

Supporting Information

**Facile and large-scale synthesis of polymorphic graphdiyne
catalyzed by transition metal salts for organic pollutants
removal**

Jianhui Zhu^a, Desheng Liu^a, Changsheng Li^{a,b}, Bingjie Zhang^a, Jianli Wang^a,

Wenjuan Wu^a, Jiawen Ji^a and Yongqiang Ma^{a,*}

^a Department of Applied Chemistry, College of Science, China Agricultural University, Beijing, 100193, China

^b Engineering Research Center of Plant Growth Regulator, Ministry of Education & College of Agronomy and
Biotechnology, China Agricultural University, Beijing, 100193, China

*Corresponding author. Tel: +86 (10) 62731978. E-mail: mayongqiang@cau.edu.cn (Y.Q. Ma)

Experimental details

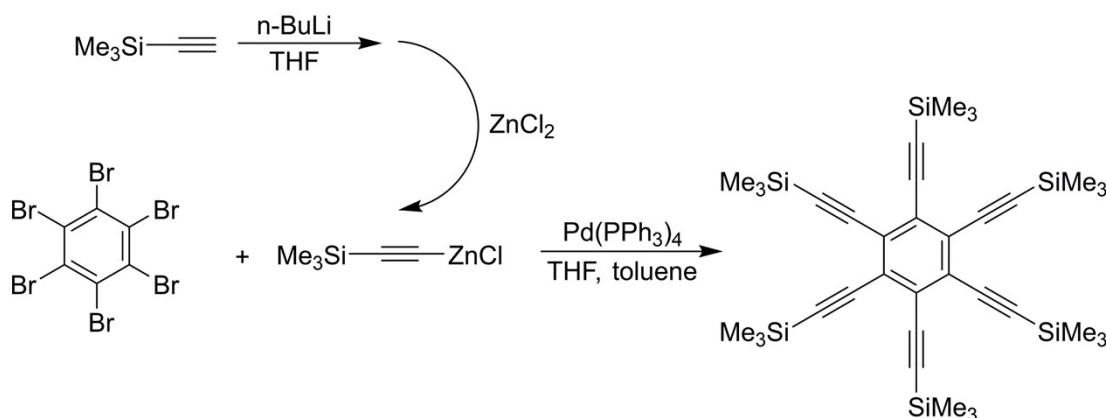
1.1 Synthetic method

1.1.1 Synthesis of monomers :

Hexakis [(trimethylsilyl)ethynyl] benzene (HEB-TMS). Molecular HEB-TMS was synthesized according to the reported synthetic route,¹ as shown in Scheme S1. In order to determine the structure and purity of the synthetic monomer HEB-TMS, ¹H NMR and ¹³C NMR detections were carried out by a Bruker 500 NMR spectrometer, and the corresponding spectrogram are exhibited in Figure S1 and S2, showing that HEB-TMS was successfully synthesized and had high purity. All chemical shifts of ¹H were in accordance with that of tetramethylsilane (TMS, $\delta = 00$ ppm) or CDCl₃ ($\delta = 7.26$ ppm) and ¹³C NMR chemical shifts were referenced to CDCl₃ ($\delta = 77.00$ ppm).

¹H NMR (500 MHz, CDCl₃, ppm): δ 0.28 (s, -Si(CH₃)₃);

¹³C NMR (500 MHz, CDCl₃, ppm): δ 127.95, 105.19, 101.00, 0.00.



Scheme S1. Synthetic route of HEB-TMS.

