## **Supporting Information for**

## Two-dimensional C<sub>60</sub> nano-meshes via crystal transformation

Yilong Lei,<sup>a,#</sup> Shaoyan Wang,<sup>a,#</sup> Zhuangchai Lai,<sup>b</sup> Xin Yao,<sup>a</sup> Yanli Zhao,<sup>a</sup> Hua Zhang,<sup>b</sup> Hongyu Chen<sup>\*a,c,</sup>

<sup>a</sup>Division of Chemistry and Biological Chemistry, School of Physical & Mathematical

Sciences, Nanyang Technological University, 21 Nanyang Link, 637371, Singapore

<sup>b</sup>School of Materials Science and Engineering, Nanyang Technological University, 50

Nanyang Avenue, 639798, Singapore

<sup>c</sup>Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech

University, 30 Puzhu South Road, Nanjing 211816, China

\*E-mail: hongyuchen@ntu.edu.sg.

<sup>#</sup>These authors contributed equally to this work.

## **Experimental details**

**Materials.**  $C_{60}$  was purchased from Sigma-Aldrich, and used without further treatment.  $CCl_4$  (A.R.), *m*-xylene (A.R.) and isopropanol (IPA, A.R.) were purchased from Beijing Chemical Agent Ltd., China. 1,2,4-trimethylbezene and 1,2,4-trichlorobenzene were purchased from Sigma-Aldrich and were used as received.

Synthesis of C<sub>60</sub> crystals including rods and plates by mixing IPA and C<sub>60</sub> stock solutions. In a typical synthesis, IPA was dropwise injected into a stock solution of C<sub>60</sub> in CCl<sub>4</sub>/*m*-xylene mixture (1 mM, 2 mL) with gentle swirling until the purple C<sub>60</sub> solution turned into turbid suspension. And then, the mixture was kept undisturbed for 10 min, afterwards dark brown precipitation was formed. When the initial solvent ratio (CCl<sub>4</sub>/*m*-xylene) was between 0:10 and 4:6 (v/v), only rods were obtained (Fig. 1c, 2a); when the ratio was between 6:4 and 10:0 (v/v), only plates (Fig. 1b, 2c); at 5:5 ratio, a mixture of plates and rods formed (Fig. 2b). The added IPA amount was dependent on the initial solvent ratio of the preparative solution, as shown in Table 1. Especially, it was set to 2 mL for 0:10 rods and 1 mL for 10:0 plates, respectively.

Crystal transformation of the C<sub>60</sub> rods and plates obtained from CCl<sub>4</sub>/*m*-xylene mixtures. The above C<sub>60</sub> crystal samples were concentrated by centrifugation at 1000 rpm and then remained in 0.3 mL of supernatant, and finally dispersed in 3 mL of transformative solution (2.7 mL IPA and 0.3 mL of supernatant) for crystal transformation.

During the transformation process of  $C_{60}$  crystals from 6:4 plates to mesh networks, the residue *m*-xylene content in the transformative solution would be an important factor for the formation of  $C_{60}$  mesh network. As a typical example, the residue CCl<sub>4</sub> and *m*-xylene in the solution was estimated to be around 4% and 2.7% v/v, respectively.

Especially, we choose the ratio of  $CCl_4/m$ -xylene = 6:4 (v/v) in stock solution as an example to clarify the detailed calculation process of the solvent ratio of  $CCl_4/m$ -

xylene/IPA (v/v/v) in transformative solution, which is shown as follow:

Firstly, the CCl<sub>4</sub>/*m*-xylene mixture with v/v = 6:4 (2 mL) is set as a stock solution. Considering that ratio of CCl<sub>4</sub> in stock solution is 60% and its corresponding volume should be 2 mL × 60% = 1.2 mL. While ratio of *m*-xylene in stock solution is 40% and its corresponding volume should be 2 mL × 40% = 0.8 mL. Then, the stock solution was diluted by 1 mL IPA to achieve C<sub>60</sub> crystals. The resultant solution was regarded as a preparative solution.

