

# **The Leading Role of Steric Hindrance Effect and Dipole-Dipole Interaction in Supperlattice Nanostructures Forming via the Assembly of Discotic Liquid Crystals**

Supporting Information for Publication

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## **1. Experimental section**

### **1.1 Materials**

All chemicals were purchased from Aladdin, and all solvents from Aldrich. All chemicals and solvents were used without further purification. Silica gel 60 (200-300 mesh ASTM) and silica gel 60 glass thin-layer chromatography was used for the purification and identification of the reaction, respectively.

### **1.2 Instrumentations**

<sup>1</sup>H-NMR spectra were recorded by a Bruker NMR spectrometer (DMX 300 MHz) in CDCl<sub>3</sub>, Chemical shifts are given as units of measurement and expressed in parts per million ( $\delta$ ) with tetramethylsilane (TMS) as a reference. Multiplicities of peaks are expressed as s = singlet, d = doublet, t = triplet, m = multiplet. The KBr pellets were used to make the test samples and the infrared spectrum (FT-IR) was recorded on a Shimadzu FTIR-8400 spectrometer by Fourier transform. Firstly, the thermal properties of discotic liquid crystals were characterized using differential scanning calorimetry (DSC) on a Netzsch DSC 200. Its optical properties were characterized by a Polarizing Microscope (POM) on a Leica DM4500P with a Linkam TMS94 hot stage. Secondly, structural characterizations of samples were characterized by 1D wide angle X-ray diffraction (1D WAXD) through a Bruker D8 Advance diffractometer equipped with a variable temperature controller, two-dimensional wide-angle X-ray diffraction (2D WAXD) using a 40KV FL tube as the X-ray source (Cu K $\alpha$ ) and the small-angle X-ray scattering (SAXS) (SAXSess, Anton Paar) equipped with Kratky block-collimation system. At last, the structure and morphology were investigated by Transmission Electron Microscope TEM (FEI Tecnai G2 20 STWIN).

## **2. Synthesis**

### **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 ethanol. The filtrate was concentrated in vacuo and subjected to a silica gel column chromatography on silica, eluting with 1:1 dichloromethane: light petroleum to give the product as pale yellow oil. (96 g, 96 %); TLC Rf: 0.55 (dichloromethane-hexane 1:1); IR (KBr):  $\nu_{\max}/\text{cm}^{-1}$  11263 (C-O-C);  $\delta_{\text{H}}$  (300MHz, CDCl<sub>3</sub>) 6.99-6.87 (m, 4H, ArH), 4.10-3.99 (t, 4H, OCH<sub>2</sub>), 1.86-1.77 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 1.58-1.47 (m, 8H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.07-0.97 (t, 6H, CH<sub>3</sub>).

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

Compound 1 (30g, 0.12mol) was added to a vigorously stirred suspension of Iron(III) chloride (62.3g, 0.46mol) in dichloromethane (200ml). The reaction occurred with vigorous evolution of gas and was quenched with methanol (300ml) after 70 min. The reaction mixture was filtered and the filtrate concentrated in vacuo to give a pale yellow powder which was subjected to a silica gel column chromatography, eluting with 1: 1 dichloromethane: light petroleum to give some pale yellow powders which were recrystallized from ethanol. (11.6g, 77%); TLC Rf: 0.44 (ethyl acetatehexane 1:6); IR (KBr):  $\nu_{\max}/\text{cm}^{-1}$  1253 (C-O-C);  $\delta_{\text{H}}$  (300MHz, CDCl<sub>3</sub>) 7.85 (s, 6H, ArH), 4.25 (t, 12H, OCH<sub>2</sub>), 1.92-1.99 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>), 2.0 (m, 12H, OCH<sub>2</sub>CH<sub>2</sub>), 1.42-1.67 (m, 24H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.07-0.99 (m, 18H, CH<sub>3</sub>).

### **2-hydroxy-3, 7, 10, 11-Pentapentyloxytriphenylene (3)**

To a cooled suspension of catechol (11g, 0.15mol) in CH<sub>2</sub>Cl<sub>2</sub> (50mL), a solution (0°C) of BBr<sub>3</sub> (28.6g, 0.11mol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was added slowly with stirring 3h under nitrogen. 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<sub>2</sub>Cl<sub>2</sub> (80 ml) and this was used for next ether cleavage reactions. A compound of 2 (14.88g, 0.02mol) was dissolved in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (200 ml) and cooled to 0°C. The B-Bromocatecholboronane solution of CH<sub>2</sub>Cl<sub>2</sub> (100ml, 0.05mol) was added under argon and the mixture was stirred at room temperature for 24h. After that it was poured over ice-water and extracted with CH<sub>2</sub>Cl<sub>2</sub>, the combined extract was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> overnight, solvent was removed under vacuum and the

crude product was purified by a silica gel column chromatography, eluting with 1: 30 ethyl acetate: light petroleum to give 3 as white powder which was recrystallized from ethanol. (3.5g, 26%); TLC Rf: 0.36 (ethyl acetate-hexane 1:4); IR (KBr):  $\nu_{\max}/\text{cm}^{-1}$  3436 (O-H), 1265 (C-O-C);  $\delta_{\text{H}}$  (300MHz,  $\text{CDCl}_3$ ) 7.93 (s, 2H, ArH), 7.83-7.76 (m, 4H, ArH), 5.92 (s, 1H, OH) 4.30-4.19 (m, 10H,  $\text{OCH}_2$ ), 2.24-2.19 (m, 10H,  $\text{OCH}_2\text{CH}_2$ ), 1.59-1.35(m, 20H,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.01-0.78 (m, 15H,  $\text{CH}_3$ ).