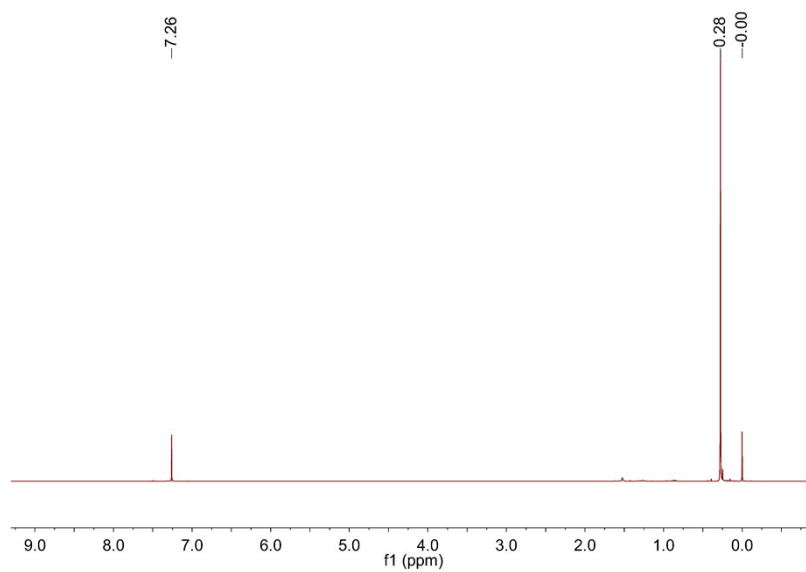


Figure S1 ^1H NMR spectrum of HEB-TMS (CDCl_3 , 500 MHz).

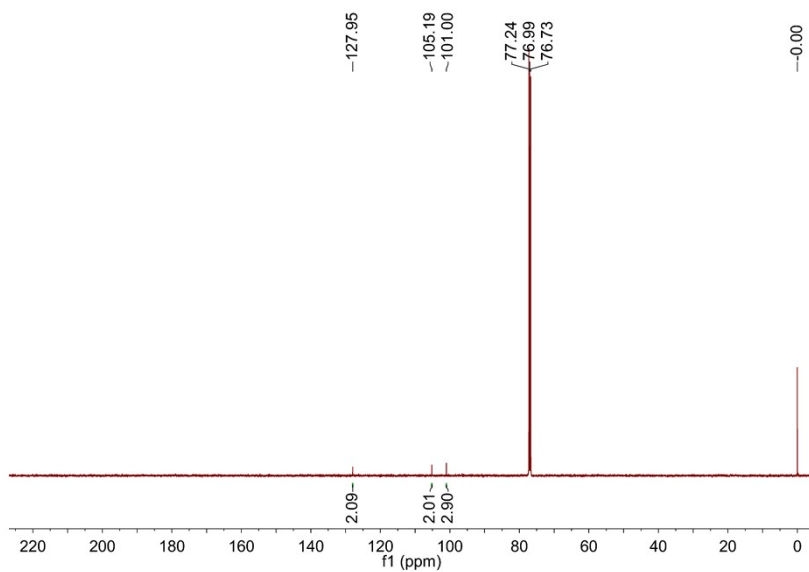


Figure S2 ^{13}C NMR spectrum of HEB-TMS (CDCl_3 , 500 MHz).

Hexaethynylbenzene (HEB). HEB-TMS (150 mg) dissolved in 50 mL THF was added 1.5 mL TBAF under nitrogen protection. The reaction was stirred at 8°C for 20 minutes. Then the reaction solution was transferred to a separatory funnel, diluted with ethyl acetate (20 mL), washed with saturated salt water (20 mL) for three times, dried with anhydrous Na_2SO_4 , and after that concentrated until dry. A yellow-brown precursor HEB was obtained by the above procedure, which was immediately used in subsequent experiments.

