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Supplementary Information for

A Facile Liquid/Liquid Interface Method to Synthesize Graphyne Analogs

Yuwei Song,[a] Xiaodong Li,[b] Ze Yang,*[b] Jing Wang,[a,b] Chunyue Liu,[a] Chipeng Xie,[b,c] Huanlei Wang*[a] and Changshui Huang*[a,b]

[a]School of Material Science and Engineering, Ocean University of China. No. 238 Songling Road, 266100, Qingdao, China.

E-mail: huanleiwang@ouc.edu.cn

[b]Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences. No. 189 Songling Road, 266101, Qingdao, China.

E-mail: yangze@qibebt.ac.cn; huangcs@qibebt.ac.cn

[c]School of Chemistry and Chemical Engineering, Hunan University of Science and Technology. No. 2 Taoyuan Road, 411201, Hunan, China.

General information

Tetrahydrofuran (THF) was dried by distillation over sodium/benzophenone. Tetrabutylamonium fluride (TBAF), trans-dichloro-bis(triphenyl-phosphine) Palladium (II) ($Pd(PPh_3)_2Cl_2$), tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) and other reagents were purchased from Acros Organics and used without further purification. Morphology details were examined using field emission scanning electron microscopy (FESEM, HITACHI S-4800) and transmission electron microscopy (TEM, HITACHI H-7650). The chemical structure of the products was characterized by Fourier transform infrared spectroscopy (FT-IR, Thermo-Fisher Nicolet iN10) and Raman spectroscopy (Thermo Scientific DXRxi, 532 nm). The X-Ray photoelectron spectrometer (XPS) was collected on VG Scientific ESCALab 220i-XL X-Ray photoelectron spectrometer, using Al K radiation as the excitation sources.

Preparation of 1,3,5-triacetylenylbenzene

Trimethylsilylacetylene (20 mL) dissolved in the THF reacts with 56 mL n-butyllithium at -78℃. After stirring for 30 minutes, 20g zinc chloride is added into the solution at low temperatures. After stirring for one hour in an argon atmosphere, the solution is added with 1g $Pd(PPh_3)_4$ and 9.6 g 1,3,5-tribromobenzene dissolved in the THF. The entire apparatus is allowed to react for 72 h at 80 ℃. Tris[(trimethylsilyl)ethynyl] benzene was prepared follow the reported method.[1,2]

Synthesis of H-GY

The 200 mg 1,3,5-triacetylenylbenzene which has been deprotected is dissolved even in the dichloromethane (CH_2Cl_2) solvent under the stirring of the glass rod.[2] Adding pure water along the wall of the instrument to form an aqueous layer. We add 150 mg $Pd(PPh_3)_2Cl_2$, 30 mg cuprous iodide and 420 mg 1,3,5-tribromobenzene into solution. The solution is dissolved as much as possible by a series of treatments such as stirring and ultrasound. The above solution was added dropwise slowly into the aqueous phase. The entire apparatus is allowed to react for 72 h at room temperature.

Synthesis of Me-GY:

The 200 mg 1,3,5-triacetylenylbenzene which has been deprotected is dissolved even in CH_2Cl_2 solvent under the stirring of the glass rod. Adding pure water along the wall of the instrument to form an aqueous layer. We add 150 mg $Pd(PPh_3)_2Cl_2$, 30 mg cuprous iodide and 476 mg 1,3,5- tribromo- 2,4,6 -trimethylbenzene into solution. The solution is dissolved as much as possible by a series of treatments such as stirring and ultrasound. The above solution was added dropwise slowly into the aqueous phase. The entire apparatus is allowed to react for 72 h at room temperature.

Synthesis of F-GY:

The 200 mg 1,3,5-triacetylenylbenzene which has been deprotected is dissolved even in CH_2Cl_2 solvent under the stirring of the glass rod. Adding pure water along the wall of the instrument to form an aqueous layer. We add 150 mg $Pd(PPh_3)_2Cl_2$, 30 mg cuprous iodide and 492 mg 1,3,5-tribromo-2,4,6-trifluorobenzene into solution.[3] The solution is dissolved as much as possible by a series of treatments such as stirring and ultrasound. The above solution was added dropwise slowly into the aqueous phase. The entire apparatus is allowed to react for 72 h at room temperature.

