Columnar liquid crystalline assembly of doubly discotic supermolecules based on tetra-triphenylene-substituted phthalocyanine[†]

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A series of doubly discotic supermolecules with four triphenylene (Tp) mesogens attached to a phthalocyanine (Pc) core *via* flexible alkyl spacers were designed and synthesized. The samples were denoted as Pc(Tp)₄. Two alkyl chain lengths (C5 and C12) in the Tp arms and two spacer lengths (C6 and C10) were used to study columnar liquid crystalline (LC) self-assemblies in Pc(Tp)₄ samples. The mesophase morphology was studied by polarized light microscopy and X-ray diffraction techniques. When the spacer length was relatively long (C10), a normal hexagonal columnar structure with the unit cell dimension close to those for the parent Tp or Pc liquid crystals was observed. The Pc columns packed either randomly or in a hexagonal superlattice in the Tp matrix. When the spacer length was short (C6), the Tp arms and the Pc core were tightly coupled together, and thus the whole supermolecules stacked together to form a super-LC column. A *column-in-column* rectangular mesophase with unit cell dimensions close to the size of the entire supermolecule was observed.

Introduction

Supermolecules, which are different from polymers, have welldefined structures and multiple functions. They represent an important class of advanced functional materials, which often self-assemble into hierarchical structures from nano- to microscales.^{1,2} An attractive category of supermolecules is liquid crystalline (LC) dendrimers or polypedes, because they have potential for optoelectronic and biological applications.3-8 Several molecular parameters play an important role in the selfassembly of LC polypedes. They include the number density of the LC mesogens at periphery, the preferred orientation of mesogenic units, the spacer length (or the degree of coupling) between the core and the mesogenic shell, and the rigidity of the core. Generally, with increasing the number density of the LC mesogens at periphery, decreasing the spacer length between the core and the mesogenic shell, and increasing the rigidity of the core, supramolecular self-assembly morphologies tend to change from calamitic to columnar, and finally to cubic (or spherical).¹

Currently, a large amount of work on LC polypedes has focused on calamitic LC mesogens, and both calamitic and columnar mesophase morphologies have been reported.^{9–36} However, fewer reports are concentrated on discotic LC polypedes, where discotic mesogens are covalently linked to the periphery of a flexible or rigid central scaffold. In a recent study, 4–64 triphenylene (Tp) mesogens were covalently linked to a flexible dendrimer core, polypropyleneimine.³⁷ A structural transition from rectangular columnar for the first generation to hexagonal columnar for the 2–5 generations was observed, and the discotic Tp mesogens and the dendrimer core microphase separated into individual columns.

In addition to flexible central scaffolds, rigid organic and inorganic molecules were also used as the central cores in discotic LC polypedes. Rigid organic central cores include a simple benzene ring,³⁸⁻⁴¹ an n-type anthraquinone,^{42,43} a p-type Tp,^{44,45} and a polyaromatic hexa-peri-hexabenzocoronene (HBC),46 to which a defined number (mostly 6 and sometimes 2, 3, or 4) of Tp,³⁹⁻⁴⁵ pentaalkyne,³⁸ or HBC⁴⁶ mesogens were attached via ester, siloxane, or ether bonds. Generally, a normal hexagonal columnar phase with a unit cell dimension close to that of the parent Tp or HBC discotic LCs was observed,40-43,45,46 suggesting that the peripheral Tp or HBC mesogens self-organized into individual LC columns regardless of the covalent linkages to the central scaffold. However, with more detailed studies, 40,41,45 a disordered superlattice, with the unit cell dimension equivalent to the size of an entire discotic LC supermolecule, was observed due to the packing of the central scaffolds. Furthermore, a broad temperature range for the columnar LC phases was obtained as compared to the parent Tp LCs.40,41,45 When three flat radial pentaalkynes were connected to a central benzene core via C11 spacers, columnar nematic phases, instead of a discotic nematic phase as found in the parent pentaalkyne molecules, were observed.38

However, discotic LC polypedes with chemically different peripheral and central polyaromatic/macrocyclic discogens are rarely studied. In this report, we covalently attached four Tp mesogens to the four corners of a central phthalocyanine (Pc) core *via* alkyl spacers with different lengths, forming a star-shaped doubly discotic LC polypede, $Pc(Tp)_4$. Different from previous reports on 1,3,5-tritriphenylene benzenetrisamides,^{40,41} where helical conformation in the hydrogen bonds along the columns was crucial to their supramolecular self-assembly, $Pc(Tp)_4$ supermolecules exhibited a reverse trend in the spacer

