# ARTICLE

# Supplemental Information

# Preparing Two-dimensional Crystalline Conjugated Polymer Films by Synergetic Polymerization and Self-assembly at Air/Water Interface

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#### 1. General Statement

**Compound synthesis:** All reactions for monomer compounds were performed under a nitrogen or ambient atmosphere in a flame-dried reaction flask. All solvents were distilled prior to use. The solvents for reaction were distilled to remove water over Na, CaH<sub>2</sub> or K<sub>2</sub>CO<sub>3</sub>. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. MS data were obtained by EI and ESI. <sup>1</sup>H and <sup>13</sup>C NMR spectra were respectively recorded at 400 and 100 MHz for CDCl<sub>3</sub> solutions. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. All reactions were carried out in dry sealed tubes under a proper atmosphere. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

**Characterizations:** Optical images were taken by Olympus microscope. Atomic Force Microscopy (AFM) analysis was conducted on a Veeco Nanoscope IV Multimode AFM (Veeco, USA). Raman spectra were recorded on a Lab RAM HR Evolution instrument (HORIBA, France) excited with a 532 nm laser. X-ray photoelectron spectroscopy (XPS) characterizations were performed on an AXIS ULTRA DLD photoelectron spectrograph (Kratos, U.K.). Confocal laser scanning microscopy (CLSM) images were recorded on the OTS-modified Si/SiO<sub>2</sub> substrates (SiO<sub>2</sub> dielectric thickness: 300 nm) using an Olympus Research inverted system microscope (FV1000-IX81, Tokyo, Japan) equipped with a charge-coupled device (CCD, Olympus DP71, Tokyo, Japan) camera. The excitation source was a xenon lamp equipped with a band-pass filter (Ex = 325 - 375 nm; Em = 425 -nm). The steady absorption spectra of crystals were recorded on a UV-2600 instrument (SHIMADZU, Japan) and the PL spectra were collected on FSL980 spectrophotometers (Edinburgh, UK) with samples on quartz slices.

Powder X-ray diffractometer (PXRD, Empyrean, PANalytic, Netherlands) was used with a tube voltage of 40 kV and a tube current of 200 mA with Cu K $\alpha$  radiation. The instrument was calibrated using  $\alpha$ -quartz as an external standard. The sample which was transferred onto the substrate of octadecyltrichlorosilane (OTS)-modified Si/SiO<sub>2</sub> substrates (SiO<sub>2</sub> dielectric thickness: 300 nm) was ground and placed into a sample holder for experiments. XRD patterns were taken in a continuous scan mode at a scanning speed of 2°/min. The poly-DHO-PBD TEM samples were suspended in ethanol and drop-casted onto a Copper grid. Transmission electron microscopy (TEM) images and corresponding selected area electron diffraction (SAED) patterns were performed on an electron microscope (JEOL JEM-1011, Japan) with an acceleration of 100 kV to gain sufficient transmission. TEM characterization was carried out in low-dose mode. The electron dose rate for diffraction pattern was limited to 0.2 e-/Å<sup>2</sup>s. The acquisition time of selected-area electron diffraction patterns was 10 – 15 s, giving a total electron dose of 2 – 3 e-/Å<sup>2</sup>. The electrical devices were measured through Keithley 4200 system connected with a probe station under ambient condition.

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# 2. Investigation of advanced direct alkyne-alkyne homocoupling for phenylacetylene under convenient ambient conditions at air/water interface

**Model-like Reaction Procedure**: Various experimental conditions for direct alkyne-alkyne homocoupling at air/water interface have been carried out with 1,4-diphenylbutadiyne (DPBD) as a model system (**Scheme 1**). Under an ambient air atmosphere at moderate temperature, an aqueous solution (5 mL) of metal salt, corresponding ligand and base was poured into the glass cylinder (10 mL), subsequently added proper oxidative. Onto the surface of this solution was sprayed gently the toluene solution of phenylacetylene (1 M, circa 100 mg mL<sup>-1</sup>, 20 µL). The screw cap of the cylinder was then closed loosely such that the organic solvent evaporated spontaneously. This series of processes resulted in the formation of alkynyl-alkynyl coupling product on the surface of the aqueous phase (**Scheme 1**), and the obtained target was detected and confirmed by Gas Chromatography (GC) analysis. The investigated detailed conditions are described in **Table S1**.

