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Enhancing conformational flexibility of dendronized triphenylene *via* diethylene glycol linkers lowers transitions of helical columnar, Frank-Kasper, and quasicrystal phases

Full-length article

Mohammad R. Imam, Mihai Peterca, Qi Xiao, Virgil Percec*

Roy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, USA

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A library of triphenylene (Tp) dendronized with self-assembling dendrons *via* a diethylene glycol linker was synthesized and the corresponding self-organizations were analyzed. They self-organize *via* a crown conformation in helical columns and spherical helices that produce hexagonal columnar, Frank-Kasper and soft quasicrystal assemblies. The same self-organizations are produced in the absence of the diethylene glycol linker except that the phase transitions and isotropization temperatures occur at lower temperatures in the presence of the linker. The incorporation of the flexible diethylene glycol linker induces also strong π-π stacking in helical columns. Spherical helices are spherical distorted short fragments of helical columns and therefore the same principles determine the thermal stability of the hexagonal columnar and of Frank-Kasper and quasicrystal assemblies except that the length of the supramolecular backbone is much longer in helical columns. A comparison of these systems with side-chain liquid crystals indicates that supramolecular dendrimers are stabilized by extended supramolecular backbone conformations. This result suggests pathways to molecularly engineer phase transitions of supramolecular dendrimers self-organized from crown conformations.

Introduction

Self-assembling dendrons adopt, depending on generation number and the multiplicity of their branching point, taper conformations that self-assemble supramolecular helical columns [1–23] and conical conformations that self-assemble supramolecular helical spheres [6–17,24–28]. An increase in dendron generation number transforms the taper shape of the dendron into half a disk or a disk-like conformation [29] that can tilt into a crown conformation. On increasing generation number, the conical dendrons become a fragment of a sphere or even an entire sphere [30]. Covalent and supramolecular polymers dendronized with self-assembling tapered dendrons self-organize

* Corresponding authors.
E-mail address: percec@sas.upenn.edu (V. Percec).
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columnar polymers [1–5,15,16,17,25,31–59]. Covalent and supramolecular polymers dendronized with self-assembling conical dendrons self-organize, at low degrees of polymerization spherical self-organizable polymers [25,53,58–60] and at high degrees of polymerization columnar self-organizable polymers [25,52,53,58,59]. When taper or conical self-assembling dendrons are connected at their apex *via* a cyclotriveratrylene (CTV), cyclotetraveratrilene (CTTV), or triphenylene (Tp), all with multiplicity six or eight, self-assembling dendrimers adopting a crown conformation are obtained. Self-assembling crown dendrimers self-organize helical columns [61–65] or spherical helices [61,64]. When self-assembling dendrons are connected to their apex with molecules containing a lower multiplicity, such as two for the case of perylenebisimides (PBI), the resulting self-assembling dendrimers generate a more complex supramolecular crown obtained from up to four dendrimers [66–68]. Regardless of the mechanism *via* which supramolecular columns are organized, they are helical [18] and the supramolecular spheres are either helical spheres or spherical helices [61,63,69]. Helical spheres and spherical helices led to the discovery of Frank-Kasper phases [6,9–14,17,21,24,25,27–30,38–40,48,51,53,70–80] and soft quasicrystals [81,82]. The most unexpected difference between Frank-Kasper phases self-organized from conical self-assembling dendrons and crown self-assembling dendrimers is that only spherical helices forming self-organizing Frank-Kasper phases exhibit the supramolecular orientational memory effect (SOM) [83–88] while the helical spheres self-organizing Frank-Kasper phases do not exhibit the SOM effect at the transition from spheres to columns. This is the most remarkable difference between these two self-organizing spherical systems. Tapered and conical dendrons are quasi-equivalent [11,25,72,73] and the transition from helical columns to helical spheres involves a multi-step process while the transition from helical columns to the spherical helix proceeds through concerted crown inversion [83–88]. In a recent publication [64] we reported that dendronized CTTV self-organize supramolecular structures with lower transition temperatures than the corresponding dendronized CTV and Tp. The higher flexibility of CTTV vs CTV and Tp was found responsible for this event. Dendronized Tp provides a very interesting supramolecular system not only because it facilitates access to helical columns and spherical helices as well as Frank-Kasper and soft quasicrystals but also because the transition from homochiral sphere to homochiral column can be mediated by donor-acceptor interactions between the donor Tp and a chiral acceptor [62]. Nevertheless, these investigations are limited in scope by the phase transition temperature close to the decomposition temperature. Here we report that incorporation of a diethyleneglycol linker between the Tp and the self-assembling dendron of the dendronized Tp enhances the conformational flexibility of the supramolecular system and lowers transition temperatures of helical columnar, Frank-Kasper and quasicrystal phases with as much as 93 to 44 °C. Therefore, the new concept reported here is complementary to the one recently reported with the conformationally flexible dendronized CTTV [64] and is expected to broaden the design capabilities of all self-organizing building blocks forming Frank-Kasper and quasicrystal phases.

Results and discussion

Synthesis of Dendronized Tp Attached to Dendrons through Diethylene Glycol Linkers. A library containing the hydrogenated 15, the semifluorinated 16 and the self-assembling dendrons 17 to 25 attached *via* a diethylene glycol linker to Tp was synthesized as briefly outlined in Fig. 1. The benzoic acids D1 to D11 were esterified with the OH group of 2 in the presence of EDAC/DPTS or DCC/DPTS to generated 3–13 in 55 to 90% isolated yields. Etherification of 14 with 3–13 was performed in a mixture of DMF-THF at 80 °C in the presence of Cs_2CO_3 to generate 15–25 in 35 to 60% isolated yields, after 16 to 24 h reaction time. Their detailed synthesis and analytical data are available in the Supplemental Information. Table 1 summarizes the results of the structural analysis of these dendronized Tp. The phases assigned in Table 1 were performed by X-ray analysis experiments summarized in Table 2, by methods developed previously in our laboratory and described in great details including for dendronized Tp [62] in original publications and review articles [6,9–14,17,21,24,25,27–30,38–40,48,51,53,70–82]. Therefore, they will not be repeated here except in cases that they provide an unusual structural event.

