## **Electronic Supplementary Information**

# Two-Dimensional Extended $\pi$ -Conjugated Triphenylene-core Covalent Organic Polymer

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#### **General Methods**

Silica gel (300-400 mesh) was used for column chromatography. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Tetrahydrofuran (THF) and toluene (Tol.) were redistilled under argon and refluxed with Na crumbs. All aqueous solutions were prepared with Milli-Q water

**S2** 

#### Characterization

Mass spectra (MS) were recorded using a Bruker time of flight mass spectrometer coupled with matrix-assisted laser desorption/ionization source (MALDI-TOF). The NMR spectra were acquired on a Bruker AV Spectrometer at 298 K in the solvents indicated. Chemical shifts are expressed in p.p.m. units relative to TMS (0.0 ppm, <sup>1</sup>H). The solid-state <sup>13</sup>C NMR spectra were acquired on Bruker Avance III with 4 mm CP/MAS probe. The functional groups of the products were also characterized by Raman spectroscopy (Hitachi X-plora, 532 nm, 0.1 mW) and Fourier transform infrared spectroscopy (FT-IR, Thermo-Fisher Nicolet Avatar330). The ultraviolet-visible (UV-Vis) absorption spectra in a diffuse reflection mode were recorded on Cary-5000 spectrometer. The X-Ray photoelectron spectrometer (XPS) was carried out on PHI quantum-2000 [Monochromatic Al Ka X-rays (1486.6 eV) operating at 15 kV and 300 W, the base pressure:  $5.0 \times 10^{-8}$  Pa]. The spectra data were analyzed using XPS-Peak software. The argon adsorption/desorption measurements

were performed using a Micromeritics ASAP2020 gas-sorption system. The X-ray diffraction (XRD) data were recorded on a Ultima IV with Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) at a scanning speed of 10° min<sup>-1</sup>. The dynamic light scattering (DLS) analysis was performed on Zetasizer Nano ZS90. Morphology details were examined using field emission scanning electron microscopy (FE-SEM, HITACHI S-4800) and transmission electron microscopy (TEM, Tecnai F30, accelerating voltage: 300 kV). The atomic force microscope (AFM) data were collected on multimode 8 using peak force mode.

**S3** 

#### **Electrochemical tests**

The electrochemical properties of TP-COP/CNT film were evaluated using 2016 coin-type cells assembled with metal lithium as counter/reference electrodes and a solution of 1M LiTFSI-DOL/DME as the electrolyte. The free-standing TP-COP/CNT film (the mass ratio of TP-COP and CNT is 2:1) is punched into a circular disk with a diameter of 14 mm and directly used as the working electrode. The average mass of each electrode ( $\emptyset = 14 \text{ mm}$ ) is ca. 1.0 mg. The electrode is dried at 80 °C overnight in a vacuum oven before the assembly of cells. All the cells are assembled in a glove box with  $[O_2]$ ,  $[H_2O] \leq 1$  ppm. The galavnosatic charge/discharge tests are conducted on LAND cycler (Wuhan Kingnuo Electronic Co., China) with various current loading at ambient temperature. The specific capacities are calculated based on the weight of the TP-COP/CNT films. In comparison, the control experiment

regarding the electrochemical properties of CNT is also evaluated under the similar conditions (the details are shown in S10).

**S4** 

#### **Monomer preparation**

The monomer of TP-COP was synthesized<sup>1</sup> by the following route as shown in Figure S1. The chemical structure and purity of products can be characterized by the MS and NMR spectrometry (see in Figures S2-S6).

913.2 mg (4 mmol) of triphenylene (TP), 90 mg of Fe (1.6 mmol) powder were added into 20 mL of degassed nitrobenzene (Ph-NO<sub>2</sub>) before injecting 4 mL of liquid bromine (Br<sub>2</sub>). The mixture was stirred under an argon atmosphere at 160 °C for 2 hours. The reaction was quenched with diethyl ether, the precipitate was obtained and washed with diethyl ether to yield 2,3,6,7,10,11-hexabromotriphenylene (HBTP) as the white powder (Figure S1). The molecular weight of the HBTP was determined through MALDI-TOF-MS (Figure S2), indicating the successful bromination progress.

701.7 mg (1 mmol) of HBTP. 561.6 mg (0.800)mmol) of bis(triphenylphosphine)palladium(II) dichloride [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], 304.0 mg (1.6 mmol) of cuprous iodide (CuI), 419.2 mg (1.6 mmol) of triphenylphosphine (PPh<sub>3</sub>) and 1.4 mL (10 mmol) of trimethylsilylacetylene [(CH<sub>3</sub>)<sub>3</sub>SiC=CH, TMS-C=CH] were added into 80 mL of triethylamine (Et<sub>3</sub>N) and toluene (Tol.) (v:v = 1:1). The mixture was stirred under argon at 80 °C for 12 hours. When the reaction progress was completed,

the residue was purified by column chromatography to yield 2,3,6,7,10,11-hexa(trimethylsilylethynyl)riphenylene (HTMSETP) as the yellow powder (Figure S1). The structure of the HTMSETP was confirmed by MS and <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.6$  p.p.m. (s, 6H),  $\delta = 0.4$  p.p.m. (s, 54H), which was shown in Figure S4.

