

Electronic Supporting Information for

Modifiable diyne-based covalent organic framework: a versatile platform for in-situ multipurpose functionalization

Chiyao Bai, Meicheng Zhang, Bo Li, Xiaosheng Zhao, Shuang Zhang, Lei Wang, Yang Li, Ji Zhang, Lijian Ma*, and Shoujian Li*

College of Chemistry, Sichuan University, Key Laboratory of Radiation Physics & Technology, Ministry of Education, No. 29 Wangjiang Road, Chengdu, 610064, P. R. China.

*E-mail: sjli000616@scu.edu.cn (S. Li), ma.lj@hotmail.com (L. Ma); Fax: +86-28-8541 2907; Tel: +86-28-8541 2329.

1. Preparation of materials

Preparation of 2, 4-hexadiyne-1, 6-diol: A mixture of CuI (0.0095 g, 0.05 mmol), TMEDA (0.0232 g, 0.2 mmol) and Et₃N (3.0 mmol) in THF (15 mL) was sonicated for 2 min. 2-Propynyl alcohol (560 mg, 10.0 mmol) in THF (5 mL) was then added dropwise at room temperature under O₂ with stirring. After stirring for 3 h, the solvent was removed in vacuo, and the residue dissolved in diethyl ether, washed with dilute HCl, followed sequentially by saturated NH₄Cl and brine. The organic extracts were dried with MgSO₄, and the solvent was removed to give a yellow white solid. Petroleum ether/diethyl ether (10:1) was used for recrystallization to afford 2, 4-hexadiyne-1, 6-diol as a white solid.

Preparation of EtMgBr: A solution of ethyl bromide (0.20 mL, 2.7 mmol) in anhydrous Et₂O (3 mL) was added dropwise to the mixture of magnesium turnings (0.648 g, 2.7 mmol) and I₂ (0.253 g, 1.0 mmol) in anhydrous Et₂O (1.5 mL). At the very beginning the reaction required activation by heating. After reaction, it formed a light grey, clear solution.

Preparation of Cu/TCD

Cu(AcO₂)₂ (0.201 g) in EtOH (5 mL) and deionized water (5 mL) was stirred at room temperature for 30 min. TCD (0.050 g) was added, and the mixture was stirred for 12 h. Then the solid was filtered and wash with deionized and ethanol until the filtrate was colorless. The solid was dried at 50 °C under vacuum for 24 h. The loading

amount of Cu was analyzed by ICP.

Preparation of Fe/TCD

FeCl₃ (0.199 g) in EtOH (5 mL) and deionized water (5 mL) was stirred at room temperature for 30 min. TCD (0.050 g) was added, and the mixture was stirred for 12 h. Then the solid was filtered and wash with deionized and ethanol until the filtrate was colorless. The solid was dried at 50 °C under vacuum for 24 h. The loading amount of Fe was analyzed by ICP.

2.1 Batch experiment of uranium (VI) adsorption

Batch experiments were performed to study the adsorption behavior of the products toward U(VI). The as-prepared material 10 mg was added to a 50 mL Erlenmeyer flask with 25 mL of multi-ion solution containing 12 metal ions (Table S1) as well as U(VI) at a given pH and shaken at 160 rpm for 3 h at room temperature. The supernatant were separated from the solid by centrifugation. The initial and equilibrium concentrations were determined by ICP-AES.

Adsorption amount (q_e , mg/g) of U(VI) or other metal ions were calculated by the following equation:

$$q_e = \frac{(c_0 - c_e) \times v}{w} \quad (1)$$

where c_0 and c_e are the initial and the equilibrium concentration of metal ion (mg/L), respectively; v is the volume of the testing solution (L); and w is the amount of adsorbent (g).

A specific term, uranium-selectivity (S_U) was use to describe the potency and degree of the selectivity of the sorbents to uranium:

$$S_U = \frac{q_{e-U}}{q_{e-tot}} \times 100\% \quad (2)$$

where q_{e-U} is the amount of uranium adsorbed (mmol/g) and q_{e-tot} is amount of all cations adsorbed (mmol/g).

All glassware used was previously soaked overnight in 10.0 wt% HNO₃ to remove impurities that might be present and to prevent further adsorption of metal ions on the walls of glassware. All tests were carried out at least in duplicates.

