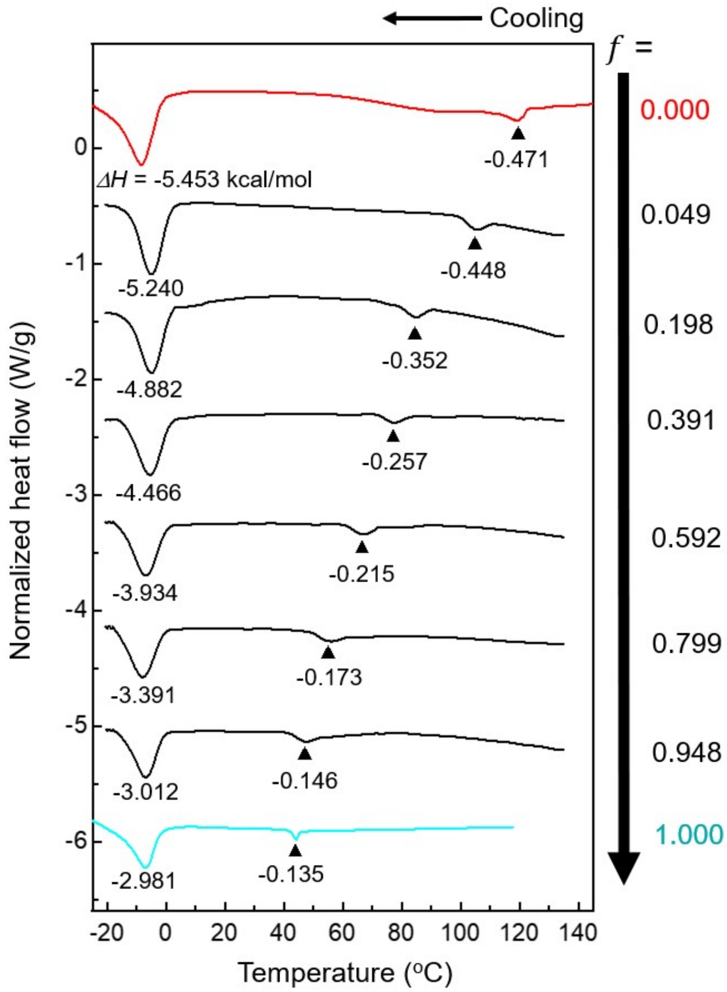

Fig. S1 DSC thermograms measured at a cooling rate of -10 °C/min from 150 to -30 °C.

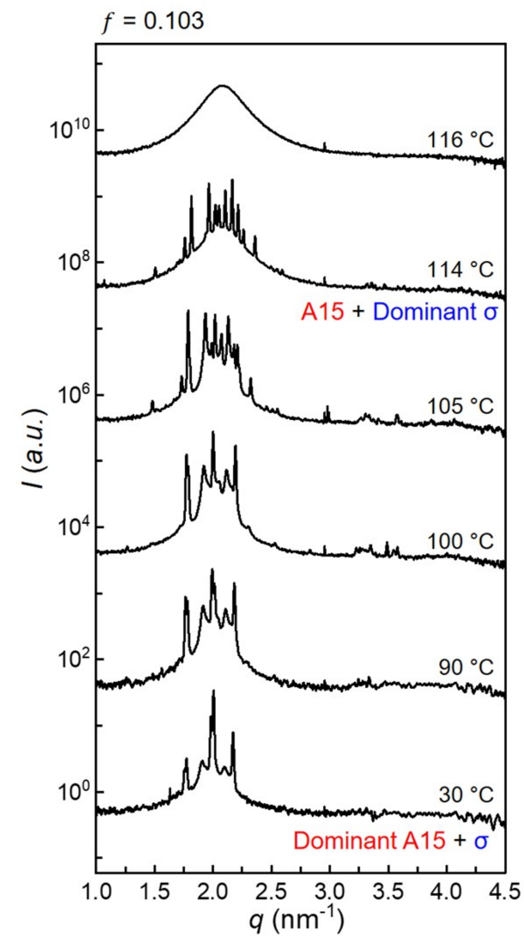

Fig. S2 SAXS intensity profiles of a dendron assembly with f = 0.103. The A15 and σ phases coexist at temperatures lower than 114 ^{o}C. However, the σ phase continues to grow at the expense of the A15 phase as the temperature increases.