(4)12G0-(EO)$_2$Tp self-organizes into a supramolecular column with a diameter of 45.9 Å (Table 2). The supramolecular columns produced by **(4)12G0-(EO)$_2$Tp** self-organize in a columnar nematic (N_c) phase. **(4)12F8G0-(EO)$_2$Tp, (3,4)12G1-(EO)$_2$Tp**, and **(3,4,5)12G1-(EO)$_2$Tp** self-assemble into supramolecular columns that self-organize in a 2-D hexagonal columnar lattice without (Φ_h) with intracolumnar order (Φ_h^{io}). At low temperature **(4)12F8G0-(EO)$_2$Tp** shows a c2mm centered rectangular columnar phase ($\Phi_{r\text{-}c}$). **(4–3,4,5)12G1-(EO)$_2$Tp, (4–3,4–3,5)12G2-(EO)$_2$Tp** and **(3,4–3,5)12G2-(EO)$_2$Tp** display a Φ_h^{io} phase at low temperatures. On increasing temperature, **(4–3,4,5)12G1-(EO)$_2$Tp** exhibits a cubic or a Frank-Kasper A15 phase. The higher temperature phases for **(4–3,4–3,5)12G2-(EO)$_2$Tp** and **(3,4–3,5)12G2-(EO)$_2$Tp** were identified as tetragonal or Frank-Kasper σ $P4_2/mnm$ phase and 12-fold QLC respectively (Table 2). However, on cooling both **(4–3,4–3,5)12G2-(EO)$_2$Tp** and **(3,4–3,5)12G2-(EO)$_2$Tp** show only the Φ_h^{io} phase. Diethylene glycol containing dendronized Tp exhibit a fewer number of higher order phases and tend to self-organize into columnar structures. Therefore, aside from increasing flexibility the diethyleneglycol linker reduces the steric effect of the dendrons at the Tp core region, relaxes the interdigitation of long alkyl chains from the periphery of the dendrons, and therefore, disfavors the formation of spherical supramolecular dendrimers and of their Frank-Kasper and quasicrystal phases.

Before continuing this discussion, we must say few words about flexibility and conformational flexibility. Conformational flexibility is determined by the rotational barrier around certain bonds and by nonbonding intermolecular or intramolecular interactions. For example, the rotational barrier around sp^3-sp^3 bonds is much lower that the rotational barrier between sp^2-sp^2 bonds. Sp^3-sp^3 bonds rotate at room temperature in the absence of intermolecular interactions. This is the case in vacuum or solution. In bulk melt state this rotational barrier increases due to intermolecular interactions. In crystal state rotational barrier of the sp^3-sp^3 bonds increases due to strong interactions. The size

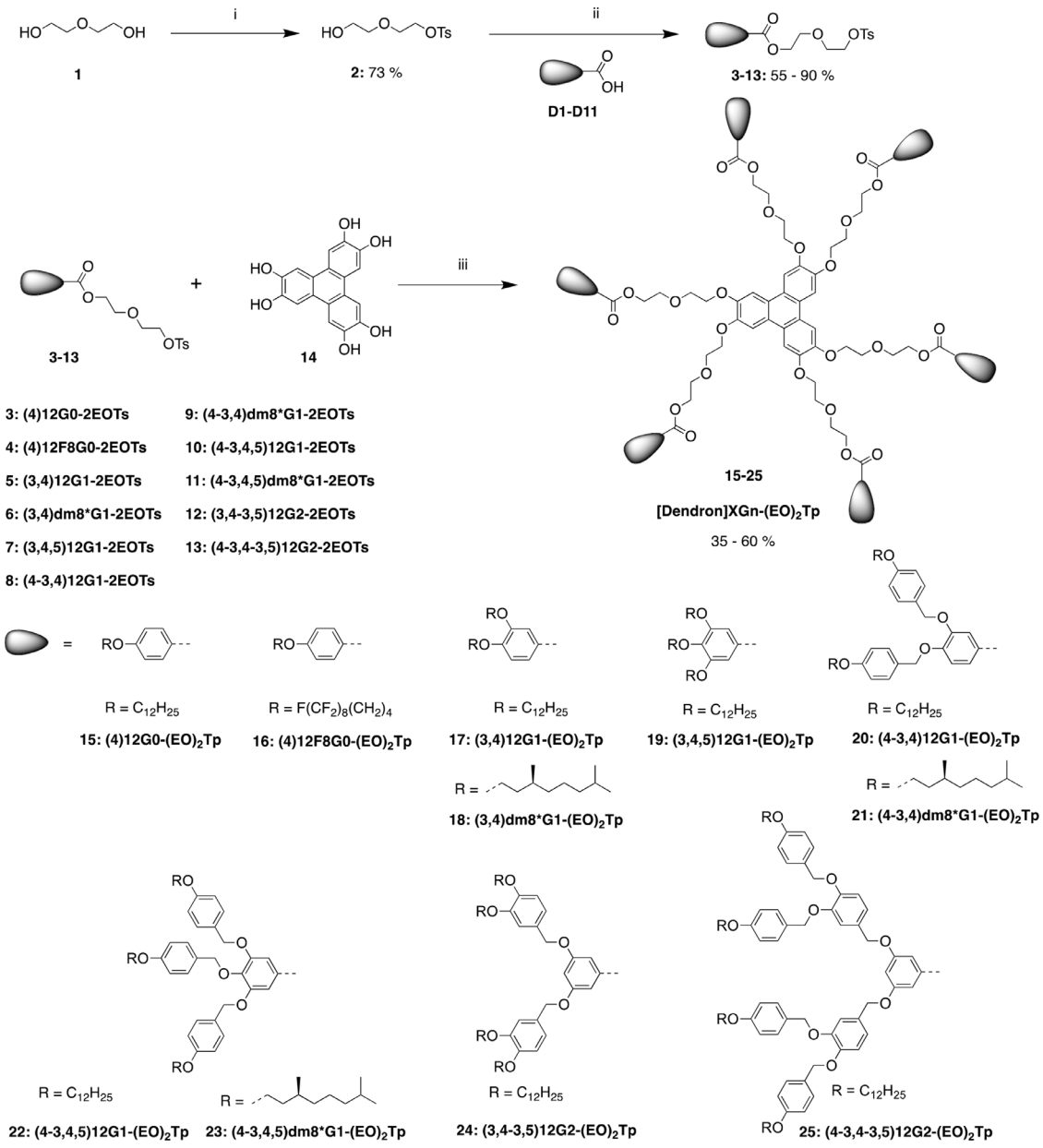

Fig. 1

Synthesis of dendronized triphenylene derivatives with diethylene glycol spacer. Reagents and conditions: i) TsCl, Et_3N. CH_2Cl_2, 23 °C, 1.5 h; ii) EDAC, DPTS, THF, 23 °C, 24 h or DCC, DPTS, CH_2Cl_2, 23 °C, 2 h; iii) Cs_2CO_3, DMF-THF, 80 °C, 16–24 h.

or molar mass of the groups attached to the sp^3-sp^3 bonds also affects their rotational barrier.