### 3. POM image and X-ray diffraction patterns of T5ON1

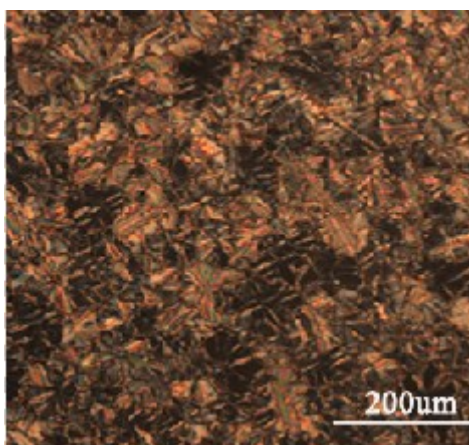


Fig. S1 POM image: T5ON1, 30°C.

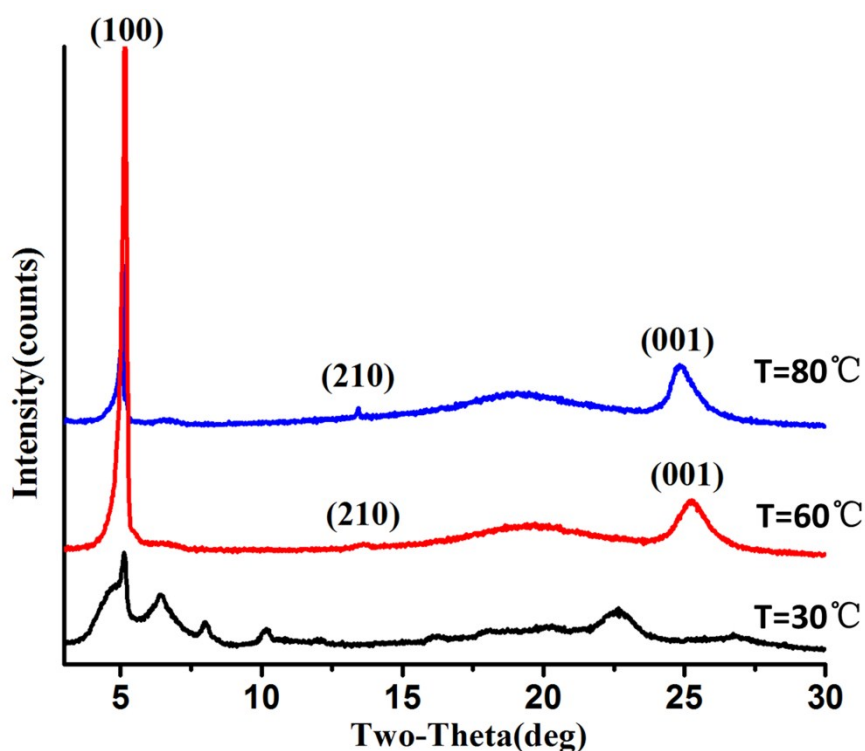


Fig. S2 1D WAXD patterns of T5ON1 at 30 °C、60°C and 80 °C.