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length-determined self-organization. When the spacer length was relatively long, a normal hexagonal columnar structure (with the unit cell dimension close to those for the parent Tp or Pc LCs) was observed, and the Pc columns packed randomly among the hexagonal Tp columns. When the spacer length was short, the Tp arms and the Pc core were tightly coupled together, and the whole $Pc(Tp)_4$ supermolecules stacked together to form a supercolumn. A *column-in-column* rectangular mesophase with unit cell dimensions close to the size of the entire supermolecule was observed.

Experimental

Materials

Monobromoalkoxytriphenylene was synthesized according to the literature with certain modifications.⁴⁰ 4-Hydroxy-1,2-benzenedicarbonitrile was purchased from TCI America. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Sigma-Aldrich. All solvents were purchased from Fisher Scientific and used without further purification.

General synthesis procedure for Pc(Tp)₄

The synthesis of novel doubly discotic supermolecules based on a Pc core and four Tp arms was achieved from cyclotetramerization of the precursor dinitriles, which is a common

method for Pc syntheses.47,48 A detailed synthetic route is shown in Scheme 1. Tp phthalonitriles were synthesized from the coupling of monobromoalkoxy-triphenylene with 4-hydroxy-1,2-benzenedicarbonitrile according to the literature with certain modifications.⁴⁹ In brief, 1.0 g of monobromoalkoxytriphenylene was added into a solution of 4-hydroxy-1,2-benzenedicarbonitrile preactivated by K₂CO₃ in DMF, and the mixture was heated at 100 °C overnight. The crude product was washed with doubly distilled water and extracted with dichloromethane three times. The combined organic phase was dried with anhydrous Na₂SO₄ and the solvent was evaporated using a rotavapor. The product was further dried in a vacuum oven to afford Tp phthalonitrile (yield 83-92%). 0.40 g of Tp phthalonitrile (0.44 mmol for 1, 0.42 mmol for 2, 0.29 mmol for 3, and 0.28 mmol for 4), 0.02 g (0.15 mmol) of CuCl₂, 5 mL of 1-pentanol, and four drops of DBU were mixed together and refluxed for 24 h. Afterwards, excess methanol was added to the reaction mixture to precipitate the target compound. The precipitate was isolated by centrifugation and washed with methanol. The crude product was further purified by column chromatography (silica gel, $CHCl_3$:hexane = 2:1 for 1 and 2, $CHCl_3$:hexane = 1:1 for 3 and 4) and recrystallized from acetone twice to give green to blue solids with yields: 69% for 1, 63% for 2, 19% for 3, and 20% for 4. Because of the paramagnetic nature of Cu²⁺ in the Pc core, quantitative molecular analysis by nuclear magnetic resonance spectroscopy could not be performed. Instead, high resolution



Scheme 1 Synthesis of Pc(Tp)₄ supermolecules with different spacer and alkyl chain lengths.

matrix-assisted laser desorption ionization–time of flight (MALDI-TOF) mass spectrometry (MS) – was performed using dithranol as the matrix. MALDI-TOF MS spectra are shown in Fig. S1–S4[†]. Sample 1: $C_{228}H_{304}CuN_8O_{28}$, calculated 3668.4 and found 3666.2. Sample 2: $C_{244}H_{336}CuN_8O_{28}$, calculated 3892.8 and found 3890.6. Sample 3: $C_{368}H_{584}CuN_8O_{28}$, calculated 5632.2 and found 5633.0. Sample 4: $C_{384}H_{616}CuN_8O_{28}$, calculated 5856.6 and found 5856.9. As we can see, the calculated values were consistent with the experimental results within experimental errors. The purity of all samples was checked by thin layer chromatography and size exclusion chromatography (SEC, see Fig. 1). Sharp unimodal peaks with polydispersity indices between 1.01–1.03 were obtained using polystyrene as the calibration standard.