3. Comparison with other modification methods

The properties of different modification methods for preparation of functional materials have been described in Table S2. It reveals that current methods have certain limitations on modification of materials. They generally have to use the related molecules containing certain active groups, *i.e.*, azide, terminal alkyne or carboxyl group, to further modify the framework skeleton of the materials by reacting with the corresponding active sites on the framework skeleton, which should not easily prepare various functional materials to satisfy the diverse needs. Conventionally, every new type of functional material requires a redesign and trips through relevant process of preparation and/or functionalization, which, in most cases, leads to be unnecessary waste of resources, increasing workload and cost. Herein, we proposed a strategy that using the carbon-carbon triple bonds as building blocks and functionalization sites to modify materials. According to the mechanism of addition reaction, compounds with multiple bonds, such as carbon-carbon triple bonds/double bonds, can react with other molecules by attaching one or two new functional groups to the carbon atoms located

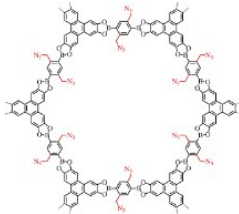
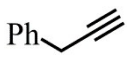
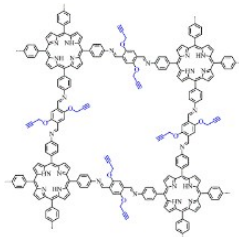
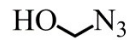
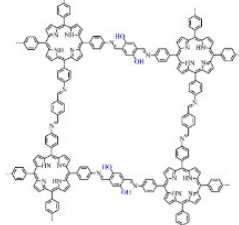
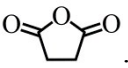
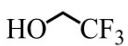
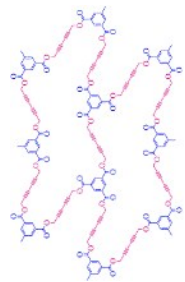
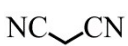
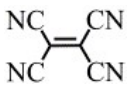

in the reacted multiple bond. In this study, diynes not only can do undergo reaction with different molecules, such as thiol, malononitrile, tetracyanoethene, and so on, to introduce desired functional groups into the framework of the platform material in situ, and to endow the material with desired functions, but also can interact with metals to form functional materials acting as catalysts or capacitors. Thus the strategy can enhance the utilization of starting materials and expand the current applications for the platform material itself.

Table S1 Compositions of the simulated nuclear industrial effluents*

Coexistent ions	Added as	Reagent purity
UO ₂ ²⁺	U ₃ O ₈	Standard reagent
La ³⁺	La(NO ₃) ₃	99.9% Metal basis
Ce ³⁺	Ce(NO ₃) ₃	99.99% Metal basis
Nd ³⁺	Nd(NO ₃) ₃	AR
Sm ³⁺	Sm(NO ₃) ₃	AR
Gd ³⁺	Gd(NO ₃) ₃ •6H ₂ O	AR
Mn ²⁺	MnO	99.5%
Co ²⁺	Co(NO ₃) ₂ •6H ₂ O	99.99% Metal basis
Ni ²⁺	Ni(NO ₃) ₂	Spectrum pure
Zn ²⁺	Zn(NO ₃) ₂ •6H ₂ O	99.99% Metal basis
Sr ²⁺	Sr(NO ₃) ₂	99.99% Metal basis
Ba ²⁺	Ba(NO ₃) ₂	AR

*References: C. R. Preetha, J. M. Gladis and T. P. Rao, *Environ. Sci. Technol.*, 2006, **40**, 3070.

Table S2 Properties of different modification methods for preparation of functional materials

Active site	Framework of materials	Molecules used to modify the materials	Properties	Ref.
-N ₃		Ph 	The molecules used to modify materials should contain certain active groups, <i>i.e.</i> , azide, terminal alkyne or carboxyl group.	1
-C≡CH		HO 		2
-OH				3
-COOH	Carbon nanotub, graphene	HO 	The materials should be modified primarily by chemical or physical methods, such as oxidation, to obtain carboxyl group.	4,5,6
-C≡C-C≡C-		NC  NC  NC  Cu, Fe	It can undergo reactions with different molecules or functional groups to prepare various functional materials according to diverse real needs.	This work

[1] A. Nagai, Z. Q. Guo, X. Feng, S. B. Jin, X. Chen, X. S Ding and D. L. Jiang, *Nat.*

Commun., 2011, **2**, 1.