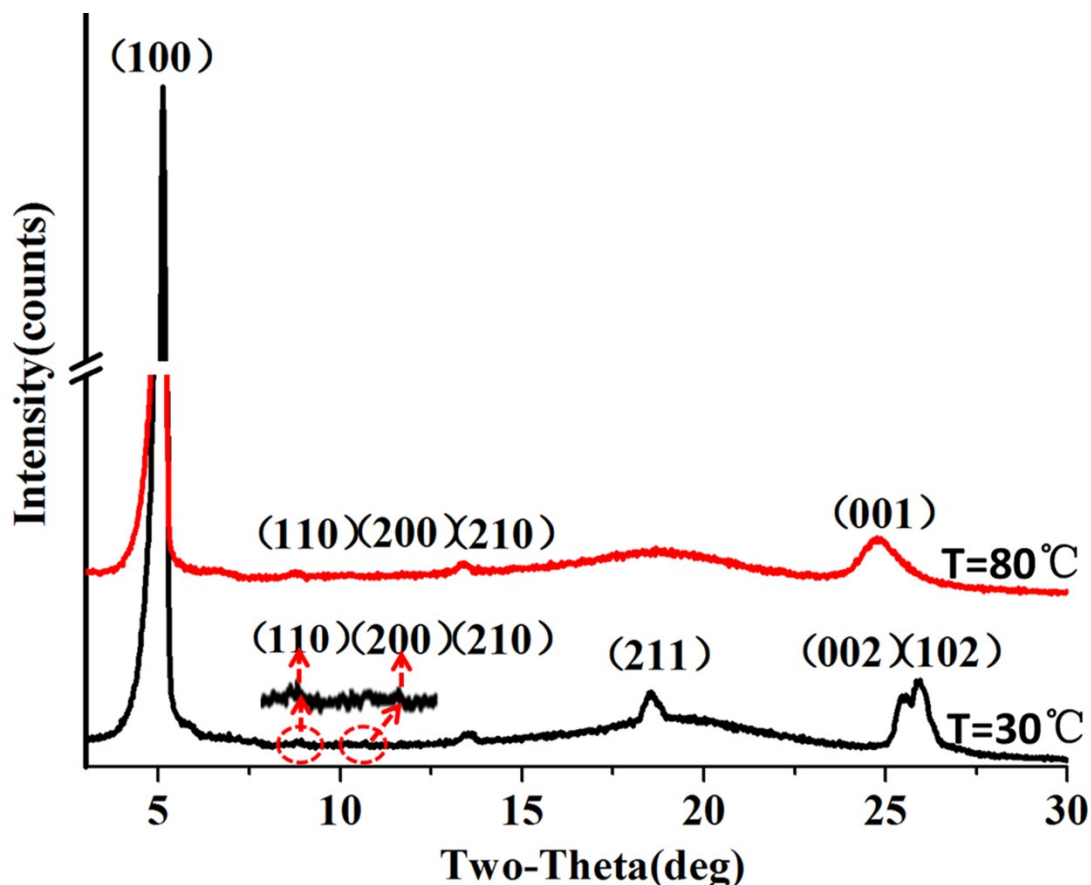


Fig. S3 1D WAXD patterns of T5EP1 at 30 °C and 80 °C.

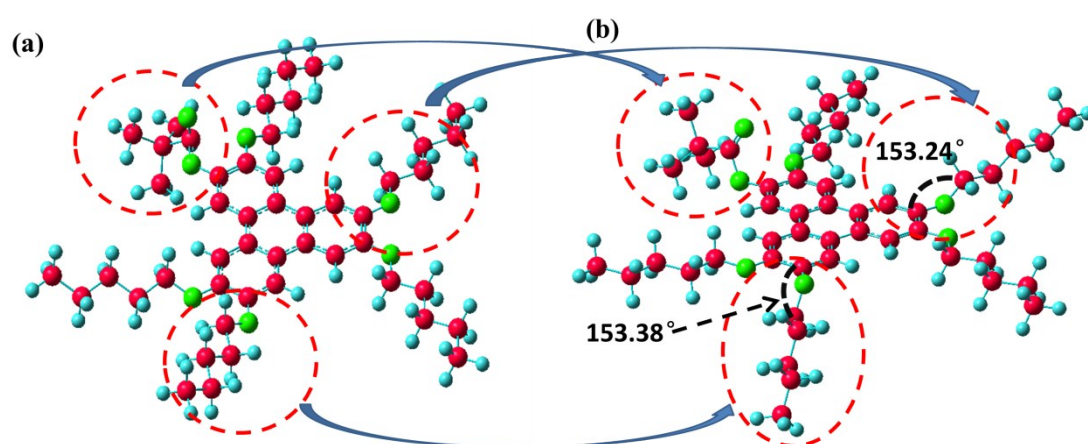
#### 4. Experimental section and full reference for Gaussian 09, results and model structure for calculation

##### 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.

Firstly, we constructed the geometrical configuration of T5EP1 by GaussView 5.0. The constructed T5EP1 was introduced into Gaussian 09 using the density function theory (DFT) theory to calculate the optimized molecular model via the B3LYP/6-31G basis sets.<sup>1,2,3</sup> The geometrical configuration of T5EP1 constructed through the GaussView 5.0 and the geometry of the T5EP1 optimized by B3LYP / 6-31G (d.p) by Density Function Theory (DFT) and Gaussian 09 Package (Revision C.01) were shown below.



**Fig. S4** (a) The geometrical configuration of T5EP1 constructed through the GaussView 5.0; (b) the geometry configuration of T5EP1 optimized by density function theory (DFT) with Gaussian 09 package (Revision C.01) at the B3LYP/6-31G(d.p) basis sets.

**Table S1.** Cartesian coordinate for the optimized structure of T5EP1.

Atom	X / Å	Y / Å	Z / Å				
C	1.44048	-5.52183	-5.53757	H	3.26455	-6.75685	-3.92579
C	0.59734	-4.72421	-6.35713	H	1.70875	-7.51229	-4.70467
C	0.92292	-3.34684	-6.59588	H	-1.21979	-4.74207	-7.55123
C	2.08838	-2.78096	-6.01255	H	-0.78934	-2.92191	-7.86682
C	2.94008	-3.5867	-5.18458	H	3.25857	-0.95637	-5.84068
C	2.61773	-4.95018	-4.94827	H	8.12437	-1.18985	0.07988
C	4.12125	-3.07516	-4.573	H	6.48866	-1.89622	0.4372
C	4.96052	-3.84177	-3.76612	H	6.70361	-0.76761	-0.97185
C	4.64828	-5.16243	-3.53727	H	9.05759	-3.49542	-0.01942
C	3.50069	-5.69985	-4.11811	H	7.48428	-4.17332	0.3244
C	1.06601	-6.88198	-5.33681	H	7.28128	-11.9237	0.42891
C	-0.07302	-7.45475	-5.9004	H	6.48313	-12.0046	-1.20161

