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Supporting information

2D Superlattice Nanostructures Formed via Self-Assembly of Discotic Liquid Crystals Dominated by Long Range Dipole-Dipole Interaction

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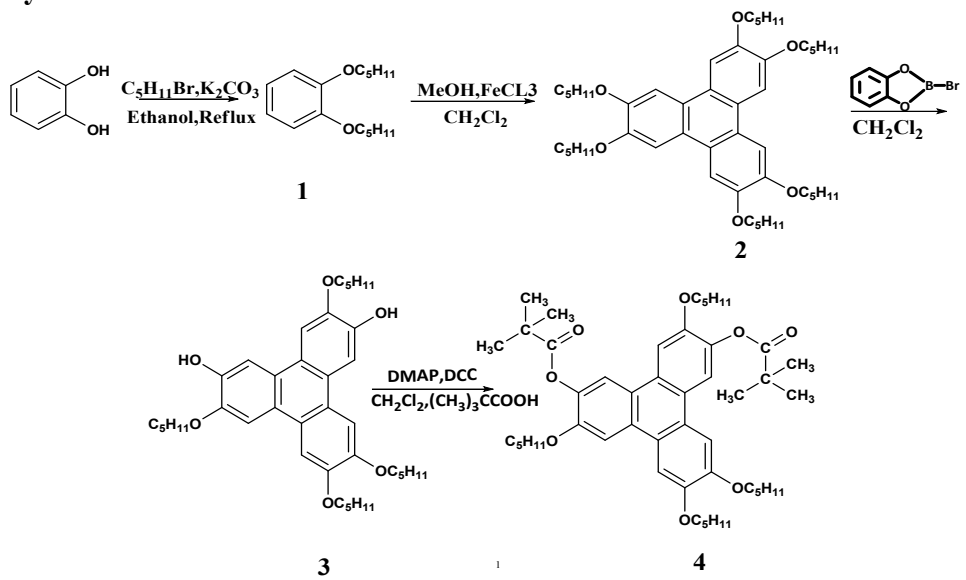
1. Materials and Physical measurements of T5EP2

Bromopentane, Catechol, Potassium carbonate, Iron(III) chloride, BBr3, Pivalic acid, Dicyclohexyl-Carbonimide (DCC) and 4-dimethylaminopyridine (DMAP) were purchased from Aladdin, and all solvents from Aldrich. B-Bromocatecholboronane was synthesized according to Kumar's reports. Unless otherwise stated, all chemicals and solvents were used without further purification.

^{1}H-NMR spectra were recorded in CDCl3 on Bruker NMR spectrometers (DMX 300 MHz), chemical shifts were given in parts per million (δ) and were referenced from tetramethylsilane (TMS). Multiplicities of the peaks were denoted as s=singlet, d=doublet, t=triplet, and m=multiplet. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 200. The samples were taken in aluminum crucibles and scanned by 10 °C/min in nitrogen atmosphere. In order to exclude the effect of thermal history, the first heating run was neglected. Polarizing optical microscopy (POM) was carried out on a Leica DM4500P microscope equipped with a Linkam TMS94 hot stage. One-dimensional wide-angle X-ray diffraction (1D WAXD) study was conducted on a Buler D8 Advance diffractometer equipped with a temperature controller. The powder sample was placed on aluminum foil and the acquired data were processed via the associated software. Small angle X-ray scattering (SAXS) studies were carried on with a high flux SAXS instrument (SAXSess, Anton Paar) equipped with Kratky block-collimation system. Two-dimensional wide-angle X-ray diffraction (2D WAXD) experiments were performed on a Bruker Axs D8 Discover diffractometer fitted with a 40KV FL tube as the X-ray source (Cu Kα) and a VANTEC 500 detector. The high resolution mass spectrums were recorded on a Bruker Apex IV FTMS mass spectrometer. Elemental analysis measurements (C, H) were performed on an Elementar Vario EL CUBE elements analyzer. Fourier transform infrared spectroscopy (FT-IR) was carried out on a Shimadzu FTIR-8400 spectrometer using KBr pellets. Samples for TEM (FEI

Tecnai G2 20 STWIN) characterization were prepared by adding one drop of Dichloromethane solution with the concentration of 5% to a 200 mesh copper grid with carbon support film. The TEM image of the sample without annealing was shown in Fig. S9.