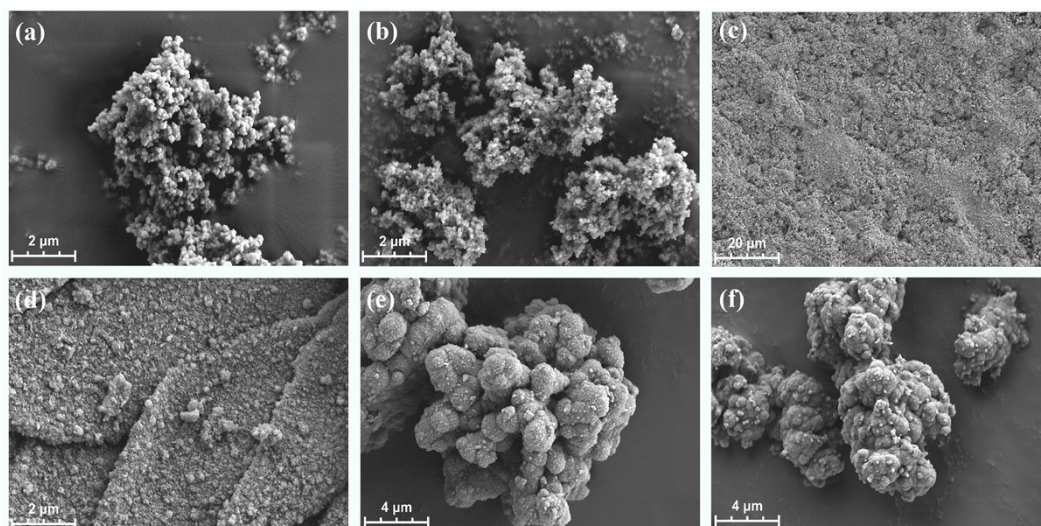


Figure S3 Low-magnification SEM images of GDY synthesized by different catalysts. (a)

CuCl; (b) CuI; (c) Cu(OAc)₂; (d) CuSO₄; (e) Pd(OAc)₂; (f) [(C₆H₅)₃P]₂·PdCl₂.

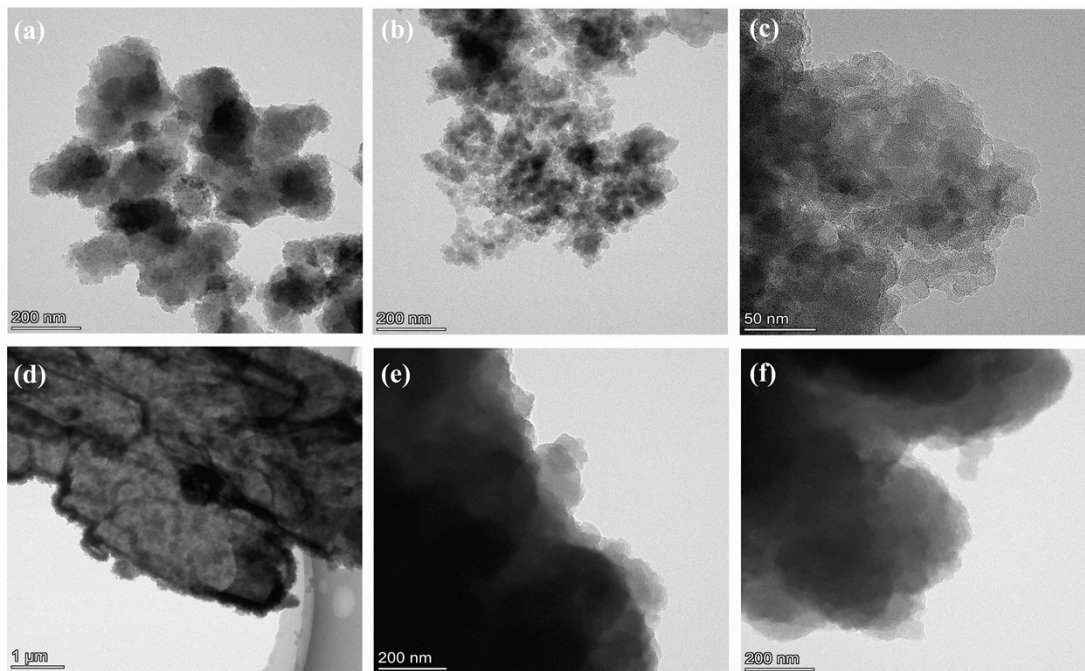


Figure S4 TEM images of GDY synthesized by different catalysts. (a) CuCl; (b) CuI; (c)

Cu(OAc)₂; (d) CuSO₄; (e) Pd(OAc)₂; (f) [(C₆H₅)₃P]₂·PdCl₂.