Instrumentation and characterization

Differential scanning calorimetry (DSC) experiments were carried out on a TA DSC-Q100 instrument. An indium standard was used for both temperature and enthalpy calibration. Approximately 3 mg sample was used for the DSC study and the scanning rate was 10 °C min⁻¹. SEC was performed on a Viscotek GPCmax VE2001 with quadruple detectors [differential refractive index (RI), UV-vis, viscometer, and light scattering, but only the differential RI detector was used in this study]. THF was used as the solvent and polystyrene standards were used for calibration. The solvent flow rate was 1.0 mL min⁻¹. MALDI-TOF MS were carried out on a Bruker Ultraflex III MALDI-TOF/TOF instrument. Polarized light microscopy (PLM) experiments were performed using an Olympus BX51P microscope equipped with

an Instec HCS410 hot stage. Fluorescence spectroscopy was performed on a Jobin-Yvon Spex Fluorolog 3-211 spectrofluorometer. Both solution and thin film samples were excited between 250 and 300 nm, respectively.

Two-dimensional (2D) X-ray diffraction (XRD) experiments were performed at the synchrotron X-ray beamline X27C at National Synchrotron Light Source, Brookhaven National Laboratory. The wavelength of incident X-ray was 0.1371 nm. The scattering angle was calibrated using silver behenate with the primary reflection peak at the scattering vector $q = (4\pi \sin\theta)/\lambda =$ 1.076 nm⁻¹, where θ is the half-scattering angle and λ is the wavelength. Fuji imaging plates were used as detectors for XRD experiments, and digital images were obtained using a Fuji BAS-2500 scanner. The typical data requisition time was 1 min. An Instec HCS410 hot stage equipped with a liquid-nitrogen cooling accessory was used for temperature-dependant X-ray experiments. One-dimensional (1D) XRD curves were obtained by integration of the corresponding 2D XRD patterns.

Results and discussion

Thermal behavior and phase morphology studied by DSC and PLM

LC phase transitions in Pc(Tp)₄ samples 1–4 were studied by DSC (Fig. 2). Upon the first cooling, the sample 1 showed a single transition at 151 °C (24.5 kJ mol⁻¹). Upon second heating, it showed a single isotropization temperature (T_i) at 173 °C (24.9 kJ mol⁻¹). In the PLM micrograph for the sample 1 at 165 °C in Fig. 3A, a branched leaf-like texture, which is typical for hexagonal columnar phases, was observed. When the spacer



Fig. 1 Size exclusion chromatography (SEC) curves for Pc(Tp)₄ samples **1–4**. A differential refractive index detector was used.



Fig. 2 Differential scanning calorimetry (DSC) first cooling and second heating curves for $Pc(Tp)_4$ samples 1–4. The scanning rate is 10 °C min⁻¹.



Fig. 3 PLM micrographs of $Pc(Tp)_4$ samples (A) 1 at 165 °C, (B) 2 at room temperature, (C) 3 at 160 °C, and (D) 4 at room temperature.

length was increased to C10, the sample **2** only showed a glass transition temperature (T_g) at -21.2 °C upon cooling. Upon heating, a weak isotropization peak was observed at 95.7 °C (8.0 kJ mol⁻¹) above the T_g (-11.2 °C), which could be attributed to a typical monotropic phase behavior. Obviously, an increase in the spacer length from C6 to C10 caused the T_i to decrease by 77 °C. Due to the very low liquid crystallinity in the sample **2**, its PLM texture in Fig. 3B only showed an irregular texture with small grains at room temperature, no matter how long it was annealed below the T_i .

Unlike samples 1 and 2, samples 3 and 4 showed richer mesophase behaviors with two major transitions (see Fig. 2). For example, upon cooling, sample 3 showed a transition peak at $147 \degree C (12.1 \text{ kJ mol}^{-1})$ and a broad peak at $6.4 \degree C (135 \text{ kJ mol}^{-1})$, respectively. Judging from the heat of transition, the high temperature (*e.g.*, $160 \degree C$) phase should be a LC phase and the low temperature (*e.g.*, $-25 \degree C$) phase should be a crystalline

Table 1 Phase transition temperatures (°C, above arrow) and heats of transition (kJ mol⁻¹, below arrow) for samples **1–4**^{*a*}