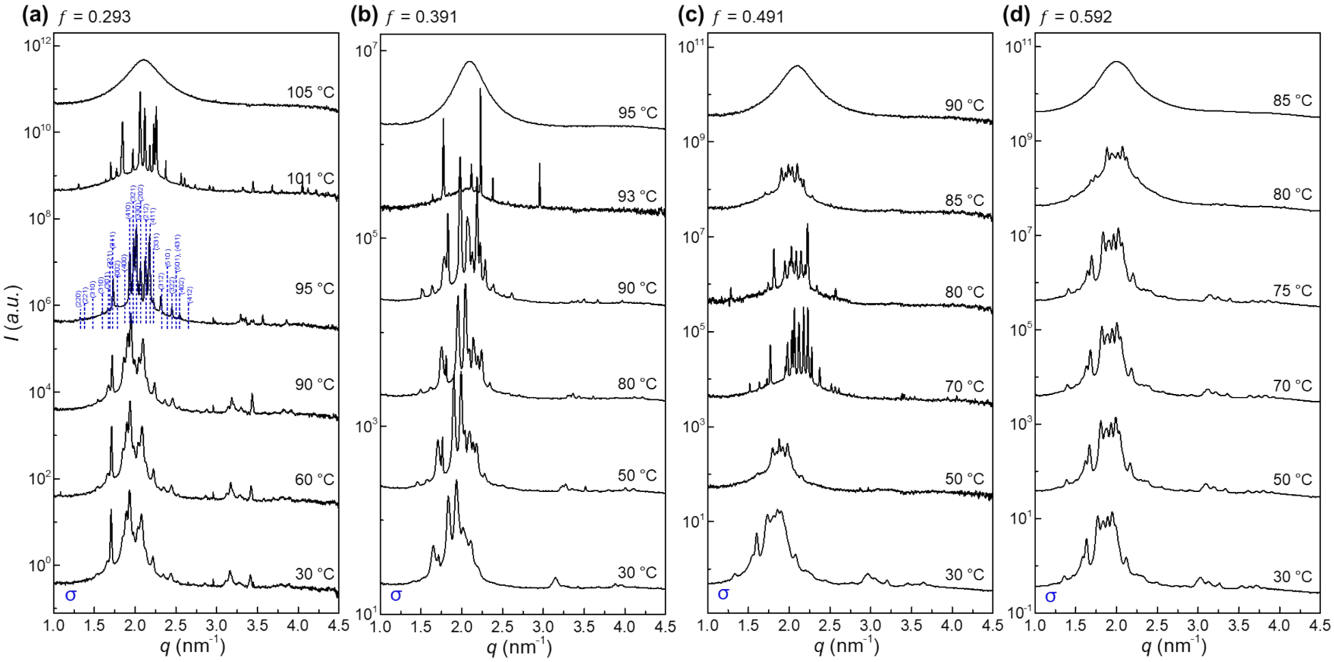

Fig. S3 SAXS intensity profiles of dendron assemblies with (a) f = 0.293 , (b) f = 0.391, (c) f = 0.491, and (d) f = 0.592, displaying that only the σ phases become an isotropic phase with increasing temperature. Miller indices of σ phase are marked on the intensity profile measured at 95 °C (a). The σ phase window extends from f = 0.198 to f = 0.592, although the characteristic intensities of σ phase diminish with increasing f.