Entry	Metal Salts (M)	Ligand (M)	Base (M)	Oxidative (eq.) <sup>[b]</sup>	Т	<i>t</i> (h)	Yield (%) <sup>[c]</sup>
					(°C)		
1				Δir	RT	<b>21</b> [d]	<5
י ר	CuCl(1.0)		KOAc (1.0)		D.Т.	24.7	×ی 97
2			KOAc (1.0)	$I_2(1.0)$	п.т. р.т	24	07
3		TMEDA (10)	KUAC (1.0)	I <sub>2</sub> (2.0)	R.I.	24	96
4	CuCl (1.0)	TMEDA (10)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	24	99
5	CuCl (1.0)	TMEDA (10)	NaOAc (2.0)	I <sub>2</sub> (2.0)	R.T.	24	91
6	CuCl (1.0)	TMEDA (10)	TEA (2.0)	I <sub>2</sub> (2.0)	R.T.	24	85
7	CuCl (1.0)	TMEDA (10)	pyridine (2.0)	I <sub>2</sub> (2.0)	R.T.	24	77
8	CuCl (1.0)	TMEDA (10)	DIPA (2.0)	I <sub>2</sub> (2.0)	R.T.	24	63
9	CuCl (1.0)	TMEDA (10)	K <sub>2</sub> CO <sub>3</sub> (2.0)	I <sub>2</sub> (2.0)	R.T.	24	N.R.
10	CuCl (1.0)	TMEDA (10)	Na <sub>2</sub> CO <sub>3</sub> (2.0)	I <sub>2</sub> (2.0)	R.T.	24	N.R.
11	CuCl (1.0)	TMEDA (10)	Ammonia (2.0)	I <sub>2</sub> (2.0)	R.T.	24	N.R.
12	CuCl (1.0)	TMEDA (10)	NaHCO <sub>3</sub> (2.0)	I <sub>2</sub> (2.0)	R.T.	24	N.R.
13	CuCl (1.0)	TMEDA (10)	KHCO <sub>3</sub> (2.0)	I <sub>2</sub> (2.0)	R.T.	24	N.R.
14	CuCl (1.0)	TMEDA (10)	None	I <sub>2</sub> (2.0)	R.T.	24	N.R.
15	CuCl (1.0)	None	KOAc (2.0)	I <sub>2</sub> (2.0)	R.T.	24	N.R.
16	CuBr (1.0)	TMEDA (10)	KOAc (2.0)	I <sub>2</sub> (2.0)	R.T.	24	83
17	Cul (1.0)	TMEDA (10)	KOAc (2.0)	I <sub>2</sub> (2.0)	R.T.	24	11
18	CuCl <sub>2</sub> (1.0)	TMEDA (10)	KOAc (2.0)	I <sub>2</sub> (2.0)	R.T.	24	92
19	Cu(OAc) <sub>2</sub> (1.0)	TMEDA (10)	KOAc (2.0)	I <sub>2</sub> (2.0)	R.T.	24	96

Table S1. Experimental conditions of the model-like reaction.<sup>[a]</sup>

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Λ	D	T	r	C	Ľ.	с.
н	n	ι.	ļ	L	L	с,