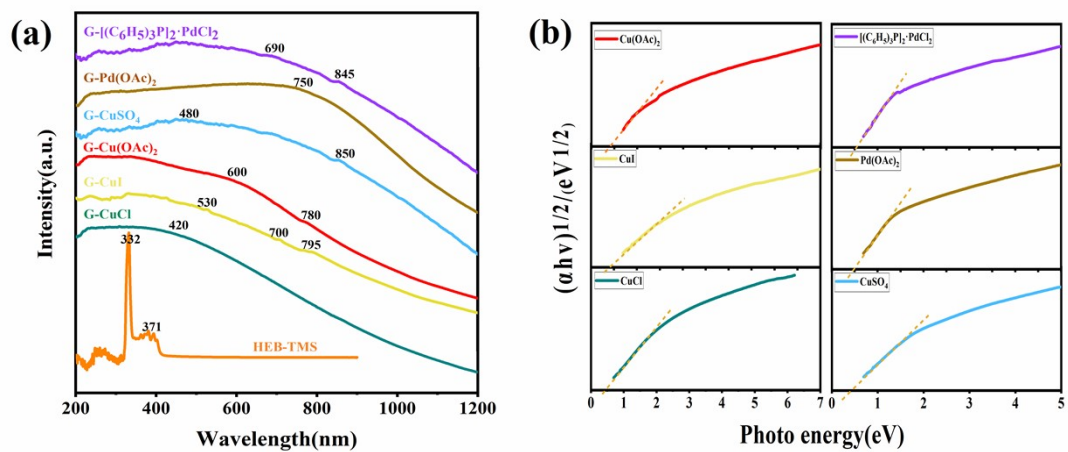


Figure S5 (a) UV-Vis absorption spectrum of GDY synthesized by different catalysts; (b) the curves of $(\alpha h\nu)^{1/2}$ versus photo energy for the band gap energy of GDYs.

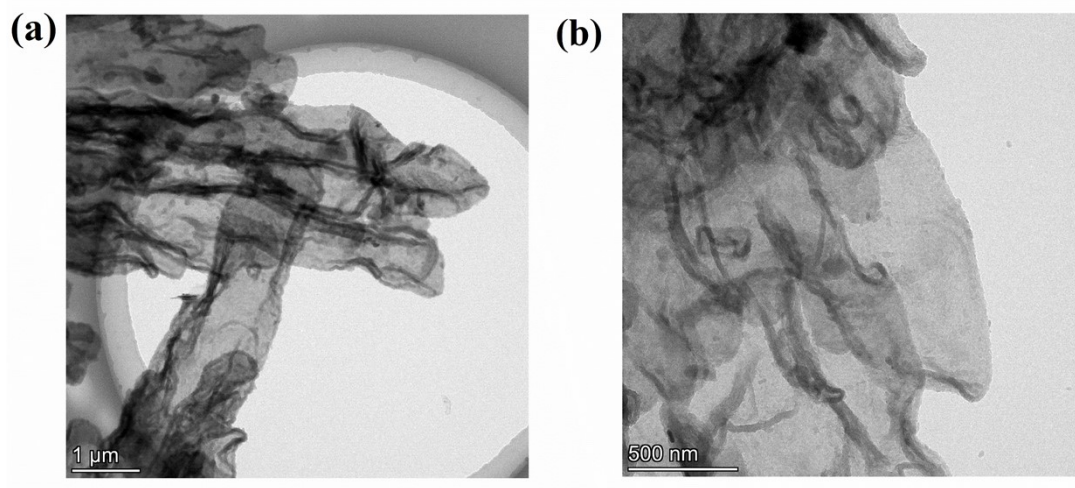


Figure S6 TEM images of GDY synthesized by different growth time. (a) 1 day and (b) 1.5 days.