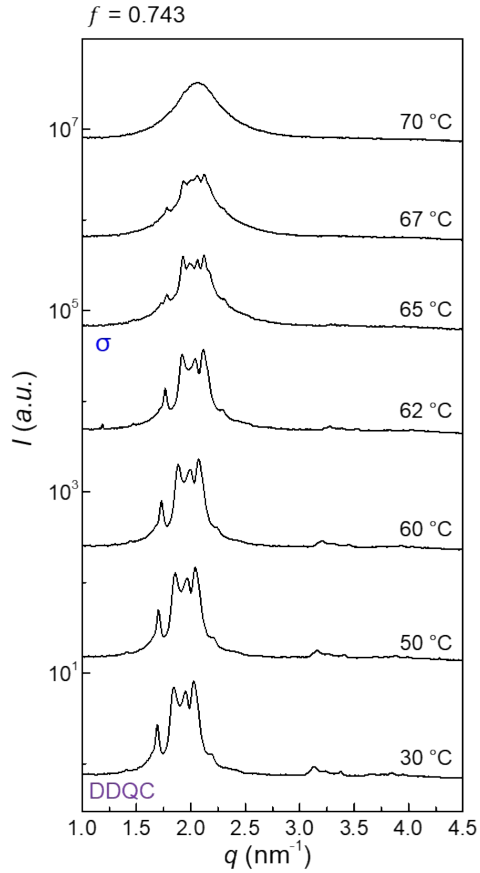

Fig. S4 SAXS intensity profiles of a dendron assembly with f = 0.743. The DDQC phase persists to 62 °C and transforms into the σ phase at 65 °C prior to becoming an isotropic phase above 70 °C. These DDQC–σ transition and isotropisation occur at slightly lower temperatures than those of f = 0.698.

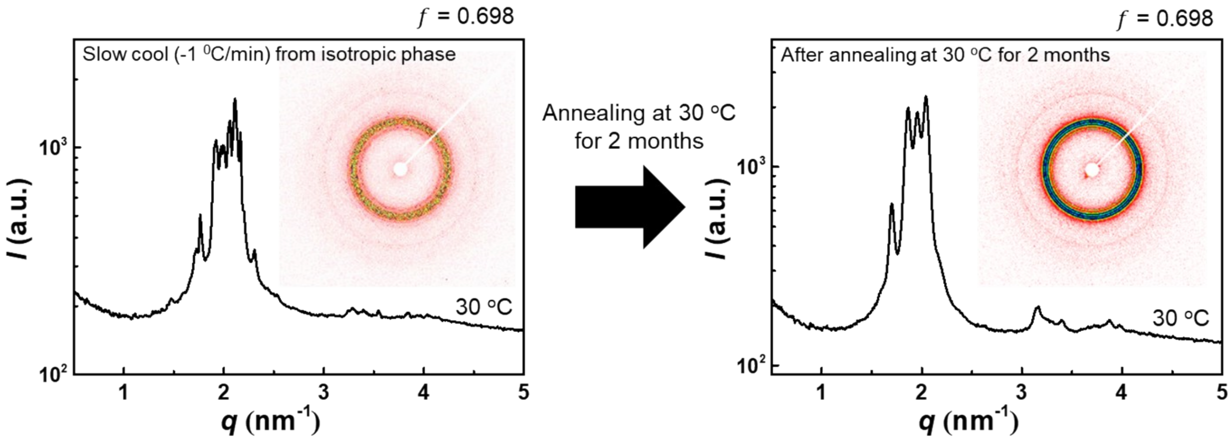

Fig. S5 SAXS intensity profiles and 2D diffraction patterns of a dendron assembly with f = 0.698 depending on the different annealing times of 1 day (left) and 2 months (right). The slow-cooling (-1 °C/min) phase from an isotropic state was not the DDQC but the σ phase (left) within the experimental time scale of 1 day. However, the DDQC phase (right) was fully recovered when the sample was reannealed at 30 °C for a long period of 2 months.