Therefore sp^3-sp^3 bonds or compounds constructed from these bonds are relatively flexible but their flexibility is determined by their state of matter. By contrast sp^2-sp^2 bonds are very rigid and rotation around this bond requires the breaking of their π bond. Considering this discussion, diethylene glycol is a very flexible molecule and therefore the attachment of a self-assembling dendron *via* a diethylene glycol linker is made *via* a more flexible bond than a benzyl ether linker (Fig. 2). In addition to its own flexibility, the steric constrains of the diethylene glycol is expected to increase the overall flexibility of the entire system more than a benzyl ether linking group.

Selected examples of TPOM textures exhibited by the dendronized Tp containing oligoethylene glycol linker are shown in Fig. 3. They exhibit the dynamics of low molas mass dendrons during analysis of their textures on TOPM and demonstrate the fast dynamic of these supramolecular assemblies.

Fig. 4 shows the wide-angle XRD pattern of the oriented fiber of **(4–3,4,5)12G1-(EO)$_2$Tp**. Analysis of the XRD pattern by Cerius2 simulation is shown in Fig. 4b and the corresponding molecular model in Fig. 4c. Fig. 4d shows the meridional plot of Fig. 4a that indicates the 4.6 Å π-π stacking of the Tp units along the axis of the pyramidal column. The correlation length ξ of the π-π stacking showing feature involves about nine Tp strata, as calculated from the full width at half maximum

Table 1

Thermal Analysis of the *2D* and *3D* Lattices Self-Organized from the Supramolecular Dendrimers Self-Assembled from Dendronized Triphenylene Containing Diethyleneglycol Linkers.

Compound	Phase transition [°C] and corresponding enthalpy changes (in parenthesis) [kcal mol^{-1}] [a]	
	Heating	**Cooling**
(4)12G0-(EO)$_2$Tp	k 49.4 (6.34) N_c 65.3 (22.50) i k_1 18.5 (7.70) k_2 26.1 (−14.10) N_c 65.0 (23.45) i	i 23.2 (−1.69) N_c 15.9 (−7.42) k
(4)12F8G0-(EO)$_2$Tp	$\Phi_{r\text{-}c}^{crystal}$ 59.1 (6.92) $\Phi_{r\text{-}c}$ 99.6 (1.11) Φ_h^{io} 191.8 (0.86) i $\Phi_{r\text{-}c}^{crystal}$ 69.1 (3.09) $\Phi_{r\text{-}c}$ 86.1 (0.25) Φ_h^{io} 191.8 (0.85) i	i 190.9 (−0.87) Φ_h^{io} 78.9(−0.11) $\Phi_{r\text{-}c}$ 48.6 (−3.78) $\Phi_{r\text{-}c}^{crystal}$
(3,4)12G1-(EO)$_2$Tp	$\Phi_h^{crystal}$ 48.1 (23.14) Φ_h^{io} 71.6 (16.40) Φ_h 93.2 (4.39) i $\Phi_h^{crystal}$ 18.1 (17.13) Φ_h^{io} 66.4 (3.08) Φ_h 93.0 (4.23) i	i 91.0 (−4.42) Φ_h^{io} 13.0 (−16.31) $\Phi_h^{crystal}$
(3,4)dm8*G1-(EO)$_2$Tp	T_g −20.7 Φ_h^{io} 70.4 (3.24) i T_g −22.1 Φ_h^{io} 70.2 (3.15) i	i 66.3 (−3.15) Φ_h^{io} −24.3 T_g
(4–3,4)12G1-(EO)$_2$Tp	Φ_h^{io} 138.3 (4.86) Φ_h 165.2 (14.14) i Φ_h^{io} 138.0 (4.74) Φ_h 165.0 (13.87) i	i 163.7 (−13.46) Φ_h 137.1 (−5.64) Φ_h
(4–3,4)dm8*G1-(EO)$_2$Tp	T_g 17.0 Φ_h^{io} 100.5 (3.06) Φ_h 142.3 (10.52) i T_g 14.1 Φ_h^{io} 99.5 (3.03) Φ_h 142.3 (10.41) i	i 140.1 (−10.42) Φ_h 97.5 (−3.19) Φ_h 8.0 T_g
(3,4,5)12G1-(EO)$_2$Tp	T_g 5.3 Φ_h^{io} 46.7 (48.86) i g_h 8.3 (5.43) Φ_h 47.5 (48.30) i	i 10.8 (−29.48) Φ_h^{io} −11.7 (−0.73) g_h
(4–3,4,5)12G1-(EO)$_2$Tp	$\Phi_h^{io\text{-}1}$ 52.1 (14.32) $\Phi_h^{io\text{-}2}$ 85.9 (22.68) Φ_h 104.3 (1.38) A15 114.2 (0.60) i $\Phi_h^{io\text{-}1}$ 51.6 (39.38) $\Phi_h^{io\text{-}2}$ 87.0 (33.42) Φ_h 105.0 (1.44) A15 114.2 (0.55) i	i 99.4 (−1.53) Φ_h 61.8 (−25.75) $\Phi_h^{io\text{-}2}$ 44.6 (−24.83) $\Phi_h^{io\text{-}1}$
(4–3,4,5)dm8*G1-(EO)$_2$Tp	Φ_h^{io} 74.5 (24.56) σ 101.0 (0.53) i Φ_h^{io} 46.5 (−3.37) Φ_h^{io} 75.0 (22.18) σ 101.0 (0.75) i	i ∼80 [b] σ 39.2 (−14.75) Φ_h^{io}
(4–3,4–3,5)12G2-(EO)$_2$Tp	Φ_h^{io} −13.3 (14.4) T_g 49.8 QLC 169.5 (21.83) i Φ_h^{io} −12.4 (15.4) T_g 54.0 QLC 169.4 (20.70) i	i 167.9 (−18.06) QLC 48.0 T_g −18.6 (−9.38) Φ_h^{io}
(3,4–3,5)12G2-(EO)$_2$Tp	Φ_h^{io} 46.3 (4.33) Φ_h 64.3 (17.44) QLC 100.8 (2.03) i T_g 37.5 Φ_h^{io} 100.6 (1.98) i	i 94.7 (−1.13) Φ_h^{io} 24.3 T_g