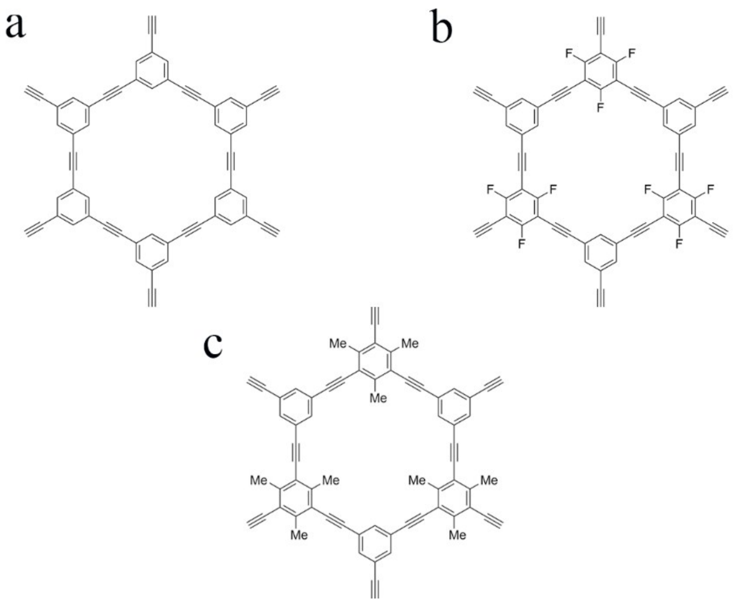

Fig. S1 Schematic diagrams of H-GY (a), F-GY (b) and Me-GY (c).

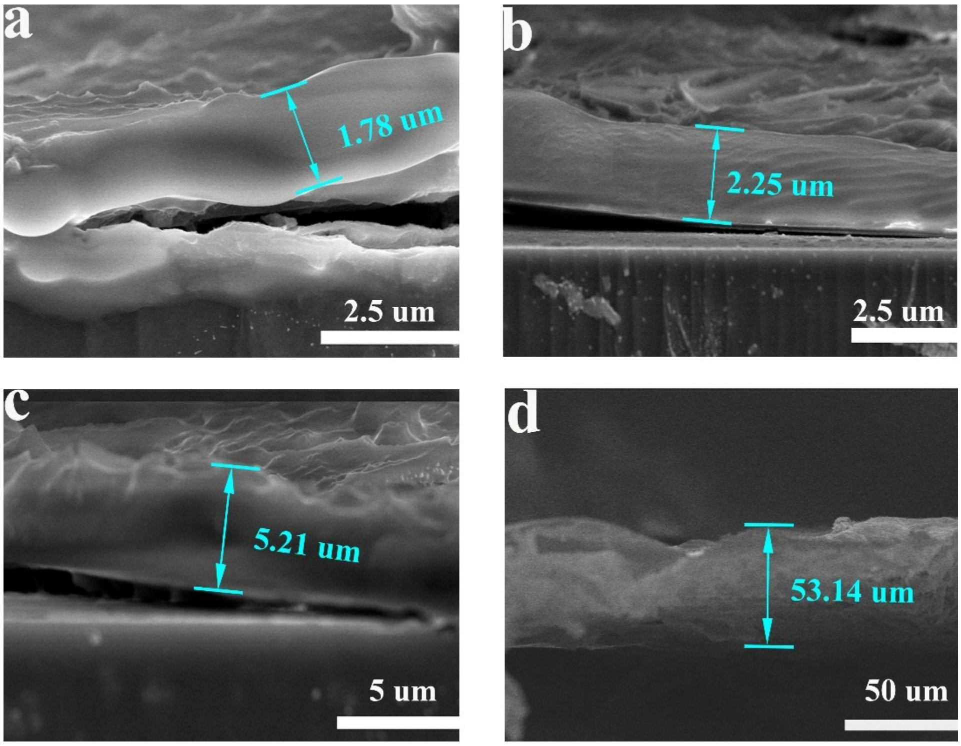

Fig. S2 The cross-sectional images of H-GY(a) Me-GY (b) and F-GY (c) films formed after one week. (d) The cross-sectional images of F-GY film formed after one month.