Sample First cooling						Second heating					
1	I —	151 24.5	$\rightarrow Col_{ho}$			Col _{ho}	$-\frac{17}{24}$	$\xrightarrow{73}$ Co	l _{hd}	$\xrightarrow{195}$ I	
2	I —	-21.2	→ g			g	-11.2	Col _{ho} –	95.7 8.0	→ I	
3	I —	147	$\rightarrow Col_{ro} -$	6.0	$\rightarrow Cr$	Cr—	37.5 7.8	$\rightarrow \operatorname{Col}_{ro}$	166	\rightarrow I	
4	I —	56.5 13.4	→ Col _{oo} -	5.8	\rightarrow Cr	Cr—	27.2 148	$\rightarrow Col_{oo}$	70.7	\longrightarrow I	
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 a Cr = crystal; g = glass; Col_{ho} =ordered hexagonal columnar phase; Col_{hd} = disordered hexagonal columnar phase; Col_{ro} = ordered rectangular columnar phase; Col_{oo} = ordered oblique columnar phase; I = isotropic.

phase. On the basis of a previous study,⁵⁰ the broad low temperature transition could be attributed to the C12 alkyl chain-induced crystallization of entire LC supermolecules. Upon heating, the crystalline phase melted with a broad peak at 9.2 °C and a sharp peak at 37.5 °C (total heat of fusion of 152 kJ mol⁻¹), respectively. Finally, the T_i was observed at 166 °C (15 kJ mol⁻¹). The PLM result in Fig. 3C showed fan-like texture at 160 °C for the sample **3**.

Similarly, upon cooling, sample **4** showed a LC formation peak at 56.5 °C (13.4 kJ mol⁻¹) and a relatively broad crystallization peak at 5.8 °C (138 kJ mol⁻¹). Upon heating, it showed a broad crystal melting peak at 27.2 °C (148 kJ mol⁻¹) and a T_i at 70.7 °C (8.8 kJ mol⁻¹), respectively. Again, the high temperature (*e.g.*, 50 °C) phase should be LC and the low temperature (*e.g.*, 0 °C) phase should be crystalline. The PLM micrograph for the sample **4** at room temperature showed a similar texture as that of the sample **2** with even smaller grains, and kept unchanged until isotropization (see Fig. 3D). Thermal behaviors and phase transitions in Pc(Tp)₄ samples **1–4** are summarized in Table 1.

Liquid crystalline self-assemblies studied by XRD

The mesophase structures in these self-assembled $Pc(Tp)_4$ supermolecules were studied by temperature-dependent 1D and 2D XRD techniques. Fig. 4A shows the 1D XRD profiles at various temperatures for the sample 1 during the second heating process after cooling from the isotropic melt. At 25 °C, a sharp reflection peak appeared at $q = 3.82 \text{ nm}^{-1}$, together with three higher order reflections, which had a q-relationship of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$. This is typical for hexagonal columnar LCs (see Table S1[†]). The distance between neighbouring columns was a = 1.90 nm. Surprisingly, this length was much smaller than the size of the entire supermolecule (\sim 5.2 nm), but was close to the size of either C5-Tp (\sim 1.7 nm)⁵¹ or C6-Pc (\sim 2.65 nm).⁵² At an even lower q, a broad halo was observed at 1.466 nm⁻¹, which corresponded to a d-spacing of 4.3 nm and was close to the size of the entire supermolecule with a flat conformation. In the wideangle region, a reflection peak was located at 18.0 nm⁻¹ (*d*-spacing = 0.35 nm), representing an ordered π - π stacking of the Tp⁵³ and/or Pc⁵² disks in the LC columns. Fig. 4B shows the 2D XRD pattern for the shear-oriented sample 1. The interdisk



Fig. 4 (A) Temperature-dependent 1D XRD profiles and (B) 2D XRD pattern on shear-oriented $Pc(Tp)_4$ sample 1 at 25 °C. The inset in (A) shows an additional magnified (×10) profile at 25 °C between 6 and 12 nm⁻¹.

reflection at 18.0 nm^{-1} (0.35 nm) oriented parallel to the shear direction, while the strong hexagonal reflection at 3.82 nm^{-1} (1.90 nm) oriented orthogonal to the shear direction. This XRD pattern indicated that the columns conformed to the shear direction and the Tp and Pc disks oriented perpendicular to the column axes.