[a] Data from the first heating and cooling scans are on the first line, and data from the second heating are on the second line. N_c: nematic columnar phase. $\Phi_{r\text{-}c}^{crystal}$: crystalline ordered centered rectangular columnar phase, $\Phi_{r\text{-}c}$: c2mm centered rectangular columnar phase, Φ_h^{io}: columnar hexagonal lattice with intracolumnar order, $\Phi_h^{crystal}$: crystalline ordered hexagonal columnar lattice, Φ_h: p6mm hexagonal columnar lattice, g: glassy phase, T_g: glass transition, i: isotropic, A15: *Pm3n* cubic lattice, σ: $P4_2/mnm$ tetragonal lattice and QLC: quasi liquid crystal. [b] This transition was observed only by TOPM and XRD experiments. [c] This phase was observed as unidentified tetragonal lattice from fiber XRD experiments. [d] Sum of enthalpies of overlapped peaks.

(fwhm): $\xi = 2\pi/\text{fwhm} = 42$ Å (Figure 4d). The azimuthal plot that integrates the region of the dendron tilt features shown in Figure 4e provided the average dendron tilt angle of 29°.

Additional examples of columnar hexagonal lattices analyzed by oriented fiber XRD experiments are shown in Fig. 5. Their XRD analysis is summarized in Table 2. The stronger π-π stacking of the Tp units of **(4–3,4)12G1-(EO)$_2$Tp** (Fig. 6), **(3,4)12G1-(EO)$_2$Tp** (Figs. 5,7), and **(4–3,4–3,5)12G2-(EO)$_2$Tp** (Figs. 5,7) in comparison with the dendronized Tp without the diethylene glycol linker demonstrates that the longer linker relaxes the packing constrains imposed by the tight arrangement of the Tp aromatic core and therefore, provides access to a mechanism that mediates π-π stacking in this new class of supramolecular assemblies.

Table 3 compares selected examples of phase transitions of dendronized Tp [62] and of dendronized Tp containing diethylene glycol linker reported here. From the analysis of these data, we conclude that incorporation of the diethylene glycol linker decreases isotropization temperatures with as much as 93 °C for **(4)12G0-(EO)$_2$Tp,** 50 °C for **(3,4)12G1-(EO)$_2$Tp**, 73 °C for **(4–3,4)12G1-(EO)$_2$Tp**, 60 °C for **(3,4,5)12G1-(EO)$_2$Tp**, 71 °C for **(4–3,4,5)12G1-(EO)$_2$Tp**, 44 °C for **(4–3,4–3,5)12G2-(EO)$_2$-Tp** and 47 °C for **(3,4–3,5)12G2-(EO)$_2$Tp** (Table 3). The minimum isotropization temperatures decrease observed are 44 °C for **(4–3,4–3,5)12G2-(EO)$_2$Tp** and 47 °C for **(3,4–3,5)12G2-(EO)$_2$Tp** (Table 3) which are for phases generated from spherical helices rather than from helical columns. More studies are required to quantify the extent of decrease in isotropization temperature mediated by flexibility.

It is interesting to remark that in the case of side-chain liquid crystal polymers a combination of long and flexible spacer with flexible backbone is responsible for the

Table 2

Structural and Retrostructural Analysis of the Supramolecular Dendrimers Self-Assembled from Dendronized Diethyleneglycol containing Triphenylene by XRD.

			Peak D-spacings [Å] and their indices							
Dendrimer	**Phase**	**T [°C]**	[a] d_{10} [b] d_{20} [c] d_{10} [d] d_{200} [e] d_{301} [f] d_{411} [g] d_{00002}	d_{11} d_{11} d_{210} d_{002} [f] d_{312} d_{12100}	d_{22} d_{20} d_{211} d_{410} – d_{10102}	d_{42} d_{21} d_{321} d_{202} – d_{12101}	**Lattice dimension or column diameter *a (a,b)* [h] [Å]**	**D_{sphere} [i] (Å)**	***t* [j] (Å)**	**μ [k]**
(4)12G0-$(EO)_2$Tp	N_c	55	[a] 45.9	–	–	–	45.9	–	–	–
(4)12F8G0-$(EO)_2$Tp	$\Phi_{r\text{-}c}$	30	[b] 64.9	51.5	25.8	21.5	$a = 131.6$ $b = 56.2$			
	Φ_h [io]	160	[c] 45.9	–	22.8	–	53.0	–	3.6	1.1
(3,4)12G1-$(EO)_2$Tp	Φ_h [io]	45	[c] 40.5	23.4	20.2	15.3	46.8	–	3.6	1.0
	Φ_h [io]	90	[c] 38.3	22.3	19.4	14.6	44.5	–	–	–
(3,4)dm8*G1-$(EO)_2$Tp	Φ_h [io]	65	[c] 34.1	19.6	17.0	–	39.3	–	3.6	0.9
(4–3,4)12G1-$(EO)_2$Tp	Φ_h [io]	95	[c] 44.7	25.8	22.3	16.9	51.5	–	3.6	1.0
	Φ_h	150	[c] 48.1	27.7	24.1	18.1	55.5	–	3.6	1.2
(4–3,4)dm8*G1-$(EO)_2$Tp	Φ_h [io]	85	[c] 43.0	24.8	21.4	16.2	49.5	–	3.6	1.0
	Φ_h	125	[c] 44.5	25.6	22.2	16.8	51.3	–	3.6	1.1
(3,4,5)12G1-$(EO)_2$Tp	Φ_h [io]	30	[c] 40.1	23.3	20.3	–	46.2	–	4.5	1.0
(4–3,4,5)12G1-$(EO)_2$Tp	Φ_h [io]	80	[c] 45.1	25.9	22.7	–	52.0	–	4.6	1.0
	A15	110	[d] 48.6	43.6	39.8	26.1	97.5	60.5	–	10
(4–3,4,5)dm8*G1-$(EO)_2$Tp	Φ_h [io]	30	[c] 41.9	24.2	20.9	–	48.4	–	4.6	0.9
	σ	96	[e] 47.1	44.9	40.2	39.5	–	–	–	–
			[f] 36.7	34.1	–	–	$a = b = 165.9$ $c = 89.8$	–	–	–
	Φ_h [io]	70	[c] 42.5	24.5	21.2	16.0	49.1	–	4.6	0.9
(4–3,4–3,5)12G2-$(EO)_2$Tp	Φ_h [io]	125	[c] 53.0	30.5	27.2	–	61.2	–	4.7	1.0
(3,4–3,5)12G2-$(EO)_2$Tp	Φ_h [io]	30	[c] 47.0	27.0	23.4	–	54.1	–	4.6	1.0
	QLC	95	[g] 44.8	41.9	40.2	38.6	89.6	–	–	–

