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### **Supplementary Information**

# In-Situ Synthesis of Electroactive Conjugated Microporous Fullerene Films Capable for Supercapacitive Energy Storage

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### **Supplementary Figures**



**Fig. S1** (a) Side view and (b) top view of the structure of the  $C_{60}$ Me5Th monomer simulated using density of function theory calculations at the B3LYP 6-31G\* level (C, white; S, yellow; H atoms were omitted).



**Fig. S2** (a) Setup of three-electrode electrochemical cell for the polymerisation of monomers to deposit CMP films on ITO, and (b) CV curves of the 1st cycle of chlorobenzene solution of  $C_{60}$ Me5Th in the presence of *n*-Bu<sub>4</sub>NPF<sub>6</sub> as electrolyte (0.1 M) at 25 °C. At the 1st positive scan,  $C_{60}$ Me5Th exhibited onset oxidative potentials at 1.15 V, which were attributed to the oxidation of thiophene units in the monomers. As the bias was higher than this potential, the polymerization occurred between thiophene cation radicals at the 2- and 5-position and yielded cationic networks via radical-radical combination. Therefore, we set the maximum potential at 1.3 V. At the first reduction scan, the peaks observed at 0.29 V were assigned to the reduction of cationic networks. We set the minimum potential as low as -0.2 V to assure the formation of neutral networks.



Fig. S3  $^{13}$ C solid-state MAS NMR spectra of C<sub>60</sub>Me5Th-CMP.



Fig. S4 FT-IR spectra of and  $C_{60}$ Me5Th (black curve),  $C_{60}$ Me5Th-CMP film (red curve) and  $C_{60}$ Me5Th-CMP powder (blue curve).





The films assumed a smooth and homogeneous surface morphology without any large particles or aggregates, as revealed by the SEM image. This smooth morphology originated from two points: (1) The conventional electropolymerization method is uncontrolled with rough film morphology; however by developing controlled electropolymerization method, we could produce porous films with high quality and smooth morphology. (2) The multi-thiophene groups benefit the formation of crosslinked films with uniform structure, thus smoothing the morphology of the films.



Fig. S6 HR-TEM images of the  $C_{60}$ Me5Th-CMP film.



**Fig. S7** (a) Nitrogen sorption isotherm curves collected at 77 K for the  $C_{60}$ Me5Th-CMP powder (solid circles: adsorption, open circles: desorption). (b) Pore size and pore size distribution profiles of the  $C_{60}$ Me5Th-CMP powder. (c) Kr sorption isotherm curves collected at 77 K for the CMP films (solid circles: adsorption, open circles: desorption).



Fig. S8 Absorption spectra of the  $C_{60}$ Me5Th-CMP film and  $C_{60}$ Me5Th spin-coated film.



Fig. S9 (a) Cyclic voltammetry profiles of the 20-nm thick  $C_{60}$ Me5Th-CMP films (red curve) and  $C_{60}$ Me5Th monomer (black curve). (b) HOMO-LUMO levels of the  $C_{60}$ Me5Th-CMP films and  $C_{60}$ Me5Th monomer.



**Fig. S10** CV curves of CMP films with different scan cycles of (a) 10 cycles, (b) 20 cycles and (c) 30 cycles. The CMP films prepared with 10 cycles exhibited the best reversibility.



**Fig. S11** (a) The relation of the monomer concentration and the absorbance, and (b) The relation of the film thickness and the absorbance.

The mass of the CMP film deposited on the ITO or GC electrode is too little to be measured by balance. Thus we estimate the mass by Lambert-Beer's law:

$$A=K \times C \times L$$
 Equation 1

(A: absorbance, K: absorption coefficiency, C: concentration, L: optical length)

For solution samples:

$$A_S = K_S \times C_S (mg ml^{-1}) \times L_S (cm)$$
 Equation 2

The L<sub>S</sub>, equal to the thickness of colorimetric cell, is 1 cm in our experiments.

From Figure S11a we could get

$$K_{\rm S} = 80.25 \text{ ml mg}^{-1} \text{ cm}^{-1}$$

For film samples:

$$A_F = K_F \times C_F (mg ml^{-1}) \times L_F (cm) = K_F \times \rho (g cm^{-3}) \times D (nm)$$
 Equation 3

(p: film density, D: film thickness)

From Figure S11b we could get

$$K_{\rm F} \times \rho \,({\rm g}\,{\rm cm}^{-3}) = 0.00163 \,{\rm nm}^{-1}$$

We suppose that the change of absorption coefficiency of C<sub>60</sub> after polymerization is negligible,

$$K_F = K_S = 80.25 \text{ ml mg}^{-1} \text{ cm}^{-1}$$

Finally we get the  $\rho$  value

$$\rho$$
=0.00163 nm<sup>-1</sup>/ 80.25 ml mg<sup>-1</sup> cm<sup>-1</sup>=0.2031g cm<sup>-3</sup>

With the density of the CMP film, the mass of a 26.3 nm-thick film is calculated to be

m= 0.2031 g cm<sup>-3</sup> × 26.3 nm × 1 cm<sup>2</sup>= 0.5342  $\mu$ g.