107.0 mg (0.13 mmol) of HTMSETP dissolved in 3 mL tetrahydrofuran (THF) was added 1.0 mL tetrabutylammonium fluoride (1 mol L<sup>-1</sup> TBAF in THF, 1.0 mmol) and stirred at room temperature for 50 min. The solution system was then diluted with dichloromethane (DCM), washed with distilled water and dried with anhydrous MgSO<sub>4</sub>. The solvent was removed in a vacuum rotary evaporation to yield raw product (Figure S1). To obtain the purified 2,3,6,7,10,11-hexaethynyltriethylamine (HETP), the raw product was recrystallization using methanol and stored in dark. The molecular weight of HETP was determined through MALDI-TOF-MS (m/z = 371.6) (Figure S5). The structure of HETP was also confirmed by the <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.7 (s, 6H),  $\delta$  = 3.6 (s, 6H) and <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  = 81.4, 82.3, 124.3, 128.4, 128.6 p.p.m., which was shown in Figure S6.

#### **S5**

#### Solution-phase synthesis of bulk TP-COP

The monomer HETP (20 mg) was dissolved in 50 mL of the degassed acetone. Under an argon atmosphere, 10 mL of  $Cu(OAc)_2$ -pyridine complex (10 mmol L<sup>-1</sup> of copper acetate and 10 mmol L<sup>-1</sup> pyridine) aqueous solution was injected into 40 mL degassed acetone. The HETP solution (0.4 mg mL<sup>-1</sup>) was added slowly via syringe pump at a speed of 10 mL h<sup>-1</sup> into above solution. Then the mixture was stirred at 60 °C for 24 hours and protected from light. Then the mixture was washed with hot acetone, DMF, and 20 % HCl (aq.) in turn and a black powder of bulk TP-COP was obtained.

**S6** 

#### Supplemental discussion of bulk TP-COP characterization

The UV-Vis absorption spectroscopy (diffuse reflection mode) was used to characterize the electronic structure of HETP and the as-prepared TP-COP (Figure S8)<sup>2</sup>. As depicted in Figure S8, the wavelength of maximum absorption ( $\lambda_{max}$ ) of monomer HETP was located at 284 nm, while the  $\lambda_{max}$  of the as-prepared TP-COP was red-shifted by 152 nm, indicating the occurrence of cross-coupling reaction.

**S7** 

#### **Exfoliation of bulk TP-COP**

The exfoliation of bulk TP-COP was performed by ultrasonication. Briefly, 10 mg of the bulk TP-COP samples was added into 20 mL of dimethyl formamide (DMF). The mixture was ultrasonically dispersed for 30 min and kept undisturbed overnight. The supernatant of the dispersion was ultrasonicated at a frequency of 20 kHz for 40 min (10 min effective pulse ultrasonication) on cell disruption system. The exfoliated TP-COP (E-TP-COP) nanosheets were well-dispersed in DMF and formed a colloidal solution, which could be proved by Tyndall effect (inset of Figure 2f).

#### **TP-COP** film synthesized by interfacial polymerization

To produce TP-COP films (Figure S14), under an argon atmosphere at room temperature, a DCM solution containing freshly prepared HETP ( $30 \ \mu g \ mL^{-1}$ , 5 mL) was added into a glass cylinder with a diameter of 18 mm. The solution was then covered with pure water (5 mL) such that a two-phase system formed. An aqueous solution (150  $\mu$ L) of catalytic copper acetate-pyridine complex was injected gently to the water. Then the catalytic phase containing  $300 \ \mu$ mol L<sup>-1</sup> of copper salt were formed. The reaction system was kept undisturbed for 24 h in dark, and a pale yellow film of the TP-COP was generated at the interface, which labeled as TP-COP (30-300) film (inset of Figure S17b). The aqueous layer was then replaced with water, and the organic layer was replaced with DCM, in order to remove the unreacted monomer and remainder catalysts. Then the both aqueous and organic phases were removed and the resultant TP-COP (30-300) film was suspended in ethanol. The suspension was cast dropwise on various substrates for further measurement.