Thus, the solvent ratio of CCl<sub>4</sub>/*m*-xylene/IPA (v/v/v) in the preparative solution =  $\frac{V_{CCl_4}}{V_{stock} + V_{IPA}} : \frac{V_{xylene}}{V_{stock} + V_{IPA}} : \frac{V_{IPA}}{V_{stock} + V_{IPA}} = \frac{1.2 \text{ mL}}{2 \text{ mL} + 1 \text{ mL}} : \frac{0.8 \text{ mL}}{2 \text{ mL} + 1 \text{ mL}} : \frac{1.0 \text{ mL}}{2 \text{ mL} + 1 \text{ mL}} = 6:4:5$ 

Next, the preparative solution was centrifuged and 0.3 mL supernatant was remained. Finally, 0.3 mL supernatant was dispersed in 2.7 mL IPA and the resultant solution was regarded as a transformative solution.

Ratio of CCl<sub>4</sub> in transformative solution =  $\frac{V_{CCl4}}{V_{total}} = \frac{0.3 \text{ mL} \times \frac{V_{CCl4}}{V_{stock} + V_{IPA}}}{2.7 \text{ mL} + 0.3 \text{ mL}} = 4.0\%$ Ratio of *m*-xylene in transformative solution =  $\frac{V_{xylene}}{V_{total}} = \frac{0.3 \text{ mL} \times \frac{V_{xylene}}{V_{stock} + V_{IPA}}}{2.7 \text{ mL} + 0.3 \text{ mL}} = 2.7\%$ Ratio of IPA in transformative solution =  $\frac{V_{IPA}}{V_{total}} = \frac{2.7 \text{ mL} \times \frac{V_{IPA}}{V_{stock} + V_{IPA}}}{2.7 \text{ mL} + 0.3 \text{ mL}} = 93.3\%$ Thus, the final solvent ratio of CCl<sub>4</sub>/*m*-xylene/IPA (v/v/v) in transformative solution is 4.0:2.7:93.3.

The molar ratio of the incorporated solvent to  $C_{60}$  for  $C_{60}$  crystals at different  $CCl_4/m$ -xylene ratios was determined by thermal gravimetric analysis (TGA) performed in a nitrogen atmosphere. It can be expected that two stages of solvent loss should be included in the  $C_{60}$  solvate crystals, namely, the removal of the solvent molecules at lower temperatures and the subsequent sublimation of the  $C_{60}$  matrix at higher temperatures. In view of the possible overlap between the two processes, we first performed the TGA analysis for a pure  $C_{60}$  sample under similar experimental conditions, as shown in Fig. S4a. It is obvious that the raw  $C_{60}$  powder starts to lose weight at a temperature of 420 °C, suggesting that the weight loss of the  $C_{60}$  solvate

crystals below this temperature is due to the removal of solvent molecules. By means of this temperature as a reference point, we have examined the solvent content incorporated within the C<sub>60</sub> crystal. It can be determined that the 10:0 plates contained 4.0% w/w CCl<sub>4</sub> (Fig. S4c), whereas the 0:10 rods contained 9.3% w/w *m*-xylene (Fig. S4b). Accordingly, the molar ratio of CCl<sub>4</sub> to C<sub>60</sub> and *m*-xylene to C<sub>60</sub> in the two C<sub>60</sub> crystals is estimated to be 1:5 and 2:3, respectively. Meanwhile, TGA data of 6:4 plates showed two stages of solvent loss, about 2.2% and 8.3% w/w, respectively (Fig. S4d).

Synthesis of crossed  $C_{60}$ ·trimethylbezene-based nano-meshes. Crossed  $C_{60}$ ·trimethylbezene-based nano-meshes were achieved following similar experimental procedures to the synthesis of  $C_{60}$ ·xylene-based nano-meshes except the initial solvent ratio (CCl<sub>4</sub>/1,2,4-trimethylbezene) was 8:2.