C	-0.88969	-6.68227	-6.69424	H	5.51656	-11.523	0.26098
C	-0.55714	-5.34663	-6.91452	H	6.89773	-9.45765	0.4933
C	0.11629	-2.49827	-7.40818	H	7.8643	-9.93924	-0.96929
C	0.41608	-1.15878	-7.65139	H	5.78658	-9.91148	-2.35114
C	1.54494	-0.61069	-7.08639	H	4.82001	-9.42989	-0.88854
C	2.35987	-1.40884	-6.28522	H	6.20118	-7.36456	-0.65622
O	6.06987	-3.29354	-3.21403	H	7.16775	-7.84615	-2.11882
C	6.21792	-3.2787	-1.88433	H	4.12373	-7.33638	-2.03747
O	5.32817	-3.68074	-1.17301	H	5.08928	-7.81858	-3.50054
C	7.18203	-1.57341	-0.37138	H	6.32986	6.07464	-7.97432
C	8.1511	-3.86326	-0.45285	H	6.84293	4.43058	-8.55398
O	5.44641	-5.93075	-2.75708	H	6.7066	4.76478	-6.7721
C	6.51318	-11.4613	-0.23066	H	4.24461	5.08685	-7.02118
C	6.86768	-10.0009	-0.47765	H	4.38093	4.75266	-8.80306
C	5.81663	-9.36824	-1.38019	H	5.30739	2.48922	-8.30735
C	6.17113	-7.90781	-1.62718	H	5.17106	2.82342	-6.52547
C	5.12008	-7.27515	-2.52971	H	2.70906	3.14549	-6.77454
O	1.86031	0.68865	-7.30616	H	2.84539	2.81129	-8.55642
C	6.27183	4.98145	-7.7735	H	3.63499	0.88251	-6.2785
C	4.8157	4.53598	-7.80166	H	3.77231	0.54756	-8.06017
C	4.73629	3.04009	-7.52686	H	-2.31051	5.5408	-11.6587
C	3.28016	2.59462	-7.55503	H	-1.50721	5.64347	-10.032
C	3.20074	1.09872	-7.28023	H	-0.54061	5.16196	-11.4946
O	-0.39389	-0.4058	-8.43432	H	-1.89848	3.07898	-11.7058
C	-1.53459	5.09248	-10.9986	H	-2.86508	3.56049	-10.2432
C	-1.8711	3.62997	-10.7392	H	-0.78197	3.56749	-8.86925
C	-0.80935	3.0165	-9.83591	H	0.18462	3.08598	-10.3319
C	-1.14586	1.55399	-9.57644	H	-1.17324	1.003	-10.5431
C	-0.08411	0.94053	-8.67318	H	-2.13984	1.48452	-9.0805
O	-2.00315	-7.21338	-7.25474	H	0.90959	1.00957	-9.16971
C	-7.61693	-6.24813	-9.63421	H	-0.05599	1.4917	-7.70664
C	-6.46106	-7.15416	-9.23095	H	-8.43469	-6.86231	-10.0733
C	-5.34205	-6.31373	-8.63008	H	-7.26306	-5.50928	-10.3876
C	-4.18619	-7.21976	-8.22683	H	-7.99755	-5.71094	-8.73681
C	-3.06718	-6.37934	-7.62596	H	-6.81493	-7.893	-8.47752
O	-0.37239	-8.75594	-5.66949	H	-6.08044	-7.69135	-10.1284
C	-4.74068	-13.0423	-4.86139	H	-4.98819	-5.57489	-9.38351
C	-3.2862	-12.6012	-4.95864	H	-5.72267	-5.77654	-7.73268
C	-3.226	-11.1022	-5.22068	H	-4.54006	-7.95861	-7.4734
C	-1.77152	-10.6611	-5.31792	H	-3.80557	-7.75695	-9.12423
C	-1.71132	-9.16198	-5.57996	H	-3.44797	-5.84283	-6.72822
				H	-2.71351	-5.63991	-8.37891
				H	-4.78468	-14.1378	-4.66989

				H	-5.23721	-12.5	-4.02588
				H	-5.26283	-12.8116	-5.81685
				H	-2.78968	-13.1436	-5.79414
				H	-2.76406	-12.8319	-4.00317
				H	-3.72253	-10.5598	-4.38517
				H	-3.74814	-10.8715	-6.17614
				H	-1.27499	-11.2034	-6.15343
				H	-1.24938	-10.8918	-4.36246
				H	-2.20785	-8.61962	-4.74446
				H	-2.23346	-8.93128	-6.53543
				H	8.37144	-4.69634	-1.08715
				C	7.49633	-2.75974	-1.27325
				H	4.37703	-2.04999	-4.74184
				C	8.4478	-2.31731	-2.40045
				H	8.65924	-3.15129	-3.03659
				H	7.9857	-1.54028	-2.9728
				H	9.35953	-1.95297	-1.97513

## 5. TEM and POM images

We provided POM images and TEM images of unannealed sample and annealed sample (Fig. S5). According to the changes in the texture of Fig.S5(c) and (d), the ordering degree of the TEM samples after annealing can be greatly improved. Generally, the annealing process was a regular progress for the self-assembly of discotic liquid crystal and was very helpful to form an ordered structure. Fig. S5 (e) and (f) were TEM images of annealed and unannealed samples, respectively. From the TEM images obtained from the unannealed samples, it can be seen that no large-area ordered nanostructures formed. From TEM image of the annealed samples, large-area ordered nanostructure can be seen clearly. Therefore, the annealing process can promote the hierarchical self-assembly to form ordered nanostructures.