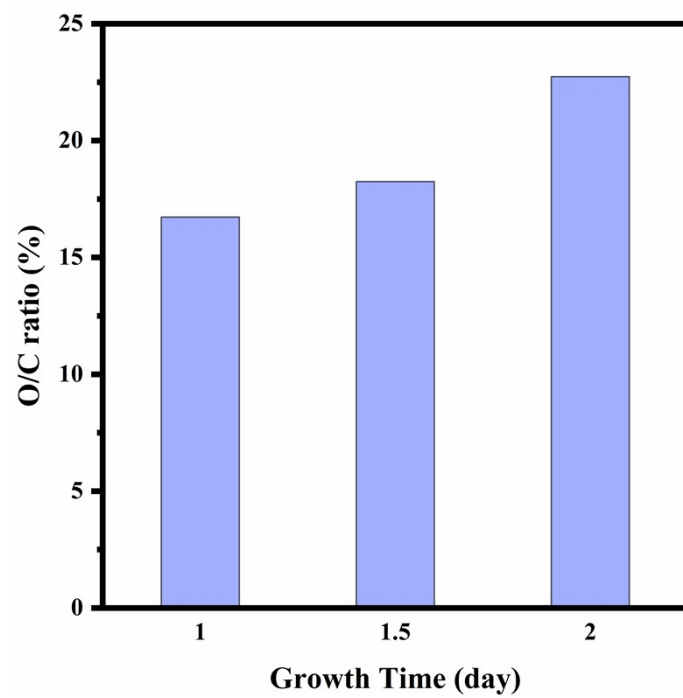


Figure S7 O/C ratio of GDY synthesized at different growth time in XPS.

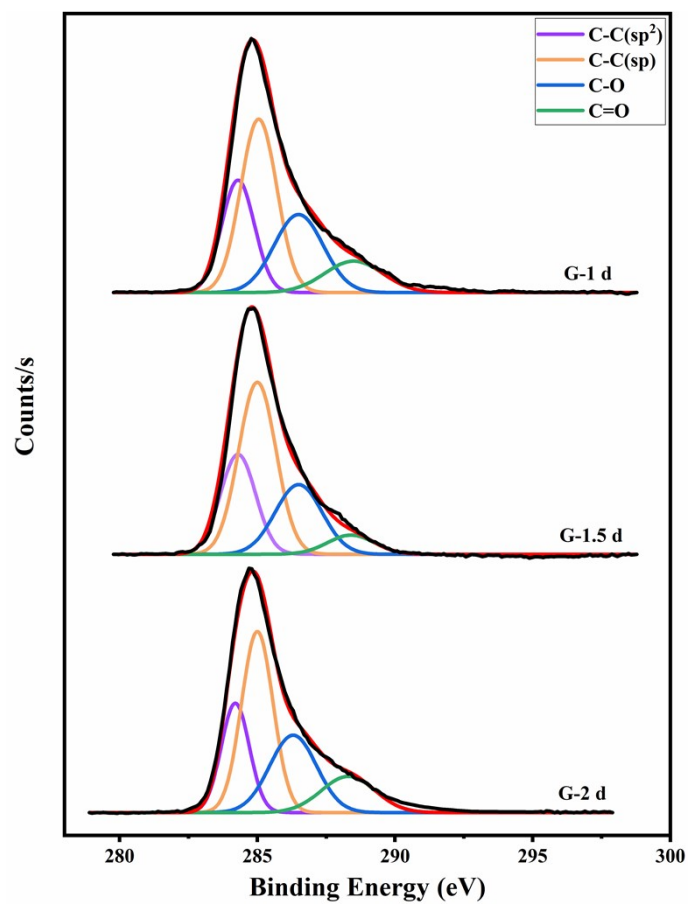


Figure S8 C1s XPS of GDY synthesized at different growth time.

1.2 Dye adsorption test

1.2.1 Solution standard curve preparation

The absorbances of Rhodamine B solution (RhB) and methyl orange solution (MO) with concentrations of 20 mg/L, 10 mg/L, 5 mg/L, 1 mg/L, 0.5 mg/L and 0.01 mg/L at the maximum absorption wavelength were measured respectively. The dye concentration was taken as the horizontal axis and the absorbance value as the vertical coordinate to perform linear fitting, and the standard curves of RhB and MO were obtained respectively.

1.2.2 Adsorption experiment

Adsorption experiments were carried out in centrifuge tubes, containing RhB or MO (20 mg/L) in the 10 mL aqueous solution separately. After that, 10 mg of GDY powder prepared under different catalysts and different growth time was added into the above dye solution respectively, and the centrifuge tubes with the mixture were placed on a vortex oscillator for vortex for 15 min at 2500 r/min at room temperature, and then centrifuged for 5 min at 3800 r/min. The supernatant was taken to be measured.