[a] d-spacing index for nematic columnar lattice (N_c). [b] d-spacings with indices for c2mm centered rectangular columnar lattice ($\Phi_{r\text{-}c}$). [c] d-spacings with indices for p6mm hexagonal columnar lattice (Φ_h). d-spacings with indices for cubic lattice (A15). [e,f] d-spacings with indices for $P4_2/mnm$ tetragonal lattice (σ). [g] d-spacings with indices for quasi liquid crystal (QLC). [h] For the Φ_h phase lattice dimension (a) is same as the column diameter. For the $\Phi_{r\text{-}c}$ LC phase lattice dimensions a and b are given. For the A15 lattice, $a = b = c$. [i] sphere diameter calculated for A15 phase. [j] average column strata thickness calculated from the oriented fiber XRD patterns. [k] number of dendrimers per supramolecular sphere or per column strata (t) calculated for the p6mm hexagonal using, for the phase using, where $\rho = 0.96$ ($g \bullet cm^{-3}$) -experimental density, N_A- Avogadro's number, and M_{wt}- molecular weight. XRD peaks position and intensity analysis was performed using Datasqueeze Software [89] (version 2.1) that allows background elimination and Gaussian, Lorentzian, Lorentzian squared, or Voigt peak-shape fitting. Indexing of d-spacings was done as reported previously [72].

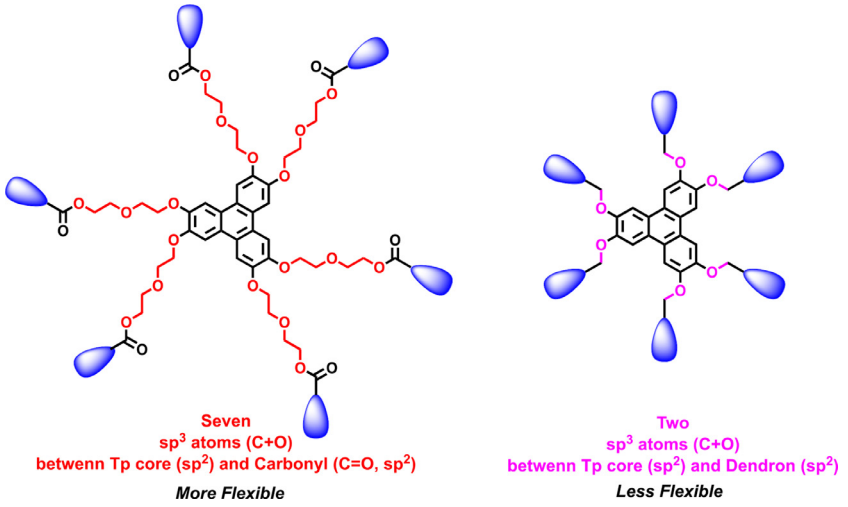

Fig. 2

Comparation of the flexibility between dendronized Tp with diethylene glycol linker (left) and previous reported dendronized Tp (right) [62].

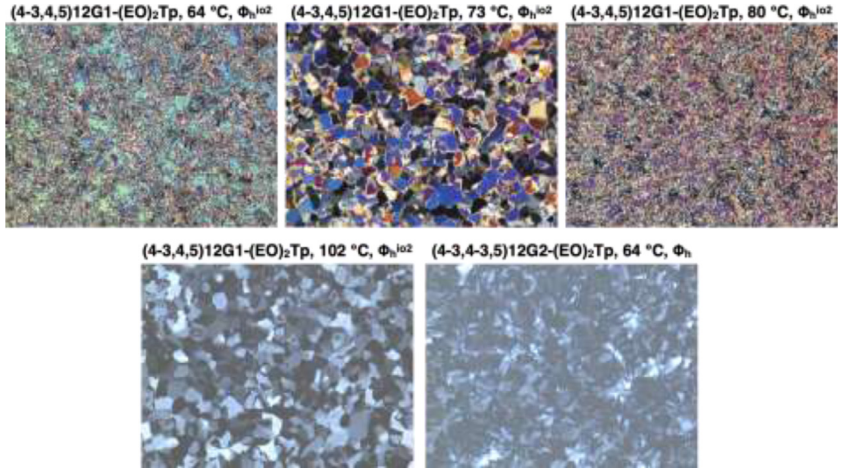

Fig. 3

TPOM textures of selected molecules in their columnar phases at the temperatures indicated.