20	CuSO <sub>4</sub> (1.0)	TMEDA (10)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	24	99
21	CuSO <sub>4</sub> (1.0)	TMEDA (10)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	12 <sup>[e]</sup>	99
22	CuSO <sub>4</sub> (1.0)	TMEDA (2)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	12	99
23	CuCl (1.0)	TMEDA (2)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	12	24
24	NiCl <sub>2</sub> (1.0)	TMEDA (2)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	12	N.F.
25	ZnCl <sub>2</sub> (1.0)	TMEDA (2)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	12	N.F.
26	Bi(NO <sub>3</sub> ) <sub>3</sub> (1.0)	TMEDA (2)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	12	N.R.
27	Ni(OAc) <sub>2</sub> (1.0)	TMEDA (2)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	12	N.F.
28	FeCl <sub>3</sub> (1.0)	TMEDA (2)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	12	N.F.
29	CoSO <sub>4</sub> (1.0)	TMEDA (2)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	12	N.F.
30	K <sub>4</sub> Fe(CN) <sub>6</sub> (1.0)	TMEDA (2)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	12	N.R.
31	Pb(NO <sub>3</sub> ) <sub>2</sub> (1.0)	TMEDA (2)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	12	N.R.
32	AgNO <sub>3</sub> (1.0)	TMEDA (2)	KOAc (2.0)	l <sub>2</sub> (2.0)	R.T.	12	N.R.
33	CuSO <sub>4</sub> (1.0)	TMEDA (2)	KOAc (2.0)	l <sub>2</sub> (2.0)	40	12 <sup>[d]</sup>	90
34	CuSO <sub>4</sub> (1.0)	TMEDA (2)	KOAc (2.0)	l <sub>2</sub> (5.0)	40	12	99
35	CuSO <sub>4</sub> (0.5)	TMEDA (1)	KOAc (1.0)	l <sub>2</sub> (10)	40	12	98
36	CuSO <sub>4</sub> (0.1)	TMEDA (0.2)	KOAc (0.2)	l <sub>2</sub> (10)	40	12	82
37	CuSO <sub>4</sub> (0.1)	TMEDA (0.2)	KOAc (0.2)	l <sub>2</sub> (50)	40	12	94
38	CuSO <sub>4</sub> (0.1)	TMEDA (0.2)	KOAc (0.2)	l <sub>2</sub> (50)	40	4 <sup>[e]</sup>	94
39	CuSO <sub>4</sub> (0.1)	TMEDA (0.1)	KOAc (0.2)	l <sub>2</sub> (50)	40	4	87
40	CuSO <sub>4</sub> (0.1)	TMEDA (0.2)	KOAc (0.2)	l <sub>2</sub> (100)	40	4	99

[a] If not otherwise noted, the reaction conditions are as follows: phenylacetylene in toluene (1 M, 20  $\mu$ L) and metal salts, ligand, base, oxidative in water (5 mL) under air. [b] eq. = equivalent to phenylacetylene. [c] The yield was determined by GC with dodecane as an internal standard. [d] No toluene detected by GC analysis when the reaction acted either at R.T. for 24 h or at 40 °C for 12 h. [e] A little toluene detected by GC analysis when the reaction acted either at R.T. for 12 h or at 40 °C for 4 h. TMEDA = tetramethylethylenediamine, TEA = triethylamine, DIPA = diisopropylamine, R.T. = room temperature, N.R. = no reaction, N.F. = target was not be found but another unhoped reaction happened. Quant. = quantitative to phenylacetylene.

# 3. Synthesis of DEBHB monomer precursor



Scheme S1. Synthesis procedure for DEBHB.

# 1,4-Bis(hexyloxy)benzene (1)



Under an air atmosphere, KOH (4.0 g, 71 mmol), and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>•5H<sub>2</sub>O (8.6 g, 35 mmol) were dissolved in water (20 mL) in a 100 mL round-bottom flask with stirring. When the flask was cooled on an ice bath, hydroquinone (3.8 g, 34 mmol) and TBAB (0.5 g, 1.6 mmol) were added. The mixture was stirred until most of the solid had dissolved. Then, 1-bromohexane (10 mL, 71 mmol) and toluene (10 mL) were added, and the mixture was refluxed with vigorous stirring for 48 h. Once complete by TLC analysis, the mixture was allowed to cool to r.t., and the aqueous layer was extracted once with toluene (10 mL). The combined organic layers were washed with brine (40 mL) and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure until the residue solidified. The residue was recrystallized from methanol to give the title compound **1** as white flaky crystals (9.3 g, 97% yield):<sup>[11]</sup> H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 0.93 (t, *J* = 6.8 Hz, 6H), 1.25-1.40 (m, 8H), 1.40-1.50 (m, 4H), 1.78 (tt, *J* = 6.6, 6.8 Hz, 4H), 3.92 (t, *J* = 6.6 Hz, 4H), 6.85 (s, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  = 14.0, 22.6, 25.7, 29.4, 31.6, 68.6, 115.3, 153.2 ppm. EI-MS: m/z (%) 278 (M<sup>+</sup>, 100); HRMS m/z (ESI) calcd for C<sub>10</sub>H<sub>10</sub>NO (M+H)<sup>+</sup>: 278.2246, found 2278.2244.