Fig. S12 The cathodic CV peak currents and anodic CV peak currents at different scan rates (acetonitrile as solvent, 0.1 M TBAAsF<sub>6</sub> as electrolyte).



Fig. S13 The Bode spectra of the CMP pseudocapacitors.



**Fig. S14** The equivalent circuits of the impedance spectra of CMP films under (a) open circuit potential, (b) oxidation potential of PTh, and (c) reduction potential of  $C_{60}$ . (The parameter of the equivalent circuits see Table S3).



**Fig. S15** The capacitive properties of the CMP films as a capacitor in the two-electrode system (0.1 M TBAAsF<sub>6</sub>/acetonitrile as the electrolyte system). (a) Galvanostatic charge–discharge curves at different current densities. (b) The mass specific capacitance at different current densities. (c) The self discharge curve of the two-electrode capacitor.



Fig. S16 Cycling stability of CMP films upon charging/discharging at a current density of 30 A g<sup>-1</sup>.



**Fig. S17** (a) CV curves of  $PC_{60}$  pseudocapacitors at different scan rates, (b) impedance spectra of  $PC_{60}$  films, (c) galvanostatic charge–discharge curves at different current densities, and (d) capacitance at different current densities.

## Supplementary Tables

| Compounds                 | Wavenumber (Strength) | Assignment                                 |  |  |  |
|---------------------------|-----------------------|--|--|--|--|
|                           | 1792 (w)              | C=C stretching hand of henzene             |  |  |  |
| C <sub>60</sub> Me5Th-CMP | 1592 (w)              |  |  |  |  |
|                           | 1435 (w)              | - C-C stratching hand of this hand         |  |  |  |
|                           | 1229 (w)              | C-C stretching band of thiophene           |  |  |  |
|                           | 1158 (m)              | C-C vibration band of thiophene            |  |  |  |
|                           | 1051 (s)              |  |  |  |  |
|                           | 971 (s)               | C-H deformation band of thiophene (3-H)    |  |  |  |
|                           | 774 (m)               | C-H deformation band of benzene            |  |  |  |
|                           | 697 (w)               | C-S stretching band of thiophene           |  |  |  |
|                           | 470 (s)               | C-H deformation band of thiophene (3-H)    |  |  |  |
|                           | 1801 (w)              |  |  |  |  |
|                           | 1590 (s)              | C=C stretching band of benzene             |  |  |  |
|                           | 1445 (s), 1414 (s)    |  |  |  |  |
|                           | 1236 (s), 1190 (m)    | C=C stretching band of thiophene           |  |  |  |
|                           | 1088 (w)              | C-C vibration band of thiophene            |  |  |  |
| C <sub>60</sub> Me5Th     | 1036 (m)              |  |  |  |  |
|                           | 940 (w)               | C-H deformation band of thiophene (3-H)    |  |  |  |
| Monomer                   | 870 (s)               | C-H vibration band of benzene              |  |  |  |
|                           | 851 (s)               |  |  |  |  |
|                           | 824 (s)               | C-H deformation band of thiophene (2-H)    |  |  |  |
|                           | 753 (s), 728 (s)      | C-H deformation band of benzene            |  |  |  |
|                           | 700 (s)               | C-S stretching vibration band of thiophene |  |  |  |
|                           | 611 (m)               | C-H deformation band of thiophene (2-H)    |  |  |  |
|                           | 492 (w)               | C-H deformation band of thiophene (3-H)    |  |  |  |

Table S1 Assignment of IR bands of the  $C_{60}Me5Th$ -CMP films and the monomer

| Porosity              |                | Band gap |                 |                  |                          |                          |                    |                    |                    |
|-----------------------|----------------|----------|-----------------|------------------|--------------------------|--------------------------|--------------------|--------------------|--------------------|
| CMD film              | Surface        | Pore     | Pore            | Optical band gap |                          | Electrochemical band gap |                    |                    |                    |
|                       | area           | size     | volume          | $\lambda_{\max}$ | $\lambda_{\text{onset}}$ | Egopt                    | НОМО               | LUMO               | EgEC               |
|                       | $[m^2 g^{-1}]$ | [nm]     | $[cm^3 g^{-1}]$ | [nm]             | [nm]                     | [eV] <sup>a)</sup>       | [eV] <sup>b)</sup> | [eV] <sup>b)</sup> | [eV] <sup>c)</sup> |
| C <sub>60</sub> Me5Th | 605            | 0.6      | 0.66            | 224              | 675                      | 1.04                     | 5.62               | 2 74               | 1 00               |
| СМР                   | 093            | 0.0      | 0.00            | 334              | 075                      | 1.64                     | -3.02              | -3.74              | 1.00               |
| C <sub>60</sub> Me5Th |                |          |                 | 202              | 501                      | 2.12                     | 5 70               | 2.50               | 2.20               |
| monomer               |                |          |                 | 282              | 581                      | 2.13                     | -3./8              | -3.50              | 2.28               |