generation of the "decoupling" of the mesogenic side groups *via* a nano-segregation of the random-coil conformation of the polymer backbone in between the smectic layers [90–102]. This combination of flexible backbone and flexible spacer induces the highest decoupling of the mesogenic side groups from the polymer backbone and therefore, induces higher isotropization temperatures though this nano-segregation architectural model [101,102]. This trend observed in side-chain liquid crystalline polymers is the reverse of the one observed in the case of supramolecular dendrimers where conformational flexibility of the system decreases phase transition temperatures including the isotropization temperature (T_i) (Table 3) [64]. In the case of supramolecular dendrimers, a different nano-segregation model [20] constructs the supramolecular polymer system. This model is favored by an extended supramolecular polymer conformation [20, 103] rather than by a random coil distorted polymer conformation [101,102]. The flexibility of the diethylene glycol linker from the dendritic molecules discussed here may provide a similar nano-segregation of the self-assembling dendrons and the supramolecular Tp backbone that is similar to that encountered in side-chain liquid crystal polymers [90–102]. In the case of supramolecular dendrimers, a new morphology based on a supramolecular sphere or column that is most probably nano-segregated from the supramolecular polymer backbone, and that is not yet elucidated, lowers the T_i values corresponding most probably to the supramolecular dendrimer. The polymer backbone of this morphology may undergo independent motion from that of the supramolecular dendrimer, but this hypothesis must be demonstrated. This remarkable difference between these two self-organized systems deserves additional investigations since it can elucidate the scope, the limitations, and the applications of supramolecular polymers [103, 104]. The dependence of phase transitions on molecular parameters was discussed in single phases systems [105] but not in nano-segregated systems. Therefore, this new decoupling concept and morphology mediated by flexibility, reported here

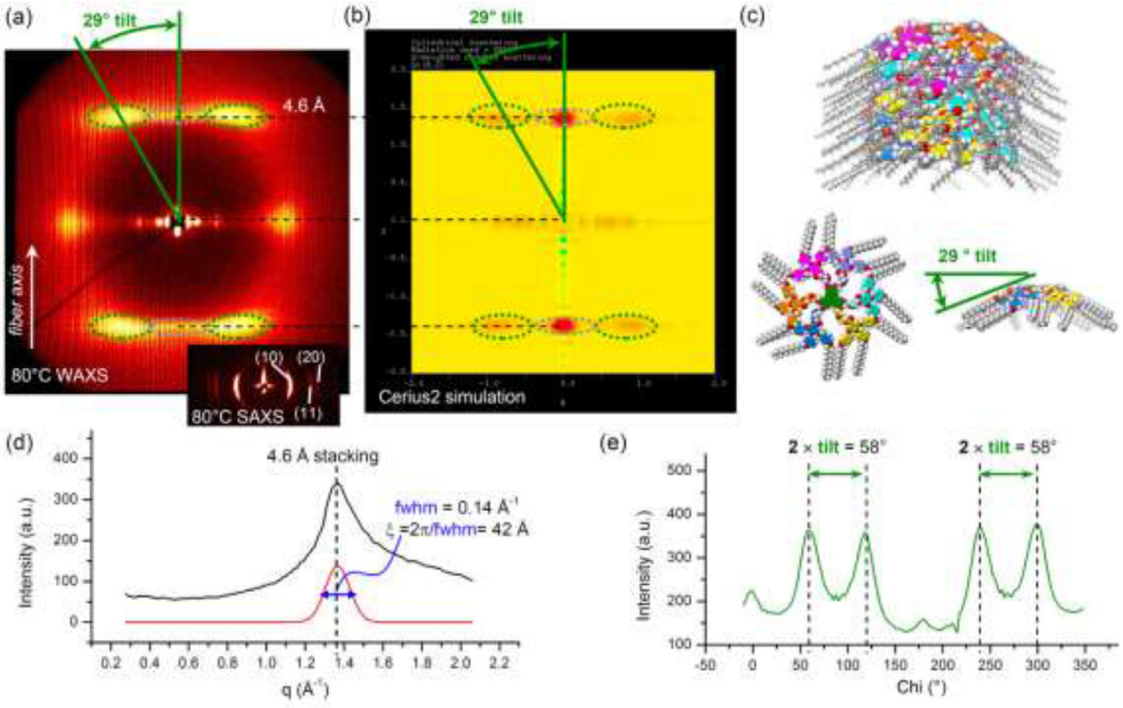

Fig. 4

Wide-angle XRD pattern collected from the oriented sample **(4–3,4,5)12G1-(EO)$_2$Tp** (a). Cerius2 simulation of the XRD fiber pattern (b) and the corresponding molecular model (c). Meridional plot indicating the stacking along the column axis features. The correlation length ξ of the 4.6 Å stacking feature is about 9 column strata as calculated from the full width at half maxima (fwhm). (d) Azimuthal plots integrating the region of the dendron tilt features (e). In a and b the tilt features are indicated.

Table 3

Thermal Analysis of Selected Dendronized Triphenylene (Tp) Molecules, and Their Phase Transition Temperatures and Enthalpy Changes.

Compound	Phase transition	T (heat) [a] (°C)	T (cool) [b] (°C)	ΔT [c] (°C)	ΔH [d] (kcal•mol^{-1})
(4)12G0-(EO)$_2$Tp	N_c – i	65	23	42	23.45
(4)12G0-Tp [e]	Φ_h^{io} – i	158	155	4	1.19
(3,4)12G1-(EO)$_2$Tp	Φ_h – i	93	91	2	0.93
(3,4)12G1-Tp [e]	Φ_h^{io} – i	143	141	2	4.23
(4–3,4)12G1-(EO)$_2$Tp	Φ_h – i	165	164	1	13.87
(4–3,4)12G1-Tp [e]	Φ_h^{io} – i	238	236	2	4.27
(3,4,5)12G1-(EO)$_2$Tp	Φ_h – i	48	11	37	48.30
(3,4,5)12G1-Tp [f]	Φ_h^{io} – σ – A15 – i	40, 96, 108	26, 86, 98	14, 10, 10	2.48, 0.43, 1.42
(4–3,4,5)12G1-(EO)$_2$Tp	Φ_h^{io} – A15 – i	87, 116	64, 82	23, 34	30.35, 0.43
(4–3,4,5)12G1-Tp [e]	Φ_h^{io} – A15 – i	105, 187	N/A, 166	N/A, 21	N/A, 1.04
(4–3,4–3,5)12G2-(EO)$_2$Tp	Φ_h^{io} – σ – i	160, 170	N/A, 167	N/A, 3	N/A, 17.82
(4–3,4–3,5)12G2-Tp [e]	Φ_h^{io} – σ – QLC – i	154, 203, 214	143, 178, 206	11, 25, 8	8.22, 0.11, 4.10
(3,4–3,5)12G2-(EO)$_2$Tp	Φ_h^{io} – QLC – i	64, 101	N/A, 95	N/A, 6	21,77, 2.03
(3,4–3,5)12G2-Tp [e]	Φ_h^{io} – QLC – A15 – i	77, 134, 148	81, 115, 141	4, 19, 7	NA, 0.25, 2,17