2. Syntheses and the molecular schemes of T5EP2



1, 2-dipentyloxybenzene (1)

1-Bromopentane (90.6g, 0.6mol) was added to a vigorously stirred solution of Catechol (22g, 0.2mol) and potassium carbonate (55g) in ethanol (300ml) under nitrogen. The reaction mixture was stirred under reflux for 24 h and filtered with copious washings of dichloromethane. The filtrate was concentrated in vacuo and subjected to a silica gel column chromatography on silica, eluting with 1:1 dichloromethane: petroleum to give the product as pale yellow oil. (96 g, 96 %); TLC Rf: 0.55 (dichloromethane-hexane 1:1); IR (KBr): vmax/cm-11263 (C-O-C); δH (300MHZ, CDCl3) 6.99-6.87 (m, 4H, ArH), 4.10-3.99 (t, 4H, OCH2),1.86-1.77 (m, 4H, OCH2CH2), 1.58-1.47 (m, 8H, OCH2CH2CH2CH2), 1.07-0.97 (t, 6H, CH3).

2, 3, 6, 7, 10, 11-hexapentyloxytriphenylene (2)

The colorless grease 1,2-dipentyloxybenzene (30g, 0.12mol) was added to a vigorously stirred suspension of iron III chloride (62.3g, 0.46mol) in dichloromethane (200ml) with concentrated sulphuric acid (2ml). The reaction

occurred with vigorous evolution of gas and was quenched with methanol (1L) after 2-3h. The reaction mixture was filtered and the filtrate concentrated in vacuo to black solid which was subjected to column chromatography, eluting with 2:1 dichloromethane: hexanes to give the product as a pale yellow solid which was recrystallized from ethanol to obtain white solid (21.8g, 73%).TLC Rf: 0.44 (ethyl petroleum ether 1:6); IR (KBr): νmax/cm-1 1253 (C-O-C); δH (300MHZ, CDCl3) 7.85 (s, 6H, ArH), 4.25 (t, 12H, OCH2), 1.92-1.99 (m, 12H, OCH2CH2), 1.42-1.67 (m, 24H, OCH2CH2CH2CH2), 1.07-0.99 (m, 18H, CH3).

2, 6-dihydroxy-3, 7, 10, 11-tetrapentyloxytriphenylene (3)

A solution (0°C) of BBr3 (28.6g, 0.11mol) in CH_2Cl_2 (10 ml) was added slowly to a cooled suspension of catechol (11g, 0.1mol) in CH_2Cl_2 (50mL) under nitrogen. After 3h, the mixture was brought to room temperature, the solvent removed and the product distilled under vacuum to give B-Bromocatecholboronane as white solid (16g, 80%). The solid was then used to make a 0.5 M solution by mixing with CH_2Cl_2 (160 ml) and this was used for next ether cleavage reactions. A compound of 2 (14.88g, 0.02mol) was dissolved in anhydrous CH_2Cl_2 (200 ml) and cooled to 0°C. The B-Bromocatecholboronane solution of CH_2Cl_2 (100ml, 0.05mol) was added under nitrogen and the mixture was stirred at room temperature for 24h. After that it was poured over ice-water and extracted with CH_2Cl_2, the combined extract was dried with anhydrous Na_2SO_4 overnight, solvent was removed under vacuum and the crude product can be purified by column chromatography. However, the separation of 2, 7-dihydroxy-3, 7, 10, 11-tetra- pentyloxy-triphenylene and 2, 6-dihydroxy-3, 7, 10, 11-tetrapentyloxy- triphenylene was very difficult. After several attempts to separate these two compounds by adjusting the ratios of petroleum ether and ethyl acetate, we found that the two compounds 2,7-dihydroxy-3,7,10,11-tetrapentyloxy- triphenylene and 2,6- dihydroxy-3,7,10,11-tetrapentyloxytriphenylene can be separated by a careful and repeated chromatography via the silica gel 60 glass thin-layer chromatography in about

1:9 ratio of the ethyl acetate and the petroleum ether: 2,6-dihydroxy-3,7,10,11-tetrapentyloxytriphenylene (Rf 0.15), 2,7-dihydroxy- 3,7,10,11-tetrapentyloxy triphenylene (Rf 0.13). (Found: C, 75.39; H, 8.60. C38H52O6 requires: C, 75.46; H, 8.67%); IR (KB*r): vmax/cm-1 3436 (O-H), 1265 (C-O-C); δH (300MHZ, CDCl3) 7.93 (s, 2*H, ArH), 7.83-7.76 (m, 4H, ArH), 5.92 (s, 2H, OH) 4.30-4.19 (m, 8H, OCH2), 2.24-2.19 (m, 8H, OCH2CH2), 1.59-1.35(m, 16H, OCH2CH2CH2CH2), 1.01-0.78 (m, 12H, CH3). HRMS (ESI): calc.m/z 605.3836 (C38H52O6), found m/z 605.3823 [M+H]+.