From Figure S15a, there were three main peaks presented in Raman spectrum of TP-COP (*30-300*) film, which corresponded to the D band (1366 cm<sup>-1</sup>), G band (1595 cm<sup>-1</sup>), and butadiyne bond (2176 cm<sup>-1</sup>), respectively. Additionally, the vibration signals of butadiyne groups were enhanced via surface-enhanced Raman spectrum (SERS) using gold nanoparticles (inset of Figure S15a)<sup>3</sup>. The FT-IR spectrum of TP-COP (*30-300*) film was displayed in Figure S15b. The almost disappearance of the acetylenic C–H vibration at 3288 cm<sup>-1</sup> could be observed, which proved the

cross-coupling reaction of HETP via interfacial polymerization. Also, in Figure S15c, the C 1s envelope of TP-COP (*30-300*) film can be fitted into four subpeaks of C=C at 284.7 eV, C=C at 285.4 eV, C–O at 287.5 eV and C=O at 288.4 eV, respectively. The XPS data confirmed that the TP-COP (*30-300*) films have both sp<sup>2</sup>- and sp-hybrid carbon, and the area ratio of C=C and C=C is close to 3:2.

The wrinkled film observed from TEM image (Figure S16a) suggested the flexible nature of TP-COP (*30-300*) film. HRTEM image clearly disclosed the lattice fringes of the as-synthesized multilayer TP-COP (*30-300*) film with an interlayer distance of 3.8 Å (Figures S16b-S16c), which was consistent with that of the TP-COP synthesized in solution-phase (Figures 2a and S13c). All characterization methods above confirmed the same structures of the TP-COP samples synthesized by solution polymerization and interfacial polymerization.

The TP-COP films by interfacial polymerization were denoted as TP-COP (*x-y*), where *x* represented *x* µg mL<sup>-1</sup> of HETP in organic phase and *y* represented *y* µmol L<sup>-1</sup> of copper complex in aqueous phase. With adding different amounts of *x* and *y*, the thickness of as-synthesized TP-COP (*x-y*) films can be tuned using interfacial polymerization. As shown in Figure S17, increasing the added amounts of monomer HETP and copper complex to the reaction system, the thicker TP-COP films were consequently produced. The thickness of the as-prepared TP-COP (*x-y*) films could be estimated from AFM analysis. The thickness of the films ranged from 0.9 nm to 56.7 nm according to the increment of *x* and *y* (Figure S17a). The optical microscope (OM) images and SEM images of the TP-COP (*x-y*) films with lateral sizes of up to micrometers were depicted in Figures S17b-S17c.

#### **S9**

#### Solution-phase synthesis of TP-COP/CNT

For preparing the TP-COP/CNT composite, the synthetic procedure was similar to solution-phase synthesis of bulk TP-COP with adding pristine CNT into the reaction system. Typically, the HETP (20 mg) was dissolved in 50 mL of acetone. 8 mg of CNT was dispersed in a solution containing 40 mL degased acetone and 10 mL of  $Cu(OAc)_2$ -pyridine complex aqueous solution (10 mmol L<sup>-1</sup> of copper acetate and 10 mmol L<sup>-1</sup> pyridine). The HETP solution (0.4 mg mL<sup>-1</sup>) was added slowly via syringe pump at a speed of 10 mL h<sup>-1</sup> into above dispersion. Then the mixture was stirred at 60 °C for 24 hours and protected from light. After polymerization and in-situ composition, the product was washed with hot acetone, DMF, and 20 % HCl (aq.) in turn and a black powder of TP-COP/CNT (about 24 mg) was obtained. Therefore, the weight ratio of TP-COP and CNT was about 2:1.

#### **S10**

#### **Electrochemical properties of CNT substrate**

The electrochemical properties of CNT substrate are also examined. Figure S18a shows the cyclic voltammograms (CV) curves of the CNT substrate at a scan rate of  $0.1 \text{ mV s}^{-1}$  within a voltage range of  $0.0 \sim 3.0 \text{ V}$ . Two tiny peaks at  $\sim 1.57 \text{V}/\sim 1.16 \text{V}$  and a board peak at 0.5 V appear successively in the cathodic scan while these peaks are disappeared in the sequent scans, which are ascribed to the continuous formation

of SEI. Besides, a sharp peak near 0 V in the cathodic scan and an obvious peak at ~0.19 V in the reverse are observed, which are attributed to the lithiation/delithiation of CNT. Figure S18b displays the dQ/dV profiles of the CNT substrate for the  $2^{nd}$ ,  $3^{rd}$ , and  $4^{th}$  cycle. One discharge peak (~0.012 V) and the corresponding charge peak (~ 0.07 V) are presented, in accordance with the above CV results. When serving as an anode material for lithium ion battery, as shown in Figure S18c, the CNT substrate delivers a reversible capacity of 522 mAh g<sup>-1</sup> at a current density of 0.1 A g<sup>-1</sup>. Figure S18d displays the rate capability of CNT substrate. The CNT delivers a capacity of ~522, ~399, ~332, ~272, ~226, ~170 at a current loading of 0.1, 0.2, 0.5, 1, 2, 5 A g<sup>-1</sup>, respectively. When return to the current of 0.1A g<sup>-1</sup>, it also gains a capacity of 383 mAh g<sup>-1</sup>. Long-term cycling performance of CNT substrate is also performed. As shown in Figure S18e, the CNT substrate shows a stable cycling performance and displays a capacity of 246 mAh g<sup>-1</sup> at a large current of 1 A g<sup>-1</sup>.