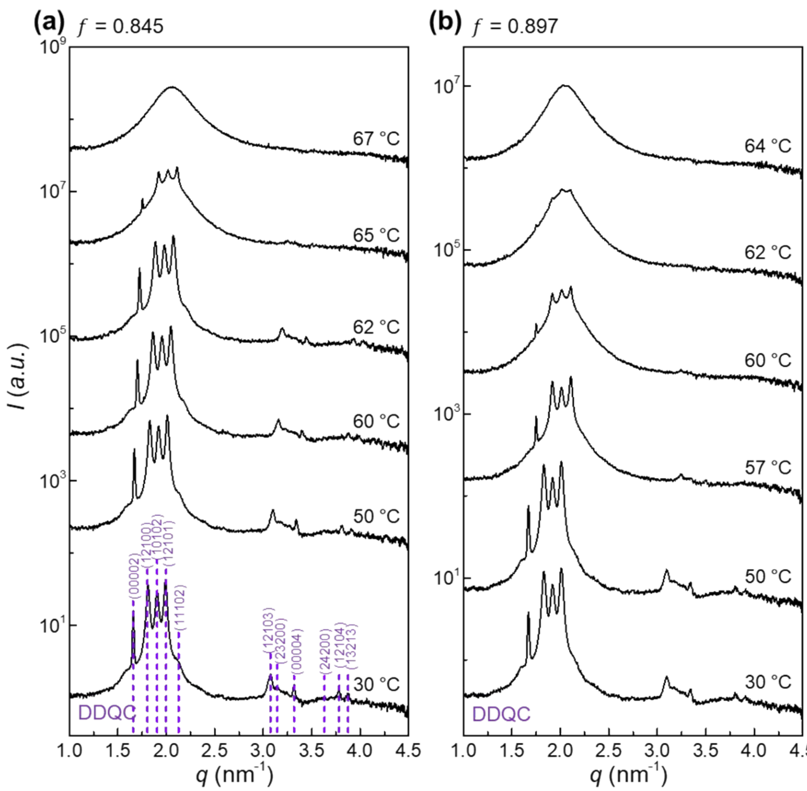

Fig. S6 SAXS intensity profiles of dendron assemblies with (a) f = 0.845 and (b) f = 0.897, displaying that only the DDQC phases become an isotropic phase with increasing temperature. Five-dimensional indices of DDQC phase are marked on the intensity profile measure at 30 ^{o}C (a).

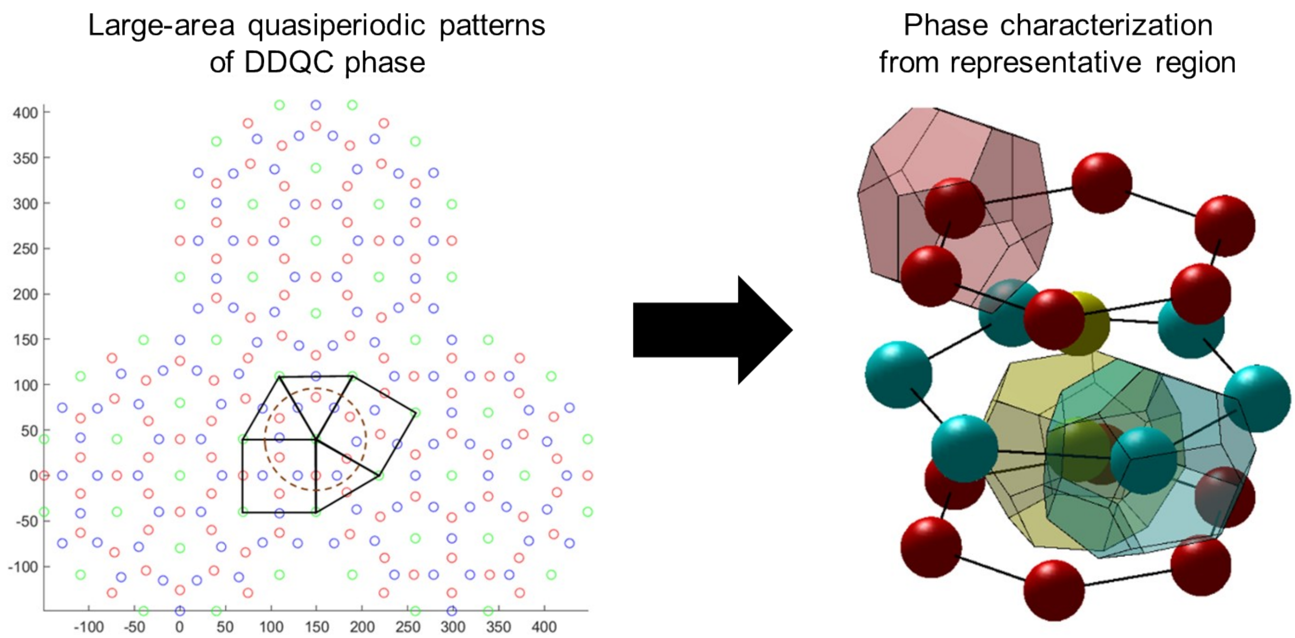

Fig. S7 ED map reconstruction process for the DDQC phase from a dendron assembly with f = 0.845 (at 30 ^{o}C). Large-area quasiperiodic patterns of DDQC phase are retrieved from its ideal fractional coordinates and the unit cell size determined from the X-ray data, which is compiled by a representative region of the quasiperiodic patterns.