2, 6-di-pivalate-tetra-pentoxy-triphenylene (4)

2, 6-dihydroxy-3, 7, 10, 11-tetrapentyloxytriphenylene (0.5g, 8.26×10^{-4} mol), dicyclohexyl-Carbonimide (DCC) and 4-dimethylaminopyridine (DMAP) were added to anhydrous dichloromethane (DCM) (15 mL) to dissolve under nitrogen. Pivalic acid (0.185g, 1.82×10^{-3} mol) was injected and the mixture immediately submerged in an oil bath at 40°C. After 12 h of reaction, the crude product was subjected to suction filtration, concentration, column chromatography and recrystallization to give the final product (0.549g, 86%); TLC Rf: 0.63 (ethyl acetate-hexane 1:8); (Found: C, 74.55; H, 8.73. C87H124O12 requires: C, 74.58; H, 8.87%); IR (KBr): νmax/cm-1 1253 (C-O-C), 1763 (C=O); 1H NMR (300 MHz, CDCl3), δ (ppm): 7.76-8.04 (d, 3H, Ar-H), 4.20-4.23 (s, 4H, OCH2), 1.95-1.87(s, 4H, OCH2CH2), 1.55-1.25(m, 17H, CH2,CH3),1-0.96 (s, 6H, CH3), HRMS (ESI): calc.m/z 773.4987 (C48H68O8), found m/z 773.4998[M+H]+.

3. ^{1}H-NMR and HRMS spectra of 2, 6-dihydroxy-3, 7, 10, 11-tetra-pentyloxytriphenylene and T5EP2.

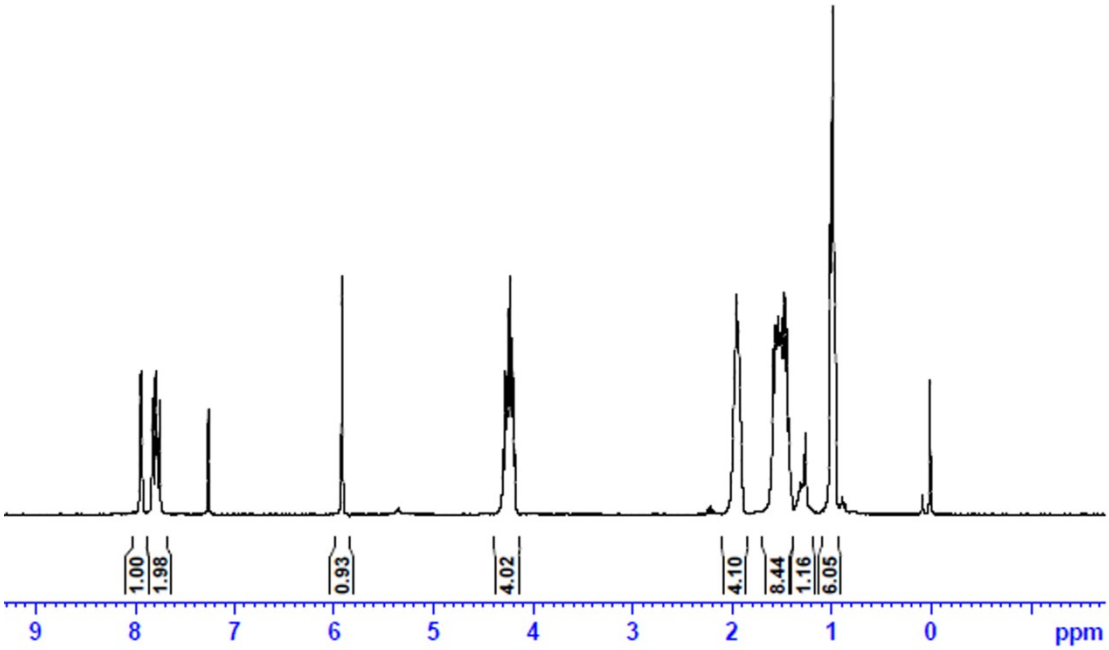


Fig. S1 1HNMR spectrum of 2, 6-dihydroxy-3, 7, 10, 11-tetrapentyloxy-triphenylene.

Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
2, 6-dihydroxy-3, 7, 10, 11-tetrapentyloxytriphenylene	C38H52O6	[M+H]+	605.3823	605.3836	-2.15