Synthesis of multi-layer hexagonal C<sub>60</sub> nano-meshes by using C<sub>60</sub> crystals formed in CCl<sub>4</sub>/IPA mixture as the initial plates. The 10:0 C<sub>60</sub> crystals with *fcc* phase were first formed in CCl<sub>4</sub>/IPA mixture using above experimental procedures. And then, the *fcc* plates were separated by centrifugation at 1000 rpm and washed one time with IPA. The freshly prepared C<sub>60</sub> plates were mixed with 200  $\mu$ L of a saturated supernatant of 0:10 C<sub>60</sub> rods formed in *m*-xylene/IPA mixture as the transformative solution, and the mixtures were allowed to stand for 10 min.

Synthesis of multi-layer hexagonal C<sub>60</sub> nano-meshes by using C<sub>60</sub>/ferrocene crystals obtained at toluene/IPA interface as the initial plates. The C<sub>60</sub>/ferrocene crystals were formed at toluene/IPA interface following the previous reported experimental procedures and were heated at 120 °C for 15 min to remove the excess ferrocene.<sup>1</sup> And then, the resulting *fcc* plates were mixed with 200  $\mu$ L of a saturated supernatant of C<sub>60</sub> rods formed in *m*-xylene/IPA mixture as the transformative solution, and the mixtures was allowed to stand for 10 min.

Synthesis of rhombic C60 nano-meshes by using C60 trichlorobenzene crystals

formed in 1,2,4-trichlorobenzene/IPA mixture as the initial plates. The rhombic  $C_{60}$ -trichlorobenzene crystals were obtained following similar experimental procedures to the synthesis of  $C_{60}$  plates formed in CCl<sub>4</sub>/IPA mixture. After that, the  $C_{60}$ -trichlorobenzene plates were separated by centrifugation at 1000 rpm and washed one time with IPA. The freshly prepared  $C_{60}$  plates were heated at 120 °C for 30 min to remove the incorporated 1,2,4-trichlorobenzene solvent. Finally, the *fcc* plates were mixed with 200 µL of a saturated supernatant of  $C_{60}$  rods formed in *m*-xylene/IPA mixture as the transformative solution, and the mixtures were allowed to stand for 10 min.

Characterization. The morphologies and sizes of the samples were examined using field-emission scanning electron microscopy (FESEM, JEOL 7600F) at an acceleration voltage of 5 kV. Prior to analysis, the samples were coated with a thin gold layer using an Edwards Sputter Coater. TEM images were obtained using a JEOL JEM-2100 electron microscope at an accelerating voltage of 200 kV. One drop of the as-prepared colloidal dispersion was deposited on a carbon-coated copper grid, and dried under high vacuum. The powder X-ray diffraction (XRD) patterns were measured by a D/max 2400 X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =1.54050 Å) operated in the 2 $\theta$  range from 3 to 30°, by using the samples spin-coated on the surface of a quartz substrate. Fourier transform infrared (FTIR) spectra were performed on Nicolet AVATAR 360 FT-IR spectrophotometer. The micro-Raman studies were measured under ambient conditions using 514.5 nm Ar ion excitation source. Thermogravimetric (TGA) curve was obtained using a STA 499 C Jupiter (NETZSCH) thermogravimetry analyzer. <sup>1</sup>H NMR spectra were measured on a Bruker BBFO-400 spectrometer. To obtain the average pore size of a nano-mesh and the width of the aligned rods, 60 and 80 samples were measured by the software of Nano Measurer 1.2, respectively. Then, the average values were exported from the reports. For the pore size, we measured the height of triangle or parallelogram. On the other hand, the width of the rod was collected by measuring the vertical distance between two opposite parallel lines of the rod in TEM image.

(1) Wakahara, T.; Sathish, M.; Miyazawa, K.; Hu, C. P.; Tateyama, Y.; Nemoto, Y.; Sasaki, T.; Ito, O. *J. Am. Chem. Soc.* **2009**, *131*, 9940–9944.