This peculiar XRD profile for the sample 1 could be explained by the very close electron densities between Tp and Pc columns in the bulk. First of all, we need to prove that Tp arms and Pc cores self-organized into microphase separated columns, instead of mixing together in one LC column. If Tp and Pc mixed together in a LC column, Föster energy transfer⁵⁴ would be facilitated by the excimer formation and the fluorescence spectrum would shift to much higher wavelengths.⁵⁵ Fig. 6 shows fluorescence spectra for C5-Tp in CH₂Cl₂, sample 1 in CH₂Cl₂, and sample 1 thin film excited at 250 nm, respectively. As we can see, the fluorescence spectra for C5-Tp and sample 1 in CH₂Cl₂ were nearly the same, with the main peak centred at 383 nm. For the sample 1 thin film, a broad fluorescence band for the Tp moiety appeared at 391 nm, almost the same as those for C5-Tp and sample 1 in CH₂Cl₂. This result suggested that the energy absorbed by Tp did not transfer to Pc. Therefore, Tp and Pc should form microphase separated LC columnar domains in the solid state.



Fig. 5 Schematic representation of the phase transformation from a normal hexagonal lattice into a super-hexagonal lattice for the sample 1 upon melting at 173 °C. The grey circles represent triphenylene columns and the black circles represent phthalocyanine columns.



Fig. 6 Fluorescence spectra for C5Tp in CH_2Cl_2 , sample 1 in CH_2Cl_2 , and sample 1 thin film excited at 250 nm, respectively.

These microphase-separated Tp and Pc columns further selfassembled into a mixed hexagonal columnar phase, as shown in the left panel of Fig. 5. Assuming the core diameters of Tp and Pc were 0.81 and 1.32 nm and the interdisk (both Tp and Pc) distance was 0.35 nm, the electron densities for the Tp and Pc columns were 649 and 616 electrons nm⁻³, respectively. These close electron densities resulted in the fact that the incident X-ray could not clearly distinguish between the Tp and Pc columns. Therefore, the major reflection was seen at 3.82 nm⁻¹ and thus the hexagonal lattice was small (a = 1.9 nm, see the left panel in Fig. 5). However, the average distance among Pc columns could still be evidenced by the halo at 1.466 nm⁻¹ because of a small electron density difference (5%) between Tp and Pc columns. This halo at low angles suggested that the packing of Pc columns among the Tp column were random (see the left panel in Fig. 5). This result is similar to the XRD observations in previous reports for 1,3,5-tristriphenylene benzenetrisamide supermolecules with relatively short spacers.^{40,41} However, we prefer not to use the term "superlattice" as in ref. 40 and 41, because no lattice existed among randomly packed Pc columns.

At 173 °C, the hexagonal columnar phase melted, as evidenced by the disappearance of the interdisk reflection at 17.4 nm⁻¹ at 145 °C. Meanwhile, the sharp reflection at 3.82 nm⁻¹ transformed into a broad halo at 3.92 nm⁻¹, representing the average distance (1.6 nm) among randomly packed Tp and Pc discotic molecules. Intriguingly, immediately after isotropization at 173 °C, another sharp reflection peak at 1.44 nm⁻¹ developed from the halo at 1.466 nm⁻¹, together with a higher order reflection at 2.45 nm⁻¹. The q-relationship for these two reflections was $1:\sqrt{3}$, suggesting a super-hexagonal lattice with a larger unit cell dimension of a = 5.04 nm (see Table S2[†]), which was nearly the same as the overall molecular size of the sample 1. Because no interdisk reflection at 17.4 nm⁻¹ was observed at 173 °C, this phase should be determined as a disordered superhexagonal lattice, and the corresponding phase transformation is depicted in Fig. 5. Based on temperature-dependent XRD experiments, this disordered super-hexagonal lattice persisted until 195 °C and completely disappeared above 200 °C. However, this transition involved too little heat to be detected by DSC (see Fig. 2). At 220 °C, three halos were observed at 1.61, 3.88, and 13.13 nm⁻¹, respectively, representing average distances



Fig. 7 (A) Temperature-dependent 1D XRD profiles and (B) 2D XRD pattern on shear-oriented $Pc(Tp)_4$ sample **2** at 25 °C. The inset in (A) shows an additional magnified (×10) profile at 50 °C between 5 and 10 nm⁻¹.

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among randomly packed Pc (3.90 nm), Tp (1.62 nm), and alkyl chains (0.48 nm) in the isotropic melt.