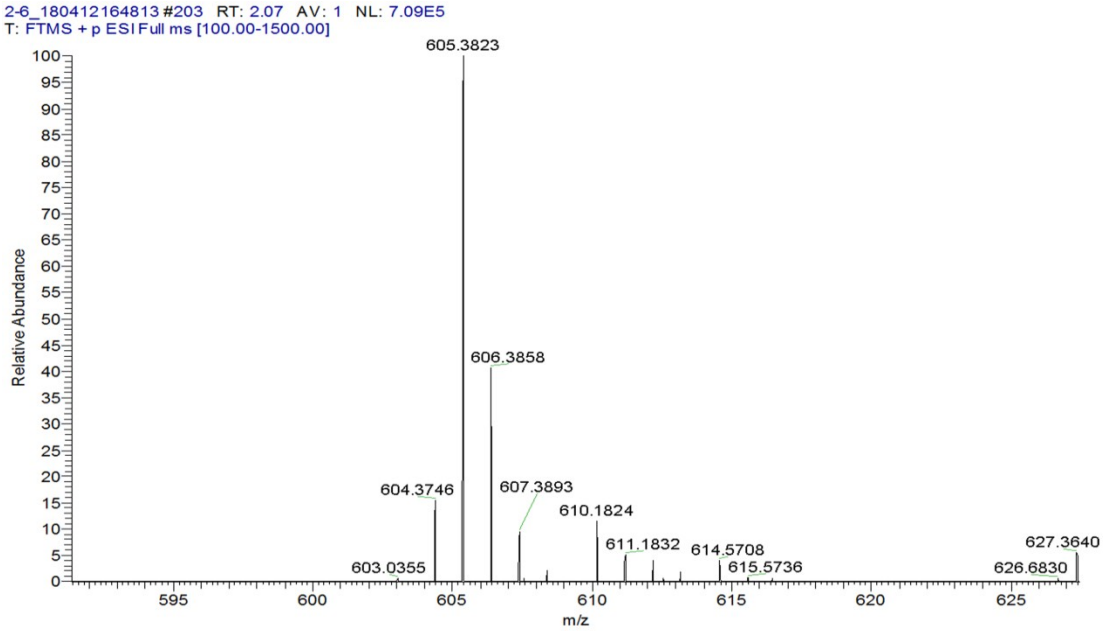


Fig. S2 HRMS spectrum of 2,6-dihydroxy-3, 7, 10, 11-tetrapentyloxytriphenylene.

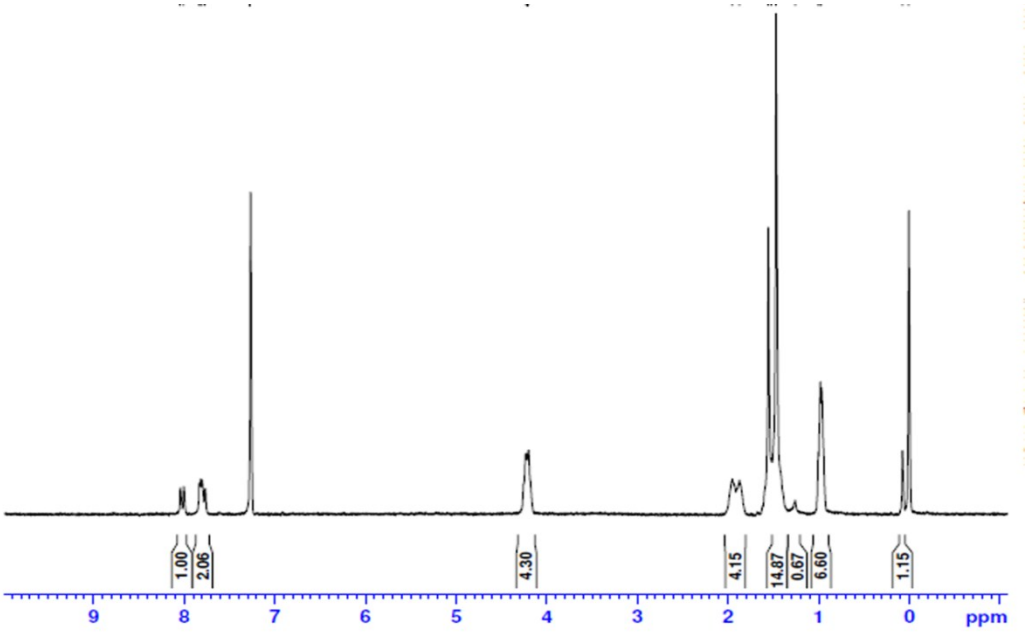


Fig. S3 1H NMR spectrum of T5EP2 in CDCl3.

Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
T5EP2	C48H68O8	$[M+H]^+$	773.4998	773.4987	1.42