Table S2 Porosity, optical, and electrochemical properties of the CMP films and monomer

<sup>a)</sup>  $E_g^{opt}$  was estimated from the onset of UV-vis spectra. <sup>b)</sup> HOMO and LUMO levels were estimated from the onset of the oxidation and reduction peaks of CV profile. <sup>c)</sup>  $E_g^{EC}$  was determined by CV.

| (a) | Rs (ohm)   | 0.89 |  |
|-----|------------|------|--|
|     | Rct1 (ohm) | 54   |  |
| (b) | Rs (ohm)   | 1    |  |
|     | Rct1 (ohm) | 53   |  |
|     | Rct2 (ohm) | 1601 |  |
| (c) | Rs (ohm)   | 0.9  |  |
|     | Rct1 (ohm) | 54   |  |
|     | Rct2 (ohm) | 869  |  |

**Table S3** The parameter of the equivalent circuits (acetonitrile as solution and  $TBAAsF_6$  as electrolyte). (a) open circuit potential. (b) oxidation potential of PTh. (c) reduction potential of  $C_{60}$ .

#### **Supplementary Materials and Methods**

**Chemicals.** *n*-Tetrabutylammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>, 98%) and *n*-tetrabutylammonium hexafluoroarsenate (*n*-Bu<sub>4</sub>NAsF<sub>6</sub>, 99%) were purchased from Alfa Aesar and were recrystallized twice and dried for 24 h under vacuum before use. The other reagents were obtained commercially and used as received. Toluene and THF were dried by distillation from sodium. 1,2-Dichlorobenzene and chloroform were dried by sodium hydride.

Synthesis of C<sub>60</sub>Me5Th. C<sub>60</sub>Me5Th was synthesized according to Scheme S1.



Scheme S1. Schematic of the synthesis of  $C_{60}$ Me5Th.

**3-(4-bromine-phenyl)-thiphene (1).** This compound was prepared according to the procedure previously reported.<sup>[S1]</sup> A mixture of 1-bromo-4-iodobenzene (1.10 g, 3.90 mmol), 3-thiopheneboronic acid (0.50 g, 3.90 mmol), tetrakis(triphenylphosphine)palladium (158.0 mg, 0.137 mmol), K<sub>2</sub>CO<sub>3</sub> (2.70 g, 19.5 mmol), toluene (10 mL), THF (10 mL), and water (5 mL) was heated at 85 °C for 20 h under Ar. After cooling to room temperature, CHCl<sub>3</sub> and water were added to the reaction mixture and the organic phase was dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure. The residue was passed a silica-gel column chromatography by using a mixture of petroleum ether and CH<sub>2</sub>Cl<sub>2</sub> (5/1 v/v) as eluent to give 760 mg (3.18 mmol, 82% yield) of **1** as colorless powder. <sup>1</sup>H NMR (ppm, CDCl<sub>3</sub>, 600 MHz, 25 °C):  $\delta$  7.53 (d, 2H, Ar-H),  $\delta$  7.46 (d, 2H, Ar-H),  $\delta$  7.45 (d, 1H, C-H),  $\delta$  7.40 (m, 1H, C-H),  $\delta$  7.36 (d, 1H, C-H).

C<sub>60</sub>Me5Th. This compound was prepared according to the reported procedure.<sup>[S2]</sup> A solution of 1

(573.6 mg, 12.4 mmol) in 8 mL of THF was added slowly to the solution of magnesium chips (60 mg, 2.5 mmol) in 2 ml THF, then stirred at room temperature for 3 h. Then the copper bromide dimethyl sulfide complex (512 mg, 2.5 mmol) was added. After stirring for 10 minutes, a solution of  $C_{60}$  (144 mg, 0.2 mmol) in 10 mL of 1,2-dichlorobenzene was added slowly. The mixture was stirred at room temperature. After 24 h the 1.24 ml (20 mmol) of iodomethane was added to the system and then stirred for 7 h at room temperature. The reaction was quenched by adding 0.1 M NH<sub>4</sub>Cl saturated solution. The mixture was filtered through a pad of silica gel (CH<sub>2</sub>Cl<sub>2</sub> as eluent). The concentrated residue was purified by flash column chromatography using a mixture of petroleum ether and CH<sub>2</sub>Cl<sub>2</sub> (5/1 v/v) as eluent, and then isolated by HPLC (toluene as eluent) to give 215 mg of  $C_{60}$ Me5Th in a yield of 70%. This product could also be synthesised in gram scale with the yield of 60-65%.