Table S1. Structural analysis of representative supramolecular dendron assemblies

Phase	**Sample**	***T*** **(°C)**	***a*** **(=*b*), *c*** **(nm)**	$\bar{R}$ **(nm)**[a]	$\bar{\mathrm{C}}$**N**[b]	$\Delta V/\bar{V}$[c]
A15 (*Pm*3*n*)	f(G2 - CH2NH2) = 0.049	101	7.19, 7.19	2.23	13.500	0.01187
	Wyckoff position	**CN**	**Number of Voronoi cell**	**Surface area of cell (nm²)**	**Volume of cell (nm³)**	**IQ**
	2a	12	2	68.74	45.38	0.749
	6c	14	6	69.71	46.85	0.766
Phase	**Sample**	***T*** **(°C)**	***a*** **(=*b*), *c*** **(nm)**	$\bar{R}$ **(nm)**	$\bar{\mathrm{C}}$**N**	$\Delta V/\bar{V}$
σ ($P4_2/mnm$)	f(G2 - CH2NH2) = 0.198	100	13.0, 6.84	2.12	13.467	0.04127
	Wyckoff position	**CN**	**Number of Voronoi cell**	**Surface area of cell (nm²)**	**Volume of cell (nm³)**	**IQ**
	2a	12	2	57.55	35.62	0.744
	4f	15	4	63.28	42.43	0.786
	8j	14	8	61.28	40.00	0.767
	8i	12	8	59.27	37.48	0.746
	8i’	14	8	62.04	40.75	0.766
Phase	**Sample**	***T*** **(°C)**	***a*** **(=*b*), *c*** **(nm)**	$\bar{R}$ **(nm)**	$\bar{\mathrm{C}}$**N**	$\Delta V/\bar{V}$
DDQC	f(G2 - CH2NH2) = 0.799	30	7.17, 7.28	2.24	13.429	0.07368
	Position	**CN**	**Number of Voronoi cell**	**Surface area of cell (nm²)**	**Volume of cell (nm³)**	**IQ**
	Top/bottom loop	12	3	64.84	42.36	0.745
	Center	14	2	69.43	47.26	0.757
	Middle loop	15	2	72.45	51.41	0.789
Phase	**Sample**	***T*** **(°C)**	***a*** **(=*b*), *c*** **(nm)**	$\bar{R}$ **(nm)**	$\bar{\mathrm{C}}$**N**	$\Delta V/\bar{V}$
C14 ($P6_3/mmc$)	f(G2 - CH2NH2) = 0.924	56	7.21, 11.8	2.19	13.333	0.09491
	Wyckoff position	**CN**	**Number of Voronoi cell**	**Surface area of cell (nm²)**	**Volume of cell (nm³)**	**IQ**
	2a	12	2	63.83	41.26	0.739
	4f	16	4	70.31	49.92	0.810
	6h	12	6	63.34	40.68	0.736

[a]The average particle volume is set to $\bar{V} = 4\pi\bar{R}^3/3 = n^{-1}\sum_{i=1}^{n} V_i$, where $\bar{R}$ and V_i are the average spherical sizes of polyhedrons and the i^{th} polyhedron volume of n particles, respectively.

[b]The average coordination number $\bar{\mathrm{CN}} = (n^{-1}\sum_{i=1}^{n}\mathrm{CN}_i)$, where CN_i is the i^{th} coordination number of n particles.

[c]The particle size diversity $\Delta V/\bar{V} = n^{-1}\sum_{i=1}^{n}|V_i - \bar{V}|/\bar{V}$.