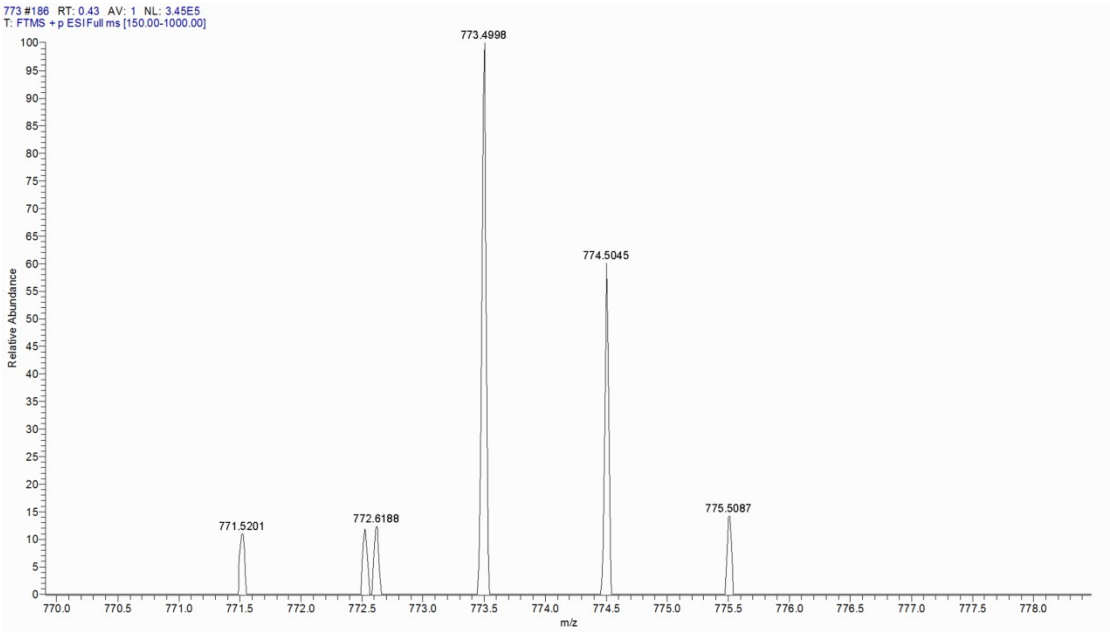


Fig. S4 HRMS spectrum of T5EP2 (4).

4. **Temperature dependent one-dimensional wide-angle X-ray diffraction patterns of T5EP2 at Colhp and Colh mesophases.**

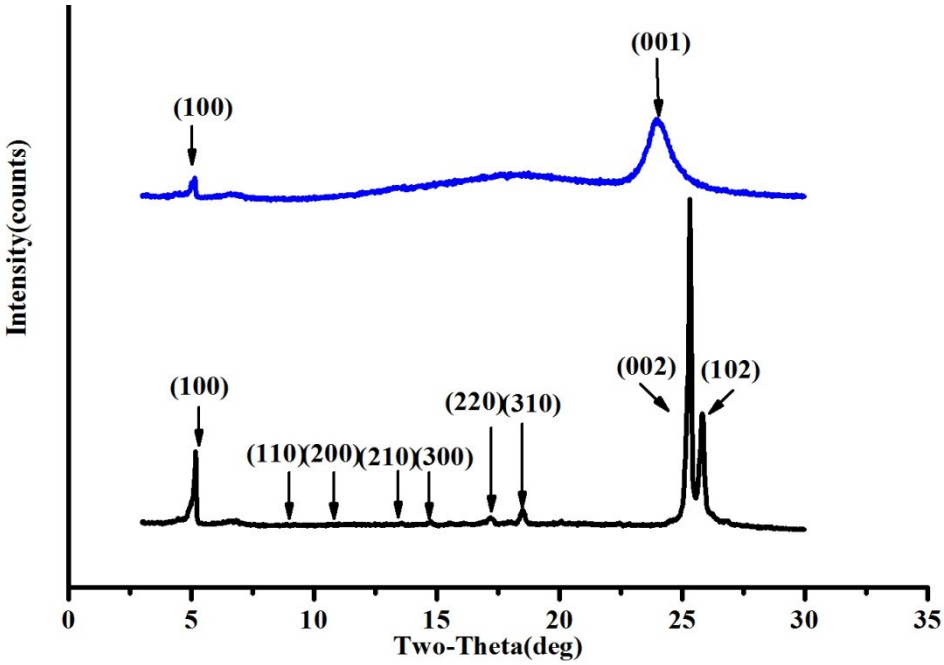


Fig. S5 1D WAXD patterns at 30°C and 100°C during the second heating

Table S1. One-dimensional wide-angle X-ray diffraction datas of **T5EP2** at at 30°C and 100°C

Sample	d-Spacing	Miller	Phase(lattice constants)
T5EP2 (30℃)	17.3	(100)	
	10.04	(110)	
	8.62	(200)	
	6.52	(210)	Col_{hp}(a=19.97Å)
	5.68	(300)	
	4.93	(220)	
	4.78	(310)	
	3.51	π-π	
	3.44	tail-tail	
T5EP2(170℃)	17.16	(100)	Col_h(a=19.81Å)
	3.71	π-π	