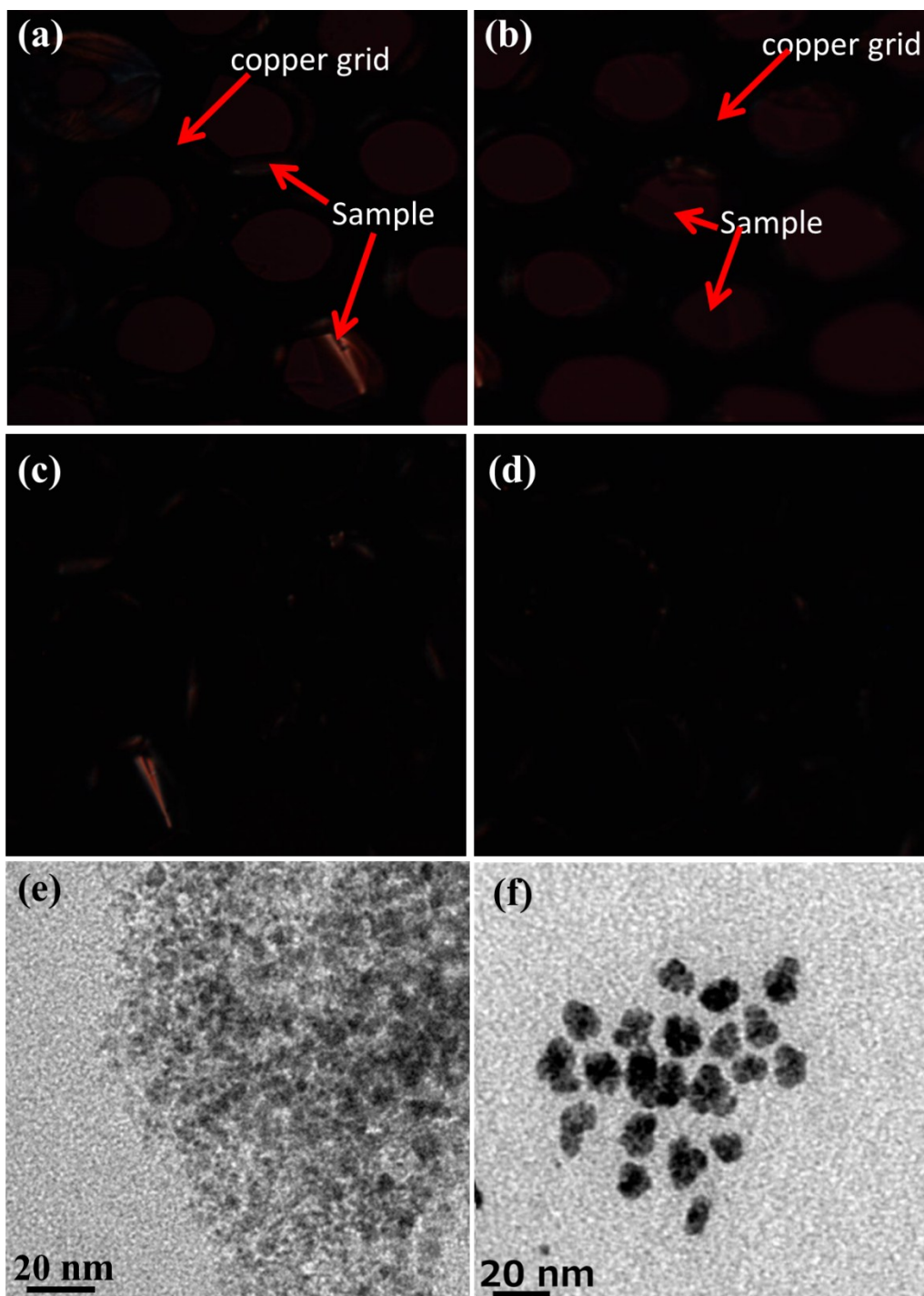


Fig. S5 The POM images of on the 200 mesh copper grid with the angle of the polarizer of 45°: unannealed sample and (b) annealed sample; the POM image of TEM sample on the 200 mesh copper grid with the angle of the polarizer of 90°: (c) unannealed sample and (d) annealed sample;(e) The TEM images of T5EP1 without the annealing; (f) the TEM images of T5EP1 after the annealing;