#### 1,4-Bis(hexyloxy)-2,5-diiodobenzene (2)



Under an air atmosphere, methanol (60 mL) was added to a 250 mL round-bottom flask equipped with a magnetic stirbar and cooled on an ice bath. Iodine monochloride (8 mL, 160 mmol) was added slowly with rapid stirring. Then, **1** (8.4 g, 30 mmol) was added. The mixture was returned to r.t., and then refluxed for 20 h. The mixture was cooled to r.t., and sodium metabisulfite was added portionwise with vigorous stirring until the dark color is gone. The reaction mixture is then portioned between hexanes (50 mL) and water (50 mL). The aqueous layer was extracted with hexanes (100 mL). The combined organic layers were washed with brine (30 mL), and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure. The residue was recrystallized from a mixture of methanol and dichloromethane by evaporation of the dichloromethane to give the title compound **2** as off-white orthorhombic crystals (14.6 g, 91% yield):<sup>[1] 1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 0.92$  (t, J = 6.8 Hz, 6H), 1.33-1.39 (m, 8H), 1.40-1.60 (m, 4H), 1.80 (tt, J = 6.5, 6.8 Hz, 4H), 3.93 (t, J = 6.5 Hz, 4H), 7.18 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta = 14.0$ , 22.6, 25.7, 29.1, 31.4, 70.3, 86.3, 122.7, 152.8 ppm. EI-MS: m/z (%) 530 (M<sup>+</sup>, 100); HRMS m/z (ESI) calcd for C<sub>10</sub>H<sub>10</sub>NO (M+H)<sup>+</sup>: 530.0179, found 530.0175.

# 2,5-Dihexyloxy-1,4-bis[(trimethylsilyl)ethynyl]benzene (3)



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Under a nitrogen atmosphere, to a solution of **2** (7.95 g, 15 mmol), Cul (0.14 g, 0.75 mmol), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.53 g, 0.75 mmol) in both dry THF (100 mL) and degassed piperidine (10 mL) was added (trimethylsilyl)acetylene (TMSA) (2.94 g, 30 mmol). The mixture was stirred at reflux for 1 h. After cooling, dichloromethane (100 mL) was added, and the white ammonium iodide precipitate was filtered off. The solution was passed through a short silica gel column using toluene as eluent. After the solvent was evaporated under reduced pressure, the white crystals **3** were obtained by recrystallization from ethanol (6.72 g, 95% yield):<sup>[2]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 0.25 (s, 18H), 0.88 (t, *J* = 6.6 Hz, 6H), 1.53-1.33 (m, 12H), 1.81-1.76 (m, 4H), 3.93 (t, *J* = 6.6 Hz, 4H), 6.88 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 154.45, 117.75, 114.45, 101.50, 100.43, 69.92, 31.99, 29.70, 26.07, 23.01, 14.43, 0.33. ppm. EI-MS: m/z (%) 470 (M<sup>+</sup>, 100); MP: 91.0-91.5 °C.