5. Experimental section and full reference for Gaussian 09, results and model structure for calculation.

Full citation for Gaussian 09 program

Ref Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

Table S2. Cartesian coordinate for the optimized structure of T5DP-2,6

Atom	X / Å	Y/ Å	Z / Å				
C	10.00013	-0.01134	-0.13837	H	10.38404	1.01888	-0.10289
C	10.87743	-1.03174	-0.50207	H	8.72845	-3.62653	-0.28273
C	10.41573	-2.32724	-0.55227	H	4.50187	1.43996	1.48936
C	9.08253	-2.58604	-0.23807	H	9.2106	2.4255	0.38933
C	8.15473	-1.57184	0.13803	H	6.91854	-4.00542	0.14004
C	8.63143	-0.23434	0.18983	H	3.86558	-0.34559	1.42037
C	6.78523	-1.85854	0.45803	H	1.05639	5.00695	3.45278
C	5.90623	-0.80484	0.82663	H	1.26234	3.5396	2.4008
C	6.38783	0.54626	0.87893	H	2.00199	3.5791	4.06114
C	7.74353	0.83006	0.56223	H	3.00068	6.48846	3.91418
C	5.55403	1.64366	1.24143	H	4.62581	6.10362	3.19794
C	6.00343	2.96196	1.29793	H	3.94507	5.0593	4.52133

C	7.31653	3.23676	0.99113	H	1.98776	6.43424	1.6408
C	8.16383	2.18986	0.63173	H	3.61411	6.04977	0.92711
C	6.25033	-3.17894	0.42363	H	2.19402	4.96572	0.59013
C	4.92373	-3.47684	0.73093	H	5.61266	-9.19451	1.09446
C	4.07233	-2.45624	1.08793	H	6.77973	-7.99997	0.37806
C	4.55823	-1.15044	1.13323	H	6.38579	-7.93457	2.15173
O	5.15795	3.96039	1.65053	H	3.3637	-8.43945	1.84285
O	4.47801	-4.75537	0.6788	H	2.88822	-6.69395	1.67155
C	3.96746	3.67038	2.18799	H	4.13857	-7.1795	2.89883
C	3.02588	4.78229	2.58066	H	3.90327	-8.52906	-0.58574
O	3.64639	2.51844	2.35888	H	3.42688	-6.78355	-0.75434
C	1.75087	4.18683	3.16316	H	5.07121	-7.33413	-1.30063
C	3.69438	5.66795	3.62384	H	17.27799	3.07461	-3.74988
C	2.68226	5.61389	1.35188	H	15.81886	3.92553	-3.07978
C	5.32292	-5.76812	0.90399	H	15.67815	2.94105	-4.60174
C	4.82654	-7.19196	0.84594	H	16.19343	0.86963	-3.3091
O	6.48311	-5.54264	1.15379	H	16.33414	1.85411	-1.78714
C	5.97878	-8.14432	1.13728	H	13.97142	2.61002	-2.05802
C	3.73055	-7.38948	1.88484	H	13.83071	1.62553	-3.57998
C	4.26959	-7.47897	-0.54221	H	14.34599	-0.44589	-2.28734
O	12.16868	-0.75159	-0.80243	H	14.4867	0.5386	-0.76539
C	16.17566	3.0136	-3.60877	H	11.98366	0.30935	-2.55837
C	15.83662	1.78156	-2.78011	H	12.12352	1.29467	-1.03687
C	14.32822	1.69808	-2.58701	H	7.17998	11.47732	0.31876
C	13.98918	0.46605	-1.75835	H	5.74391	10.52754	0.89994
C	12.48078	0.38256	-1.56526	H	6.28117	10.3951	-0.83187
O	7.78003	4.50917	1.03783	H	8.42144	9.34985	-0.08764
C	6.62473	10.51782	0.21964	H	7.88418	9.48228	1.64418
C	7.54061	9.35957	0.59267	H	5.9	8.05632	1.13734

C	6.78083	8.04661	0.45704	H	6.43726	7.92389	-0.59447
C	7.6967	6.88836	0.83007	H	8.57753	6.87864	0.14976
C	6.93692	5.5754	0.69444	H	8.04027	7.01107	1.88158
O	11.24669	-3.33853	-0.90273	H	6.05609	5.58511	1.37474
C	16.38774	-5.09017	-3.8369	H	6.59336	5.45268	-0.35707
C	15.14446	-5.37934	-3.00614	H	16.93949	-6.03881	-4.02248
C	14.38947	-4.08125	-2.7522	H	16.08704	-4.64016	-4.80944
C	13.14619	-4.37042	-1.92143	H	17.04496	-4.38058	-3.28617
C	12.39119	-3.07234	-1.66749	H	15.44517	-5.82935	-2.0336
O	2.77788	-2.71737	1.39161	H	14.48725	-6.08893	-3.55687
C	-3.18107	-1.80564	0.06205	H	14.08876	-3.63125	-3.72474
C	-2.06429	-2.42599	0.8912	H	15.04669	-3.37166	-2.20146
C	-0.71563	-1.97598	0.34519	H	13.4469	-4.82043	-0.94889
C	0.40116	-2.59633	1.17434	H	12.48897	-5.08002	-2.47216
C	1.74982	-2.14631	0.62834	H	12.09049	-2.62233	-2.64003
				H	13.04841	-2.36274	-1.11676
				H	-4.16667	-2.13451	0.46107
				H	-3.11072	-0.69622	0.11686
				H	-3.08202	-2.13269	-0.99719
				H	-2.13464	-3.53542	0.83639
				H	-2.16334	-2.09895	1.95045
				H	-0.64527	-0.86656	0.40001
				H	-0.61657	-2.30302	-0.71405
				H	0.3308	-3.70575	1.11953
				H	0.3021	-2.26928	2.23359
				H	1.82017	-1.03689	0.68315
				H	1.84887	-2.47335	-0.43091
				H	10.38404	1.01888	-0.10289