6. Double logarithmic presentations of the hole and electron photocurrent transients of T5EP1, T5E3, HAT5 and T5ON1

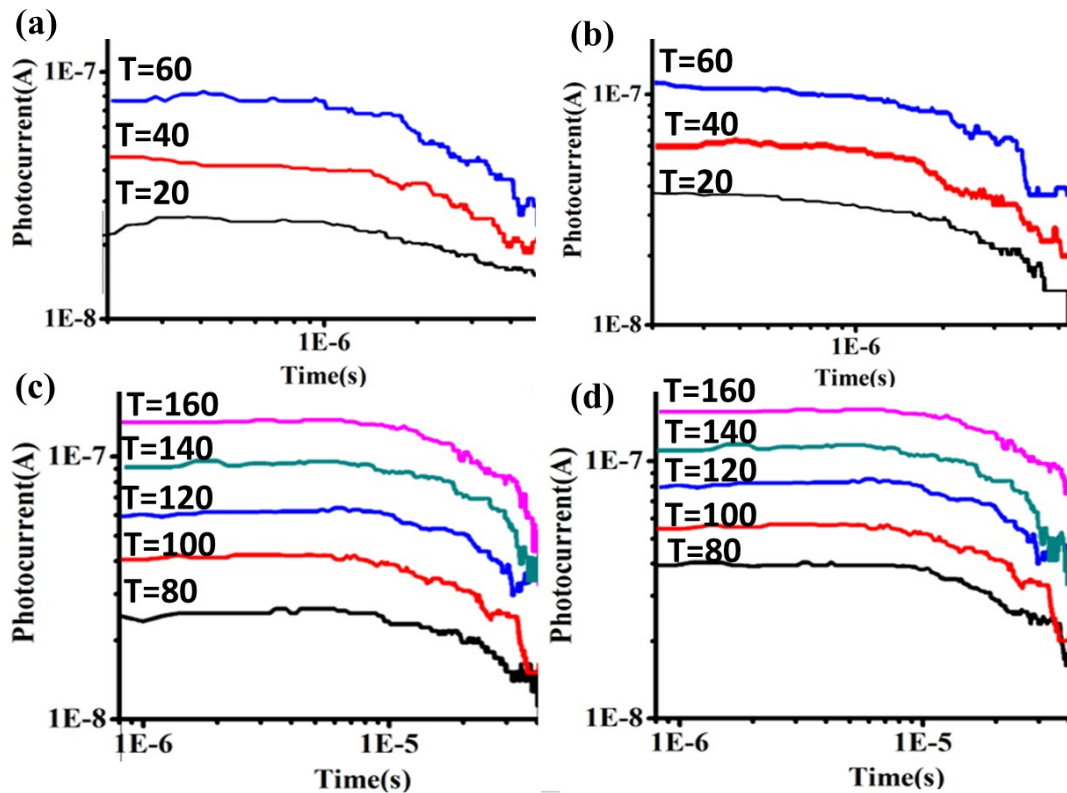


Fig. S6 Double logarithmic plot of typical transient currents  $I$  as a function of time  $t$  of T5EP1 at an electric field of  $E = 2.2 \times 10^{-4}$  V/cm: (a) and (c) the hole mobility of T5EP1 as a function of temperature; (b) and (d) the electronic mobility of T5EP1 as a function of temperature.