[a] Phase transition temperature upon heating.
[b] Phase transition temperature upon cooling.
[c] Differences between T (heat) and T (cool).
[d] Enthalpy of the phase transition.
[e] Data was published in Table 1 of Ref [62].
[f] Data was published in Table S1 of Ref [88]. Φ_h: *P6mm* hexagonal columnar liquid crystalline phase; io: intracolumnar order; A15: *Pm*3*n* simple cubic lattice; σ: $P4_2/mnm$ tetragonal lattice; QLC: Quasi-liquid crystals (12-fold); *i*: isotropic phase.

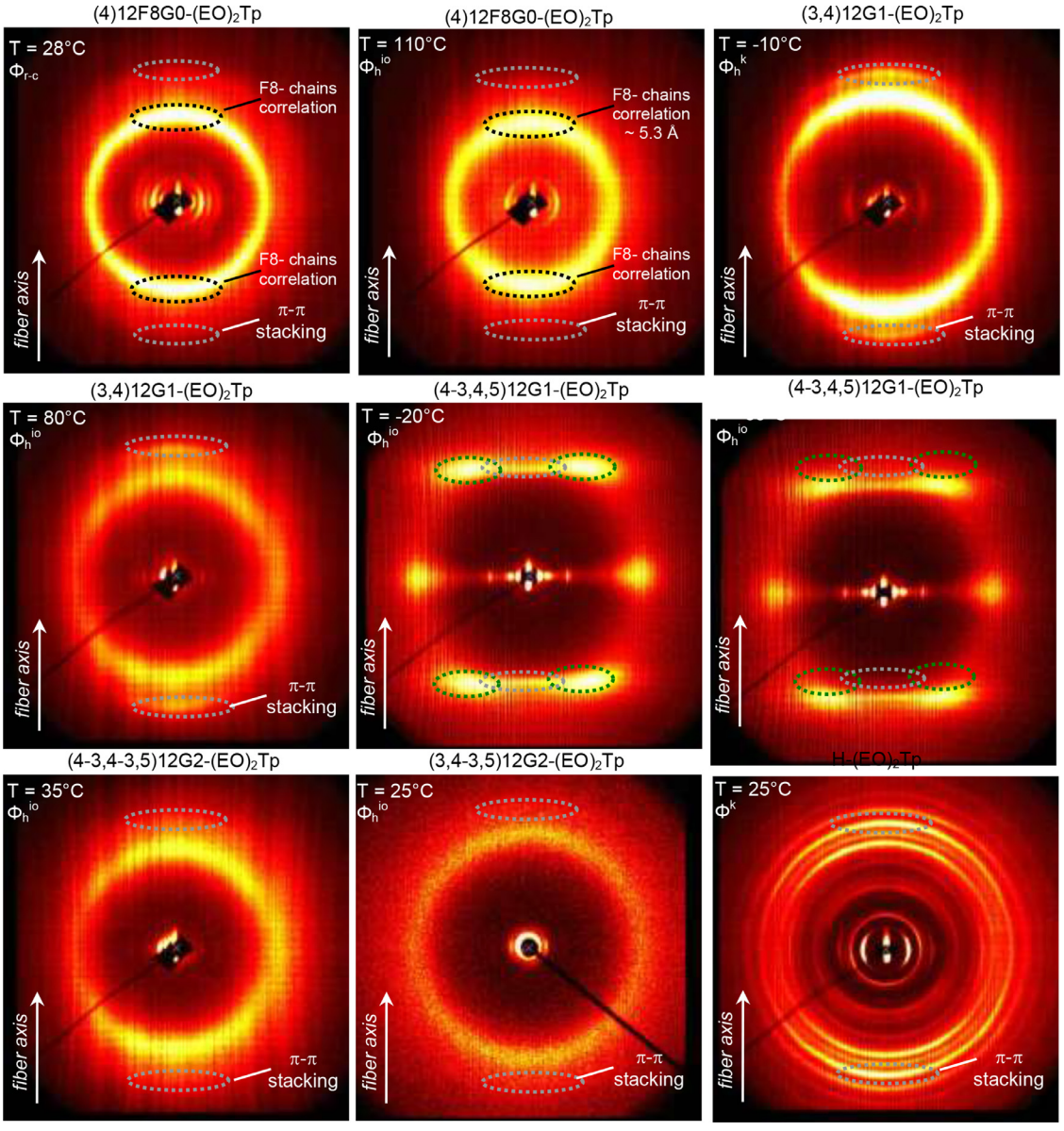

Fig. 5

Wide-angle XRD patterns collected from oriented fibers of dendronized triphenylenes attached to Tp *via* the diethylene glycol, $(EO)_2$ linker. Temperature, phases, fiber axis, stacking, helical, and tilt features are indicated.