1.2.3 Comparison with other adsorbents

The GDY with the best adsorption effect was selected from 1.4.2 to carry out the following comparative experiments. 1 g/L different adsorbents, including GDY, MWCNTs, RGO, GCB, AC, PSA, C18 and Florisil, were added into 20 mg/L RhB and MO dye solution respectively, and then the solution was vortexed for 15 min (2500 r/min) at room temperature to fully mix for adsorption. After centrifugation for 5 min (3800 r/min), the supernatant was taken to measure the absorbance respectively.

Table S1 Zeta potential of GDY synthesized at different growth time.

Growth time (day)	Zeta potential (mV)
1	-9.58
1.5	-12.00
2	-11.70

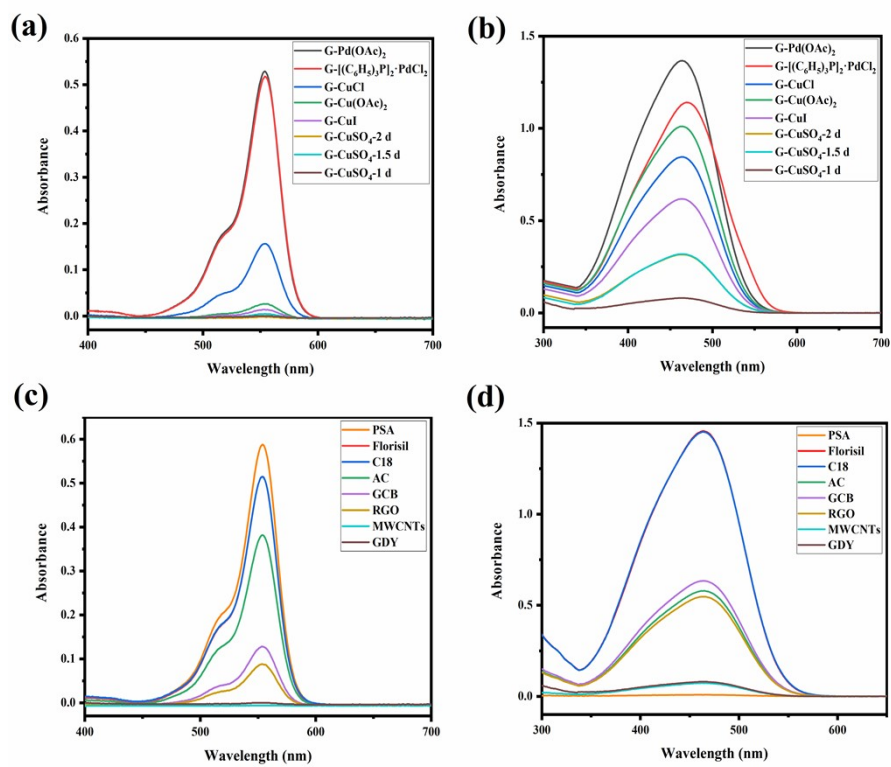


Figure S9 Curves of absorbance versus wavelength of dyes adsorbed by GDYs. (a) RhB, λ max = 554 nm; (b) MO, λ max = 464 nm. Curves of absorbance versus wavelength of dyes adsorbed by different adsorption materials. (c) RhB; (d) MO.

Table S2 HPLC-MS/MS parameters of investigated organic pollutants.

No.	organic pollutants	Prec Ion	Prod Ion (CE)	Frag (V)
1	oxytetracycline	461.2	201.1 (40) 268.3(45)	120
2	doxycycline	445.2	201 (45) 252.2 (50)	120
3	tetracycline	445.2	154.2 (25) 267.2 (40)	120
4	chlorotetracycline	479.2	286.2 (60) 303.2 (40)	115
5	acetamiprid	223.1	126.0 (20) 56 (10)	100
6	clothianidin	250.1	169.1 (10) 132.1 (30)	80
7	thiacloprid	253.0	126.0 (15) 186.0 (10)	120
8	imidacloprid	256.0	175.0 (20) 209.0 (10)	80
9	nitenpyram	271.1	224.0 (10) 56.0 (30)	100

Supplementary References

1. G. Li, Y. Li, H. Liu, Y. Guo, Y. Li and D. Zhu, *Chem. Commun.*,2010, **46**, 3256-3258.