Temperature-dependent 1D XRD profiles for the sample 2 during the second heating process are shown in Fig. 7A. A similar phase behavior as for sample 1 was observed. At 50 °C, reflections from a normal hexagonal columnar lattice were observed at 3.56 and 6.15 nm⁻¹, respectively, with a q-relationship being $1:\sqrt{3}$ (see Table S3[†]). The unit cell dimension for this small hexagonal lattice was a = 2.04 nm, slightly larger than that (a = 1.90 nm) for sample 1 because of an increase in the spacer length from C6 to C10. Again, the interdisk distance was observed at 17.6 nm⁻¹ (0.36 nm) in the wide-angle region. From the 2D XRD pattern in Fig. 6B, the same orientation of the molecular disks with respect to the column axes as in sample 1 was observed; the Tp and Pc disks were perpendicular to the LC column axes. Differing from sample 1, no disordered superhexagonal columnar phase was observed for the sample 2 upon isotropization at 95.7 °C. Three halos were observed at 1.36, 3.56, and 13.10 nm⁻¹, respectively, representing average distances among randomly packed Pc (4.62 nm), Tp (1.76 nm), and alkyl chains (0.48 nm). The difference between samples 1 and 2 could be attributed to the longer spacer length in the sample 2.

The temperature-dependent 1D XRD profiles during the second heating process for sample 4 are shown in Fig. 8A. At 50 °C, a sharp reflection was seen at 2.89 nm⁻¹ with several higher order reflections in the low-angle region. Again, this reflection corresponded to a *d*-spacing of 2.17 nm, which was close to the sizes of C12-Tp (ca. 2.5 nm)⁵⁶ and C10-Pc (ca. 3.15 nm).⁵² However, the higher order reflections could not fit into a hexagonal lattice as in samples 1 and 2. Instead, they fitted to an oblique lattice with unit cell dimensions: a = b = 2.19 nm and $\gamma = 97^{\circ}$ (see Table S4[†]), and the corresponding Miller indices were labelled in Fig. 8A. This result indicated that Tp and Pc columns assembled (or mixed) into an oblique lattice, rather than a hexagonal lattice as shown in the left panel of Fig. 5. Comparing with sample 2, this difference is clearly a result of an increased alkyl arm length (C12) for the sample 4. At even lower q values, a broad halo was seen at 1.31 nm⁻¹, corresponding to the average distance (4.80 nm) among randomly packed Pc columns. Note that this distance was close to the entire supermolecule size. In the wide-angle region, the interdisk reflection was seen at 17.9 nm^{-1} , which corresponded to a *d*-spacing of



Fig. 8 (A) Temperature-dependent 1D XRD profiles and (B) 2D XRD pattern on shear-oriented $Pc(Tp)_4$ sample **4** at 40 °C.

0.35 nm. In the 2D XRD pattern in Fig. 8B, the (10)/(01) reflection oriented orthogonal to the shear direction, while the interdisk reflection was parallel to the shear direction. Again, this indicated that the Tp and Pc disks were perpendicular to the column axes.

At -50 °C, entire supermolecules of the sample **4** crystallized due to the crystallization of C12 alkyl chains. However, the major feature of the oblique columnar packing did not change, as seen in Fig. 8A. After heating to 125 °C, the oblique columnar phase disappeared. Three halos were observed at 1.39, 2.93, and 13.32 nm⁻¹, corresponding to average distances among randomly packed Pc (4.53 nm), Tp (2.15 nm), and alkyl chains (0.47 nm), respectively.

The sample 3 displayed a completely different mesophase structure from those of samples 1, 2, and 4. This is evidenced from the temperature-dependent 1D XRD profiles during the



Fig. 9 (A) Temperature-dependent 1D XRD profiles and (B) 2D XRD pattern on the shear-oriented $Pc(Tp)_4$ sample 3 at 100 °C.

short spacer



Fig. 10 Schematic representations of the supramolecular self-assembly of $Pc(Tp)_4$ supermolecules 1–4 with short and long spacers, respectively. 2D unit cells are shown with dotted lines.