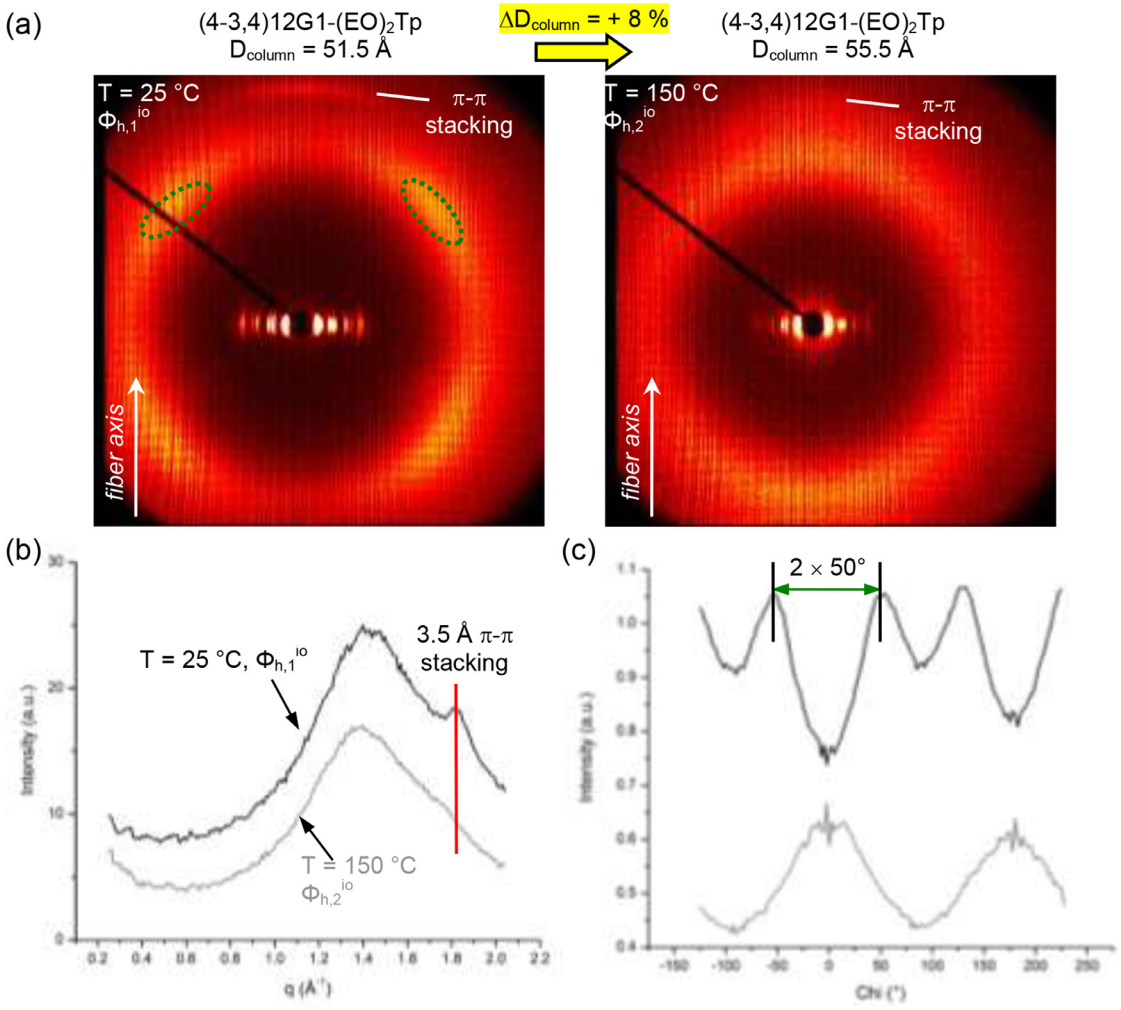

Fig. 6

Wide-angle XRD fiber pattern of **(4–3,4)12G1-(EO)$_2$Tp** collected at the indicated temperatures (a) and their corresponding meridional (b) and azimuthal (c) plots. The unusual increase of the column diameter at the transition $\Phi_{h,1}^{io}$-$\Phi_{h,2}^{io}$ which is accompanied by the disappearance of the diffuse WAXS features marked by the green circles is indicated in (a).

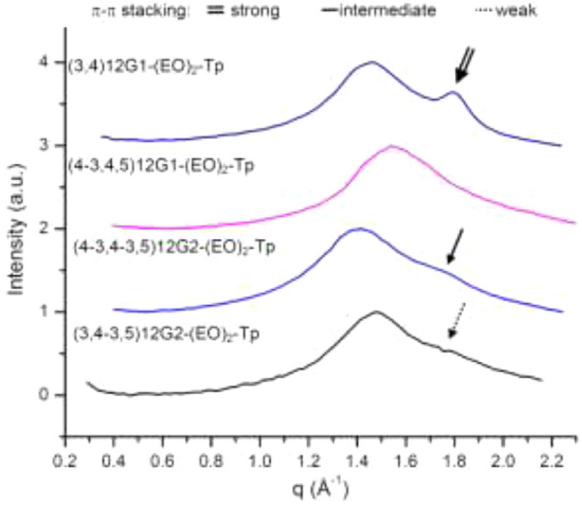

Fig. 7

Meridional plots of the oriented fiber x-ray diffraction collected at 25 °C from the dendronized triphenylenes with diethylene glycol linker. The π-π stacking features and their relative intensities are marked.

and in a previous publication [64], requires substantial research investigations in order to be elucidated. This manuscript just brings the experimental evidence for it and provides a potential hypothesis but not a definitive explanation that is not part of the scope of this publication. Supramolecular polymers including dendrimers resemble biological supramolecular systems [72,73,77,106–111] that do not adopt random coil conformations.

Conclusions

A library of self-assembling dendrons was attached to Tp *via* diethylene glycol linkers and the resulting self-organizations were compared with those of the corresponding systems generated with the same self-assembling dendrons attached directly to the Tp apex. Incorporation of the diethylene glycol linker enhances the flexibility of the supramolecular dendrimer system, decreases phase transitions temperatures and in the case of helical columns induces strong π-π stacking. The behavior of this supramolecular system resembles the one in which the rigid Tp or CTV was replaced by CTTV [64]. Therefore, regardless

of the mechanism, enhanced flexibility lowers phase transition temperatures and facilitate the design of experiments that are limited by transition temperatures close to decomposition temperature. A comparison of the concept elaborated here with the one functioning in the case of side-chain liquid crystal polymers, in which the reverse trend is observed, indicates that extended supramolecular backbone conformation is optimum for supramolecular dendrimers and most probably general for all supramolecular polymers while a distorted backbone conformation optimizes the self-organization of side-chain liquid crystal polymer systems. The new concepts discussed and elaborated here are of great importance for the Frank-Kasper phases in soft matter [112–143], and the entire field of complex molecular systems [72,73,106–111,144–149].

Declaration of Competing Interest

The authors declare no competing interests in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.giant.2022.100098.

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