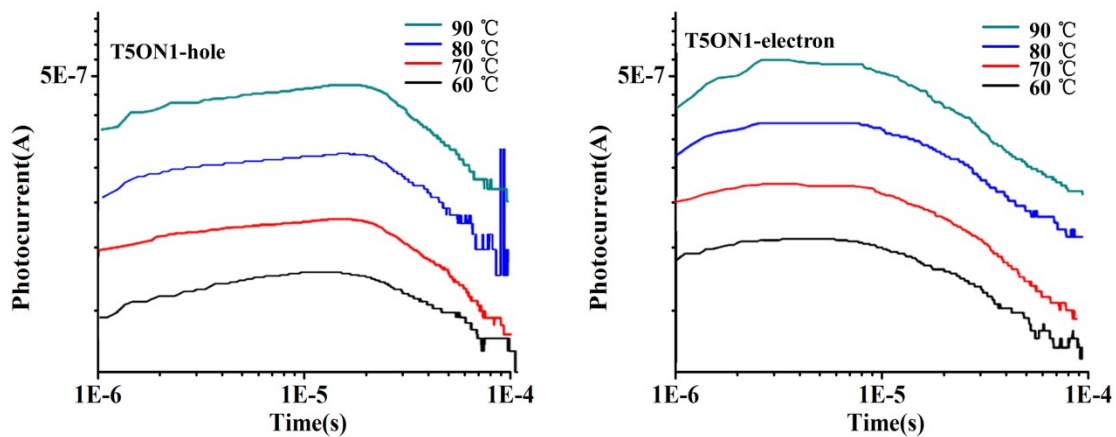
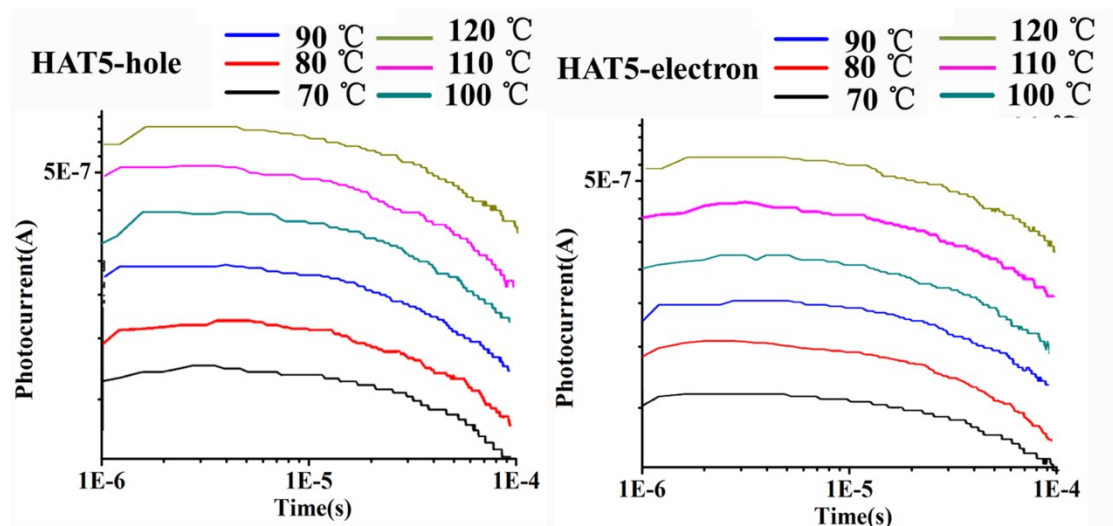
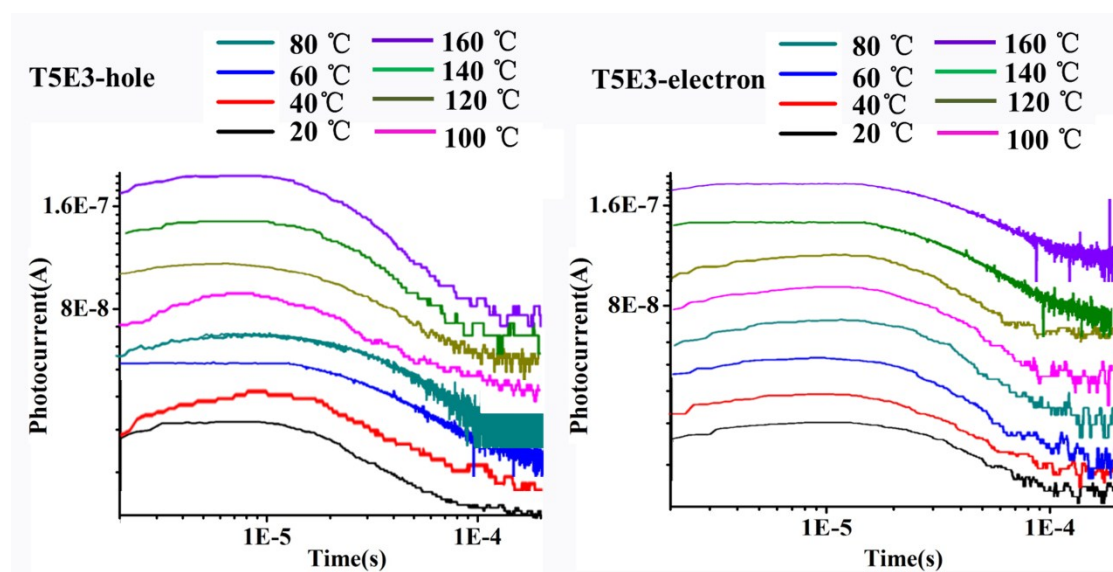


Fig. S7 Double logarithmic plot of typical transient currents  $I$  as a function of time  $t$  of T5ON1 at an electric field of  $E = 2.2 \times 10^{-4}$  V/cm: the hole and electron mobilities of T5ON1 as a function of temperature.