## **Supporting Figures:**



**Fig. S1. TEM images of C**<sub>60</sub> **crystals synthesized at different CCl**<sub>4</sub>/*m*-**xylene ratio.** TEM images of C<sub>60</sub> crystals synthesized at different CCl<sub>4</sub>/*m*-xylene ratio (a, 3:7; b, 5:5; c, 8:2; d, 6:4) before crystal transformation.



Fig. S2. SEM images of C<sub>60</sub> rods synthesized at different CCl<sub>4</sub>/*m*-xylene ratio. SEM images of C<sub>60</sub> rods synthesized at different  $CCl_4$ /*m*-xylene ratio (a, b, 0:10; b, d, 1:9), before (a, c) and after washing by IPA (b, d).



Fig. S3. SEM images of C<sub>60</sub> crystals formed by evaporating small aliquots of the precipitate solutions. SEM images of C<sub>60</sub> crystals formed by evaporating small aliquots of the precipitate solutions at different  $CCl_4/m$ -xylene ratio (a, b, 6:4; c, d, 3:7) in air.



**Fig. S4. The average pore size of a nano-mesh and the width of the aligned rods.** (a) The average pore size of mesh is around 330 nm, and (b) the width of the rods from the mesh network is about 650 nm.



**Fig. S5. TGA characterization of C60 crystals.** TGA curves of (a) c<sub>60</sub> powder and (b-d) crystals involving (b) 0:10 rods, (c) 10:0 plates, and (d) 6:4 plates.

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**Fig. S6. FT-IR spectra of C**<sub>60</sub> **crystals.** FT-IR spectra of C<sub>60</sub> crystals involving (black) 10:0 plates, (red) 0:10 rods, (blue) 6:4 plates, and (cyan) mesh networks.



Fig. S7. <sup>1</sup>H NMR spectra of C<sub>60</sub> crystals. <sup>1</sup>H NMR spectra of C<sub>60</sub> crystals involving (pink) 0:10 rods, (cyan) 6:4 plates, and (blue) mesh networks. The blue and red dashed boxes show the corresponding <sup>1</sup>H NMR peaks originated from -CH- and -CH<sub>3</sub> groups of *m*-xylene, respectively.

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Fig. S8. Enlarged SEM image of the out-of-plane vertical rods on the mesh networks. Enlarged SEM image of the 6:4 plates after 4 rounds of washing were transferred to an IPA solution with 2% v/v *m*-xylene for 30 min. The dashed lines highlight the orientation of the horizontal rods.

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**Fig. S9. Crystal transformation of 5:5** C<sub>60</sub> **plates.** SEM images of C<sub>60</sub> mesh networks at (a and c) low- and (b and d) high-magnification formed by transferring the 5:5 plates after 4 rounds of washing into an IPA solution with *m*-xylene (1% v/v) for 24 h.



Fig. S10. Crystal transformation of C<sub>60</sub> plates obtained from CCl<sub>4</sub>/IPA mixture after solvent washing. SEM images of C<sub>60</sub> plates obtained in (a and b) CCl<sub>4</sub>/IPA mixture; (c and d) after 4 rounds of washing; the washed plates of c and d were transferred into IPA solutions (e and f) with *m*-xylene (1% v/v); and (g and h) with *m*-xylene (2% v/v) for 24 h.



Fig. S11. Crossed C<sub>60</sub>-trimethylbezene-based nano-meshes formed by crystal transformation. SEM images of C<sub>60</sub> crystals synthesized at  $CCl_4/1,2,4$ -trimethylbezene = 8:2 before (a) and after crystal transformation (b and c).



Fig. S12. Rhombic C<sub>60</sub> nano-meshes formed by using C<sub>60</sub>•trichlorobenzene crystals as the initial plates. SEM images of C<sub>60</sub> crystals obtained in 1,2,4trichlorobenzene/IPA mixture (a); the C<sub>60</sub> trichlorobenzene plates after heat treatment were mixed with a saturated supernatant of C<sub>60</sub> rods formed in *m*-xylene/IPA mixture (b and c) for a few minutes.