<sup>1</sup>H NMR (ppm, CDCl<sub>3</sub>, 600 MHz, 25 °C): δ 7.91 (d, 5H, C-H), δ 7.80 (d, 5H, C-H), δ 7.60 (m, 10H, Ar-H), δ 7.51 (s, 5H, C-H), δ 7.43 (m, 10H, C-H), δ 1.61 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (ppm, CDCl<sub>3</sub>, 600 MHz, 25 °C): 159.18, 156.15, 152.00, 150.71, 147.78, 146.85, 144.71, 143.82, 142.76, 141.82, 140.47, 137.48, 135.77, 134.37, 129.38, 128.35, 127.68, 125.89, 125.57, 125.22, 119.68, 61.35, 59.87, 57.01, 28.68. MS (MALDI-TOF, SIN): m/z: cal.: 1531.16; found: 1531.44.

**Methods.** <sup>1</sup>H and <sup>13</sup>C NMR were recorded using a Bruker AVANCE HD III 600M spectrometer operating in deuterated chloroform solution at 298 K. Chemical shifts were reported as  $\delta$  values (ppm) relative to an internal tetramethylsilane (TMS) standard. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Electrochemical experiments were performed on a CHI 760D electrochemical workstation. FT-IR spectra were measured using an IFS 66V/S Fourier transform infrared spectrophotometer. The film thickness was measured on a Veeco dektal150 profilometer. HR-TEM experiments were performed on a TEM JEOL 2100F with an acceleration voltage of 300 kV. N<sub>2</sub> sorption isotherm measurements were performed on micromeritics@model ASAP2020M at 77 K. HPLC experiments were performed on LC-9130 liquid chromatograph.

Synthesis of CMP films. The C<sub>60</sub>Me5Th-CMP films were synthesized by electropolymerization of C<sub>60</sub>Me5Th (0.8 mg mL<sup>-1</sup>) in a three-electrode system using glassy carbon or ITO as the working electrodes, a titanium plate as the counter electrode, and an Ag/Ag<sup>+</sup> as the reference electrode; a

mixture of chlorobenzene and acetonitrile (4/1 v/v) containing TBAAsF<sub>6</sub> was used as the electrolyte (0.1 M), and the electropolymerization was conducted using multicycle cyclic voltammetry in the potential range from -0.2 to 1.3 V, whereas the film thickness was controlled by regulating the number of cycles. After polymerization, the films were washed with acetonitrile to remove the unreacted monomers and doped electrolytes. The films were subsequently dried under flowing  $N_2$  and stored under  $N_2$  in the dark.

For the infrared spectroscopy (IR) and high-resolution transmission electron microscopy (HR-TEM), the CMP films were prepared on ITO by electrolysis of the monomer for 200 s at 1.3 V, followed by the application of a potential at -0.2 V for another 200 s to neutralize the cationic species. After polymerization, the films were washed with acetonitrile to remove the unreacted monomers and doped electrolytes. The films were subsequently dried under flowing N<sub>2</sub> and stored under N<sub>2</sub> in the dark. This method yields micrometer-thick films that can easily peel off electrodes to form freestanding films with sufficient mass for analysis.

Synthesis of  $C_{60}$ Me5Th-CMP powders. The  $C_{60}$ Me5Th-CMP powders were synthesized by the oxidative coupling polymerization as reported by the literature.<sup>[S3]</sup>  $C_{60}$ Me5Th (150 mg, 0.098 mmol) was dissolved in 20 mL of anhydrous chloroform and then transferred dropwise to a suspension of ferric chloride (410 mg, 2.53 mmol) in 20 mL of anhydrous chloroform. The solution mixture was stirred at room temperature for 1 d under nitrogen protection. Then 100 mL of methanol was added to the above reaction mixture to quench the reaction. The resulting mixture was kept stirring for another hour and the precipitate was collected by filtration. After washed with methanol, the obtained solid was stirred vigorously in hydrochloric acid solution (37 %) for 2 h. The suspension was then filtered and washed with water and methanol (50 mL × 3, respectively). After extracted in a Soxhlet extractor with methanol for 24 h, and then with tetrahydrofuran for another 24 h, the desired polymer was collected (93% in yield) and dried at 110 °C under vacuum overnight.

### **Supplementary References**

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