## 1,4-diethynyl-2,5-bis(hexyloxy)benzene (DEBHB)



Under an air atmosphere, methanol (30 mL) and KOH (2 mL, 5 N) were added to a stirred solution of 3 (2.82 g, 6 mmol) in THF (20 mL). After the mixture was stirred at r.t. for 2 h, the solvent was evaporated, and the residue was poured into 100 mL of water and extracted with hexane twice. The combined hexane layer was washed with water and brine and dried over anhydrous magnesium sulfate. After the solvent was removed, purification by column chromatography of the mixture gave the pure DEBHB as pale yellow solid (1.82 g, 93% yield):<sup>[2]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 6.95 (s, 2H), 3.97 (t, *J* = 6.6 Hz, 4H), 3.33 (s, 2H), 1.84-1.75 (m, 4H), 1.50-1.26 (m, 12H), 0.90 (t, *J* = 6.6 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 154.43, 118.26, 113.75, 82.75, 80.19, 70.13, 31.90, 29.50, 25.97, 22.96, 14.37 ppm. EI-MS: m/z (%) 326 (M<sup>+</sup>, 100); MP: 71.1-72.0 °C.

## 4. Synthesis and characterizations of poly-DHO-PBD via interfacial reaction

Under an ambient air atmosphere at 30 °C, an aqueous solution (5 mL) of copper(I) sulphate (0.3 M), TMEDA (0.6 M) and potassium acetate (0.3 M) was poured into the glass cylinder (10 mL), subsequently added iodine tablets(>100 eq. to DEBHB). Onto the surface of this solution was sprayed gently the dibutylether solution of DEBHB (10 mg mL<sup>-1</sup>, 30 µL). The screw cap of the cylinder was then closed loosely such that the organic solvent evaporated spontaneously over 3 days, giving yellow-orange poly-DHO-PBD compound. It should be stated that decreasing the reactant concentrations was favorable for the formation of more ordered poly-DHO-PBD micro/nanostructures due to the better synergetic effect of polymerization and assembly (**Figure S1**). When the reactant concentrations were reduced to 1 mg mL<sup>-1</sup>, and even much lower 0.3 mg mL<sup>-1</sup>, crystalline micro/nano-belts/sheets of poly-DHO-PBD with diameters

of tens micrometers could be first obtained along with the occurrence of polymerization and initial assembly process. In this case, when further carefully adding the chloroform/butyl ether mixed solvent, disordered aggregates could be solved and large-scale well-defined poly-DHO-PBD films with typical layer-by-layer growth model were finally obtained (**Figure S2**) under the effect of second-stage "solution-epitaxy" growth where the previously formed micro/nano-belts/sheets worked well as the highly-crystalline seeds and the solvent disordered aggregates as the new solute molecules (**Figure 1d**). The obtained poly-DHO-PBD films were washed for many times, which were then tansferred onto desired substrates for following characterizations and device construction. The detailed experimetal conditions are also summarized in **Table S2**.

Table S2 Three typical reaction conditions tried in experiment for preparation of poly-DHO-PBD.

Entry	CuSO₄ (M)	TMEDA (M)	KOAc (M)	l <sub>2</sub>	Reactant Concentration	Solven t	Temperature
1	0.3 moL L <sup>-</sup> 1	0.6 moL L <sup>-</sup> 1	0.3 moL L <sup>-</sup> 1	10 Particles	10 mg mL <sup>-1</sup>	Dibutyl Ether	30 ℃
2	0.3 moL L <sup>-</sup> 1	0.6 moL L <sup>-</sup> 1	0.3 moL L <sup>-</sup> 1	3 Particles	1 mg mL <sup>-1</sup>	Dibutyl Ether	30 ℃
2	<b>0.1 moL L</b> - 1	0.2 moL L <sup>-</sup> 1	0.1 moL L <sup>-</sup> 1	3 Particles	0.3 mg mL <sup>-1</sup>	Dibutyl Ether	40 ℃



**Figure S1** Camera photos of poly-DHO-PBD products prepared via the advanced Glaser-Hay coupling reaction at air/water interface under a) reactant concentration of 10 mg mL<sup>-1</sup> and b) reactant concentration of 0.3 mg mL<sup>-1</sup>, respectively.



**Figure S2** Optical images of well-defined poly-DHO-PBD films with typical multilayer morphology.



Figure S3 FT-IR spectra of DEBHB crystals (black) and crystalline poly-DHO-PBD films (red).