				H	8.72845	-3.62653	-0.28273
				H	4.50187	1.43996	1.48936

6. Model structure of T5EP2

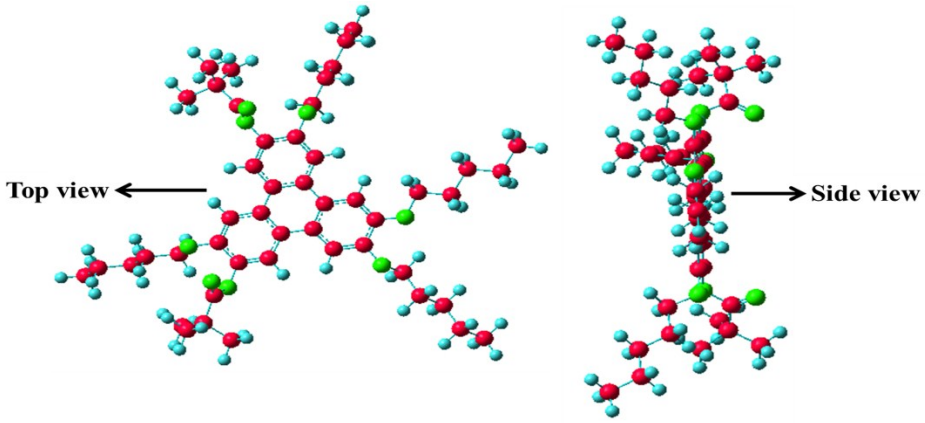


Fig. S6 Top view and side view of a molecule.

7. DSC diagram of T5EP2.

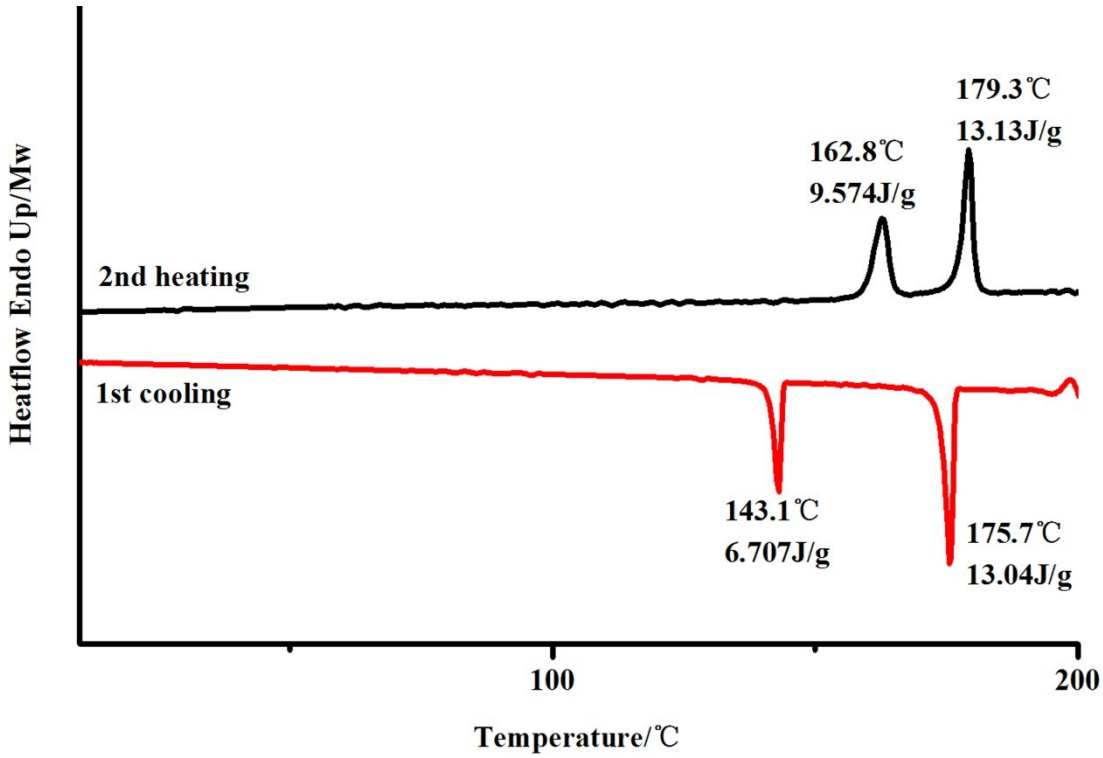


Fig. S7 DSC diagram of T5EP2.