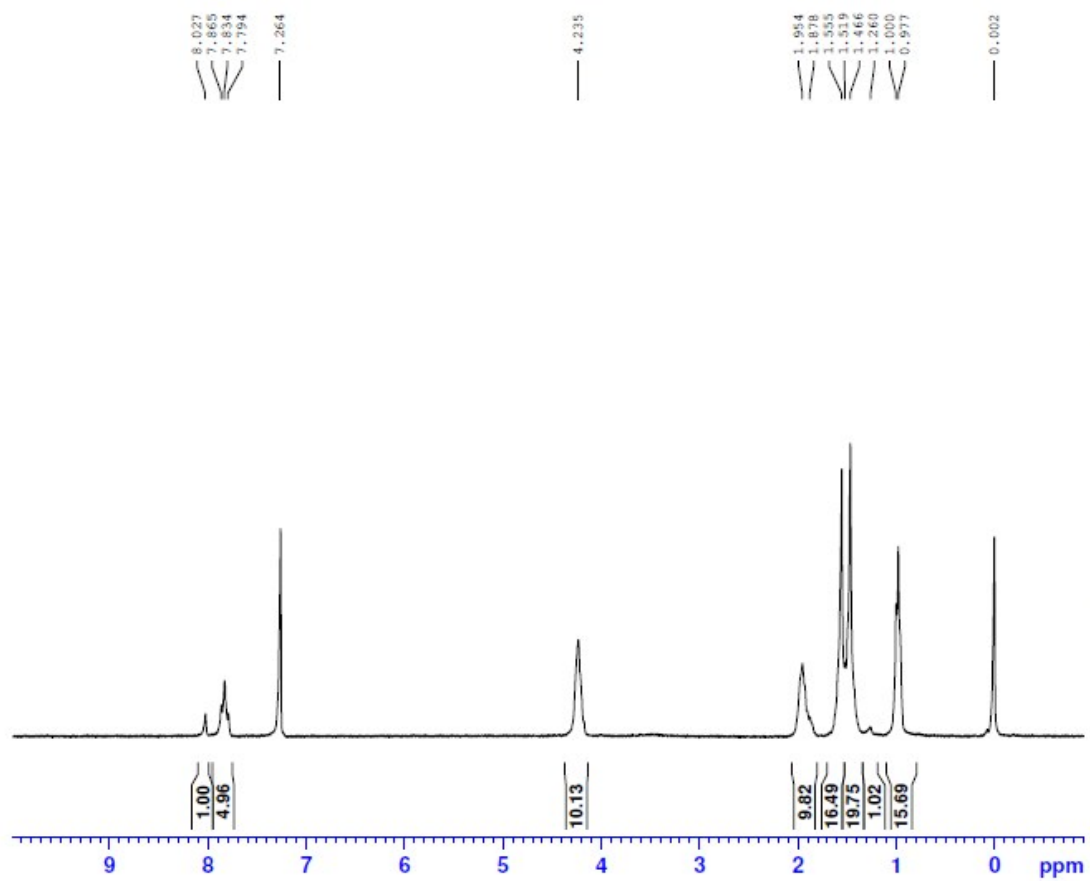


**Fig. S8** Double logarithmic plot of typical transient currents  $I$  as a function of time  $t$  of HAT5 at an electric field of  $E = 2.2 \times 10^{-4}$  V/cm: the hole and electron mobilities of HAT5 as a function of temperature.

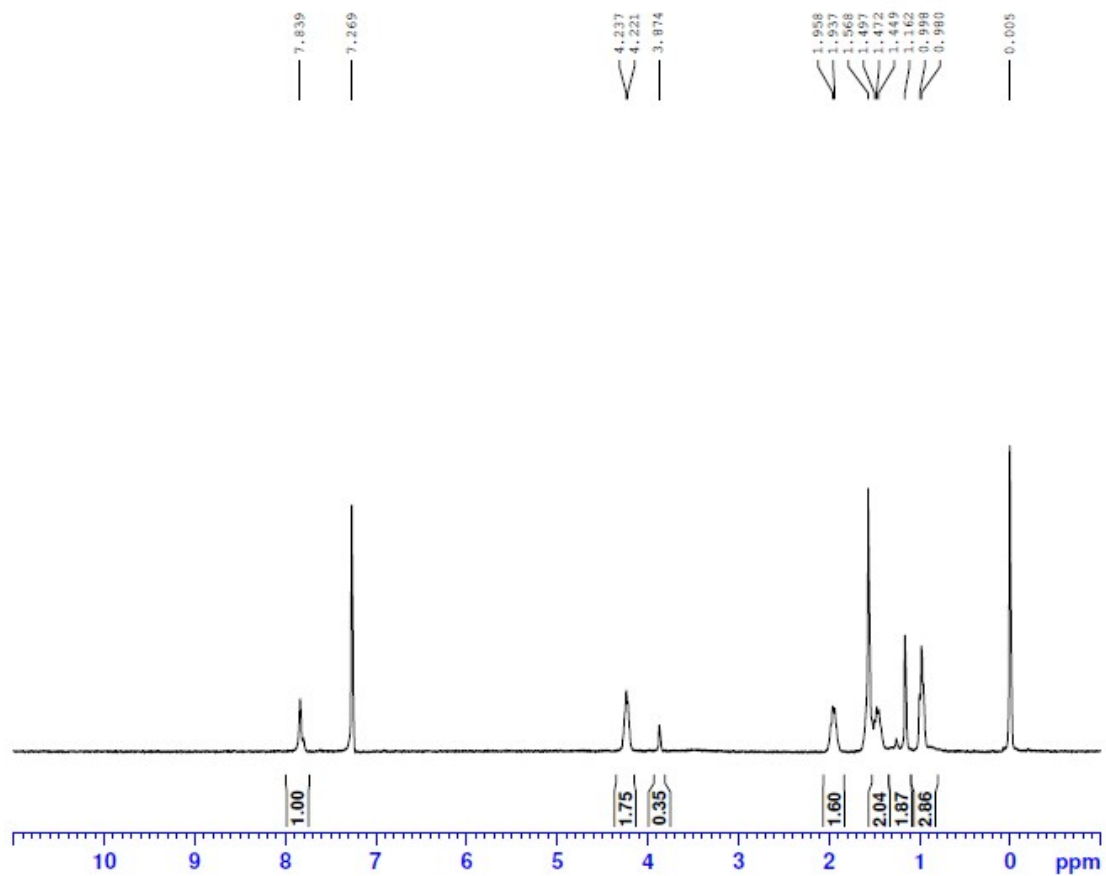


**Fig. S9** Double logarithmic plot of typical transient currents  $I$  as a function of time  $t$  of T5E3 at an electric field of  $E = 2.2 \times 10^{-4}$  V/cm: the hole and electron mobilities of T5E3 as a function of temperature.

## 7. <sup>1</sup>HNMR spectra of T5EP1 and T5ON1



**Fig. S10** <sup>1</sup>H NMR spectrum of T5EP1 in CDCl<sub>3</sub>.



**Fig. S11**  $^1\text{H}$  NMR spectrum of T5ON1 in  $\text{CDCl}_3$ .

**References:**

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- [2] A Hesselmann, G Jansen and M Schütz, *J. Chem. Phys.*, 2005, **122**, 014103.
- [3] M. W. Wong, *Chemical Physics Letters*, 1996, **256**, 391.