second heating in Fig. 9A. At 50 and 130 °C, many sharp reflections were observed in the low-angle region. To solve the LC structure, a 2D XRD experiment was performed on the shear-oriented sample 3, and the results are shown in Fig. 9B. In this 2D XRD pattern, all low-angle reflections were oriented on the equator, suggesting a 2D columnar LC phase in the sample. Both the 1D profile and 2D patterns could be fitted with a 2D rectangular symmetry with unit cell dimensions: a = 5.03 nm and b = 4.30 nm (see Table S5[†]), and Miller indices were assigned in both figures. Note that these dimensions were close to the size $(\sim 5 \text{ nm})$ of the entire supermolecules. This result is similar to those observed for 1,3,5-tristriphenylene benzenetrisamide supermolecules with relatively long spacers,^{40,41} where rectangular and oblique columnar phases were observed. At high angles, the interdisk reflection was seen at 17.7 nm^{-1} (0.35 nm) in the 1D profile and on the meridian in the 2D pattern, which was perpendicular to the (10) reflection on the equator. Therefore, the Tp and Pc disks again were oriented perpendicular to the LC columns.

At -10 °C, entire supermolecules crystallized as induced by the C12 alkyl chain crystallization. Although XRD line widths slightly increased, the fundamental rectangular structure was preserved in the sample. After isotropization at 170 °C, three broad halos were observed at 1.54, 3.25, and 13.0 nm⁻¹, corresponding to average distances among randomly packed Pc (4.08 nm), Tp (1.93 nm), and alkyl chains (0.48 nm), respectively.

Fig. 10 summarizes the supramolecular self-assembly of $Pc(Tp)_4$ supermolecules with short and long spacers, respectively. When the spacer (C6) is shorter than the Tp C12 alkyl arms, the Tp arms are tightly attached to the Pc core, and thus the supermolecules adopt a disk-like overall molecular shape when they stack parallel together. Finally, a *column-in-column* nano-structure is obtained; four Tp columns inside a super-column formed by the entire supermolecules (see the top panel of Fig. 10). When the spacer is no shorter than the alkyl arms in the Tps such as in samples 1, 2, and 4, Tp arms and Pc cores are decoupled to a great extent. Therefore, ordered hexagonal or rectangular structures with a random arrangement of the Pc cores are obtained (see the bottom panel of Fig. 10).

Our observations seem to be contradictory to those observed for hydrogen-bond stabilized 1,3,5-tristriphenylene benzenetrisamide supermolecules,^{40,41} where normal hexagonal columnar phases were observed for short spacers (C3 and C4), while oblique or rectangular superlattice columnar phases were observed for long spacers (C5 and C6) as compared to the alkyl chain length (C6) in the Tp arms. We speculate that the helical conformation of the hydrogen-bonds in the 1,3,5-benzenetrisamides may be sensitive to the length spacers between the Tp arms and the benzene core. When the spacer length is relatively short (C3 and C4), the helical conformation in hydrogen bonds may be quite open and thus Tp arms could stack together to form LC columns. This is evidenced by the ordered interdisk reflections at $2\theta \sim 25^\circ$ for short spacer length samples (see XRD profiles for T-3-Hex and T-4-Hex samples in Fig. 3 of ref. 41). When the spacer length (C5 and C6) is comparable to the alkyl chain length (C6) in the Tp, well-defined helical conformation in the hydrogen bonds prevents the ordered π - π stacking of the Tp arms. Instead, the whole supermolecules stack together with helical hydrogen bonds to form a super-column, and thus

oblique (or rectangular) columnar phases with unit cell dimensions close to the entire supermolecular sizes were observed. This is evidenced by the disappearance of the ordered interdisk reflections around $2\theta \sim 25^{\circ}$ for long spacer length samples (see XRD profiles for T-5-Hex and T-6-Hex samples in Fig. 3 of ref. 41).

Conclusions

In summary, a series of doubly discotic Pc(Tp)₄ supermolecules were designed and successfully synthesized. Columnar LC phases were observed for all samples. PLM and XRD techniques were employed to study the mesophase morphology. When the spacer length was relatively long, a normal hexagonal columnar structure with the unit cell dimension close to those for the parent Tp or Pc LCs were observed for samples 1, 2, and 4, and the Pc columns packed randomly among the hexagonal Tp columns (see the left panel in Fig. 5). Intriguingly, a hexagonal Pc superlattice was formed immediately after the isotropization of the Tp columns in the sample 1 at 173 °C (see the right panel in Fig. 5). When the spacer length was short, the Tp arms and the Pc core were tightly coupled together, and the whole $Pc(Tp)_4$ supermolecules stack together to form a super-column. A column-in-column rectangular mesophase with unit cell dimensions close to the size of the entire supermolecule was observed.

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