As shown in Fig. S2, the thickness of the cross sections of H-GY, Me-GY and F-GY are 1.78 um, 2.25um and 5.21 um. When the reaction time is prolonged, the thickness of these films will gradually increase. After one month, the thickness of F-GY film can reach up to 53.14 um (Fig. S2d).

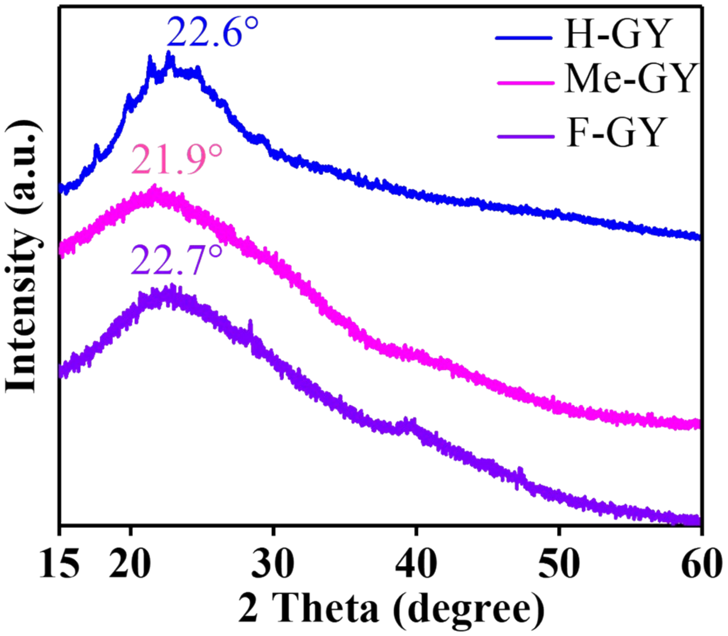

Fig. S3 XRD patterns of H-GY, Me-GY and F-GY

In the Fig. S3, the peak at 22.6° for H-GY correspond to the interlayer spacing of 3.93 Å. As calculated from Bragg equation (2dsinθ=nλ), the interlayer spacing of Me-GY and F-GY are 4.06 and 3.90 Å.

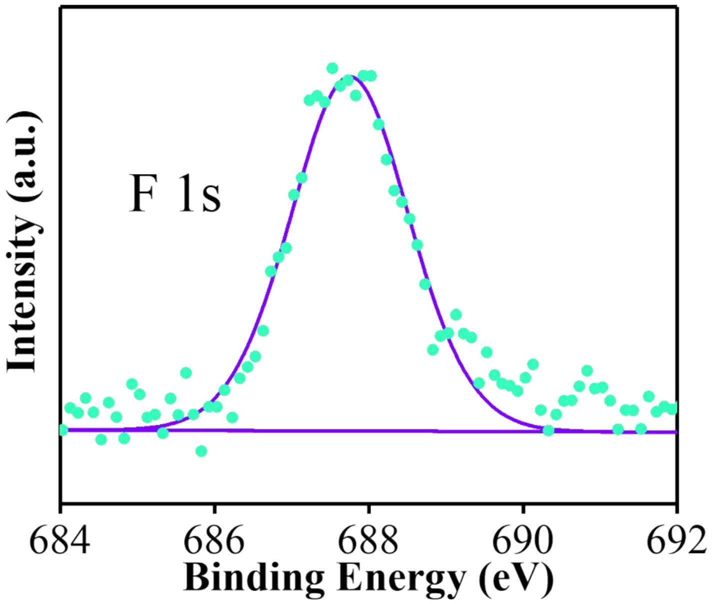

Fig. S4 XPS narrow scan for the element of fluorine in F-GY

References

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3. J. He, N. Wang, Z. Yang, X. Shen, K. Wang, C. Huang, Y. Yi, Z. Tu and Y. Li, *Energy Environ. Sci.*, 2018, **11**, 2893-2903.