Figure S1 Synthetic route of HETP.



**Figure S2** Mass spectrum of HBTP. The simulated and experimental isotopic distribution patterns of mass peak are represented in red and blue, respectively.



Figure S3 Mass spectrum of HTMSETP. The simulated and experimental isotopic

distribution patterns of mass peak are represented in red and blue, respectively.



**Figure S4** The <sup>1</sup>H NMR spectra of HTMSETP. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.6$ 

 $(s, 6H), \delta = 0.4 (s, 54H).$ 



**Figure S5** Mass spectrum of HETP. The simulated and experimental isotopic distribution patterns of mass peak are represented in red and blue, respectively.



**Figure S6** The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of HETP. <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 8.7$  (s, 6H),  $\delta = 3.6$  (s, 6H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>):  $\delta = 81.4$ , 82.3, 124.3, 128.4, 128.6 p.p.m.



**Figure S7** The FT-IR spectra of HETP and TP-COP. The stretching and bending vibrations of aromatic C–H were located at 3187 and 887 cm<sup>-1</sup>, respectively. Peaks at 1000-1500 cm<sup>-1</sup> may be contributed to the asymmetric stretching mode of C–C bonds.



Figure S8 The UV-Vis spectra of HETP and TP-COP.



Figure S9 The solid-state <sup>13</sup>C NMR spectra of HETP and TP-COP.



Figure S10 (a) The argon adsorption-desorption isotherm of bulk TP-COP, which gives a BET surface area of 241.2 m<sup>2</sup> g<sup>-1</sup>. (b) Micropore and mesopore size distribution curves for TP-COP analyzed Horvath-Kawazoe (HK) and Barrett-Joyner-Halenda (BJH) method, respectively.



Figure S11 The top-view of monolayer and multi-layer TP-COP.  $D_{Multi}$  is

smaller than  $D_{\text{Mono}}$ .



Figure S12 The XRD pattern of the bulk TP-COP.



**Figure S13** The SEM (a), TEM (b), and HRTEM (c-e) images revealed the layered and porous structure of bulk TP-COP. The scale bars in (a-e) indicate a scale of 5  $\mu$ m, 200 nm, 20 nm, 10 nm, and 40 nm, respectively. The boundary of TP-COP layer is marked with the red dashes. The mesopores in TP-COP are marked with blue circles.



Figure S14 The liquid/liquid interfacial polymerization for TP-COP film.



**Figure S15** (a) Raman spectra, (b) FT-IR, and (c) C 1s XPS spectrum of TP-COP (*30-300*) film. The scale bars in (a) indicate a distance of 50 μm. Inset of (a): Raman spectra of bare gold nanoparticle (purple curve) and enhanced signals of TP-COP

(30-300) film (orange curve) via SERS technique.



Figure S16 The TEM (a) and HRTEM (b, c) images of TP-COP (30-300) film. The

scale bars in (a-c) indicate a distance of 1  $\mu m,$  10 nm, and 5 nm, respectively.



**Figure S17** Morphology of the controllable synthesis of the TP-COP (x-y) films. (a) The AFM images of the TP-COP (x-y) films with corresponding height profiles. (b-c) The OM and SEM images of the as-synthesized TP-COP (x-y) films. i-iv represent for TP-COP (10-100) film, TP-COP (20-200) film, TP-COP (30-300) film, and TP-COP (40-400) film, respectively. The scale bars in (a-c) indicate a distance of 5, 25, and 10  $\mu$ m, respectively.



**Figure S18** (a) Cyclic voltammetry curves of the CNT substrate at scan rate of 0.1 mV s<sup>-1</sup> within a potential range of 0-3.0 V. (b) The corresponding dQ/dV curve profiles of the CNT substrate for the  $2^{nd}$ ,  $3^{rd}$ , and  $4^{th}$  cycle. (c) Cycling performance of the CNT substrate at a current of 100 mA g<sup>-1</sup>. (d) Rate capability of the CNT substrate at a current of 0.1, 0.2, 0.5, 1, 2 and 5 A g<sup>-1</sup>, respectively. (e) Long-term cycling of the CNT substrate a large current of 1 A g<sup>-1</sup>.

### **Supplemental References**

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