With regard to monomer DEBHB containing terminal alkynyl, a sharp peak around 2106 cm<sup>-1</sup> can be detected for terminal carbon-carbon triple bond stretching ( $v_{C=H}$ ), and when it occurs to homocoupling that most of terminal alkynyl groups transform to butadiyne linkages (peak of 2200 cm<sup>-1</sup>), this peak of few terminal alkynes as end groups in poly-DHO-PBD backbone was shifting to 2140 cm<sup>-1</sup>. For instance, the very strong stretching vibration of terminal acetyletic carbon-hydrogen ( $v_{C-H}$ ) at 3275 cm<sup>-1</sup> and terminal acetylenic carbon-hydrogen bending vibrations ( $\delta_{C-H}$ ) at both 671 and 646 cm<sup>-1</sup> in monomer DEBHB molecules were nearly weakened and disappeared respectively for poly-DHO-PBD films.



**Figure S4** Chemical structures of other diacetylene monomers investigated in this research (M1-M4 marks) and their corresponding synthesized linear poly(butadiynylene) derivatives (P1-P4 marks).



Figure S5 Optical images of well-defined corresponding poly(butadiynylene) films.



**Figure S6** UV-Vis spectra of diacetylene monomers (M1-M4 marks and black line) and their corresponding poly(butadiynylene)s (P1-P4 marks and red line), confirming the effective interfacial polymerization with formation of extended  $\pi$ -conjugation.



**Figure S7** FT-IR spectra of diacetylene monomers (M1-M4 marks and black line) and their corresponding poly(butadiynylene)s (P1-P4 marks and red line), confirming the effective air/water interfacial polymerization reaction with diagnostic peaks nearly weakened and disappeared in polymers.



**Figure S8** Raman spectra of diacetylene monomers (M1-M4 marks and black line) and their corresponding poly(butadiynylene)s (P1-P4 marks and red line), confirming the effective air/water interfacial polymerization reaction with diagnostic peaks almost completely disappeared in polymers.



**Figure S9** TEM characterizations of poly-PHO-PBD films. (a-c) Bright field images of poly-PHO-PBD films for measurement with the spot diffraction regions marked with red circles. (d-f) The obtained SAED diffraction patterns from different samples, which are identical for different samples.



**Figure S10** (a) A typical SAED pattern obtained for poly-PHO-PBD films, suggesting a systematic extinction induced by the centered symmetry feature of single-crystalline poly-PHO-PBD films. (b) The schematic of full diffraction patterns corresponding to SAED in (a), giving a central symmetric structure.



**Figure S11** Schematic of a conjugated poly-PHO-PBD chain drawn through ChemDraw software. A repeat unit distance calculated is around 9.47 Å based on DFT calculation.



**Figure S12** (a) Molecular packing structure of DEBHB precursor monomers in a unit cell in stick model. For clarity, the hydrogen atoms are deleted here. (b) Ball and stick model of one DEBHB monomer obtained from the single crystal data, giving the distance of C1-C6 of 8.037 Å. Further including one C-C distance, i.e., around 1.2 Å, the periodic length speculated for poly-PHO-PBD chain is around 9.237 Å, which is well consistent with that calculated value based on DFT.

Density functional theory (DFT) calculations are performed at the B3LYP/6-31G(d) level implemented in the Gaussian 09 software<sup>[3]</sup>. The periodic one-dimensional polymer is simulated by a fully optimized structure repeating three minimal units. The periodic length is estimated as 9.47 angstrom, which is well consistent with that with value of around speculated from its DEBHB precursor single crysta data (**Figure S12**).



Figure S13 /-V curves of single-crystalline poly-PHO-PBD film-based vertical electronic device.



**Figure S14** Summary of nine *I-V* curves obtained based on poly-PHO-PBD film-based veritcal electronic devices measured on different samples.

## Movie S1

Large-sized highly-crystalline poly-DHO-PBD films are obtained at the air-water interface under low solution concentration, which can be easily transferred with the tweezers from one culture dish to another culture dish, demonstrating excellent flexibility. The scale bar for each grid on the paper is 0.5 cm.

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