8. The determination of annealing conditions including annealing temperature, annealing duration and cooling rate of T5EP2

T5EP2 sample was annealed from 159°C to room temperature for a whole night at rate of 10°C min^{-1}, 5°C min^{-1}, and 0.5°C min^{-1}, respectively. Their optical properties were observed under POM and all POM images were obtained in the same area (fig. S8). From Fig. S8 (a) obtained via annealing at a rate of 10 °C min^{-1}, it can be observed the existence of distinct straight line defect texture. From Fig. S8 (b) obtained by annealing at a rate of 5°C min^{-1}, we found that the straight line defect texture was significantly decreased in the same area. From Fig. S8 (c) obtained by annealing at a rate of 0.5 °C min^{-1}, it was surprised to find that the straight defect texture disappeared and the viewing field was completely dark, which indicated that the domains were almost all vertically aligned. In order to obtain the most realistic and ideal results, samples of 2D WAXD and TEM were all annealed from 159°C to room temperature for a whole night at a rate of 0.5°C min^{-1} .

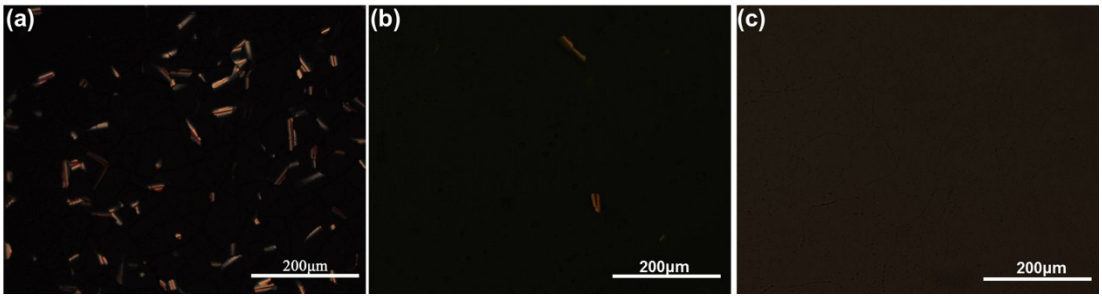


Fig. S8 The POM images of T5EP2: (a) annealing at a rate of 10 °C min^{-1}; (b) annealing at a rate of 5 °C min^{-1}; (c) annealing at a rate of 0.5 °C min^{-1}.

9. TEM image of T5EP2

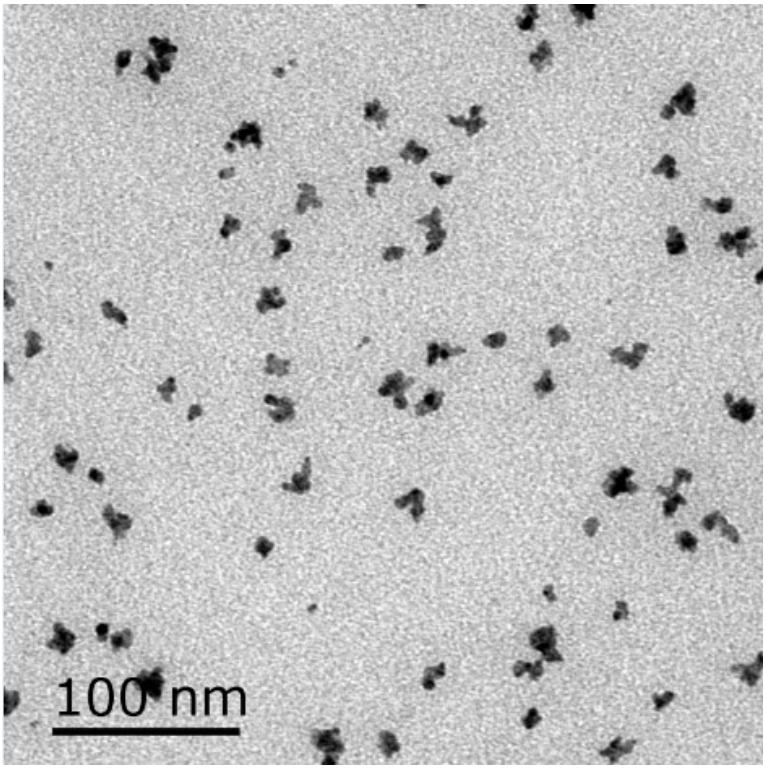


Fig. S9 TEM image of T5EP2 without annealing.