- [2] N. Huang, R. Krishna and D. L. Jiang, *J. Am. Chem. Soc.*, 2015, **137**, 7079.
- [3] N. Huang, X. Chen, R. Krishna and D. L. Jiang, *Angew. Chem.*, 2015, **127**, 3029.
- [4] J. Wang, X. Ma, G. Fang, M. Pan, X. Ye and S. Wang, *J. Hazard. Mater.*, 2011, **186**, 1985.
- [5] K. A. Wepasnick, B. A. Smith, K. E. Schrote, H. K. Wilson, S. R. Diegelmann, D. H. Fairbrother, *Carbon*, 2011, **49**, 24.
- [6] L. M. Zhang, J. G. Xia, Q. H. Zhao, L. W. Liu and Z. J. Zhang, *Small*, 2010, **6**, 537.

4. XPS spectra of C 1s and O 1s for TCD-CN and TCD-AO

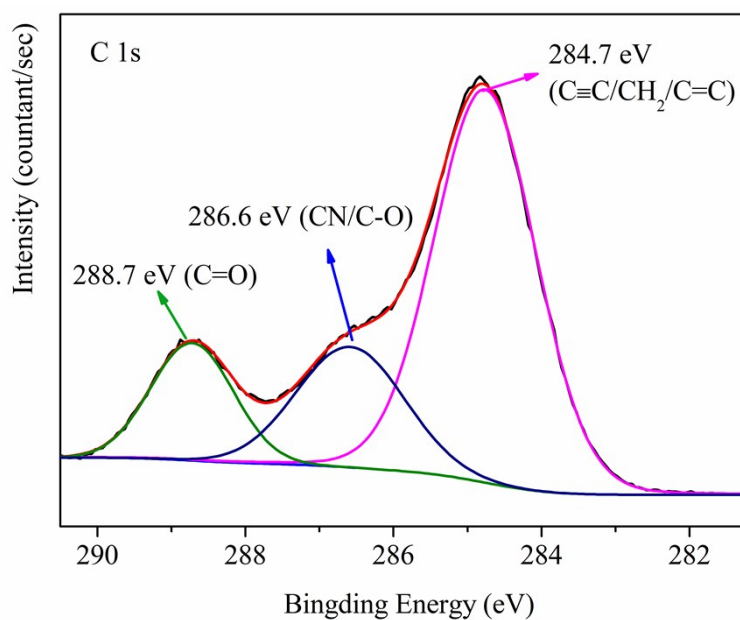


Fig. S1 XPS spectrum of C 1s for TCD-CN.

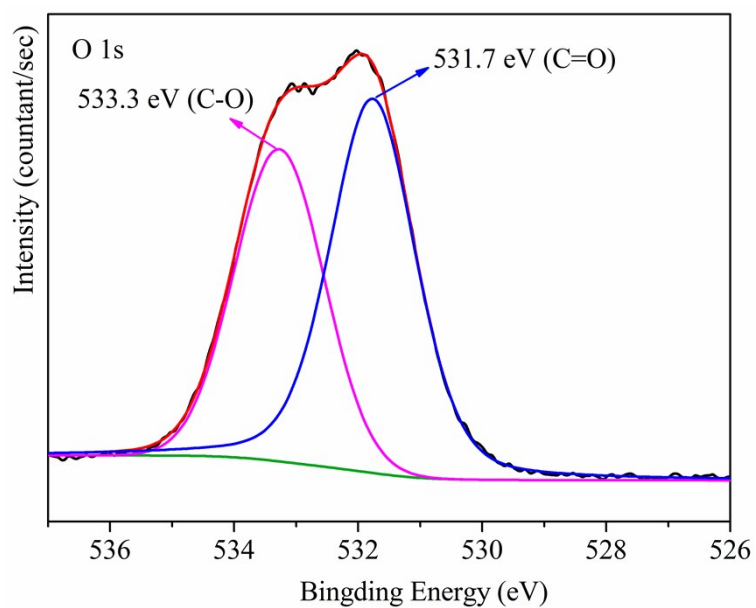


Fig. S2 XPS spectrum of O 1s for TCD-CN.

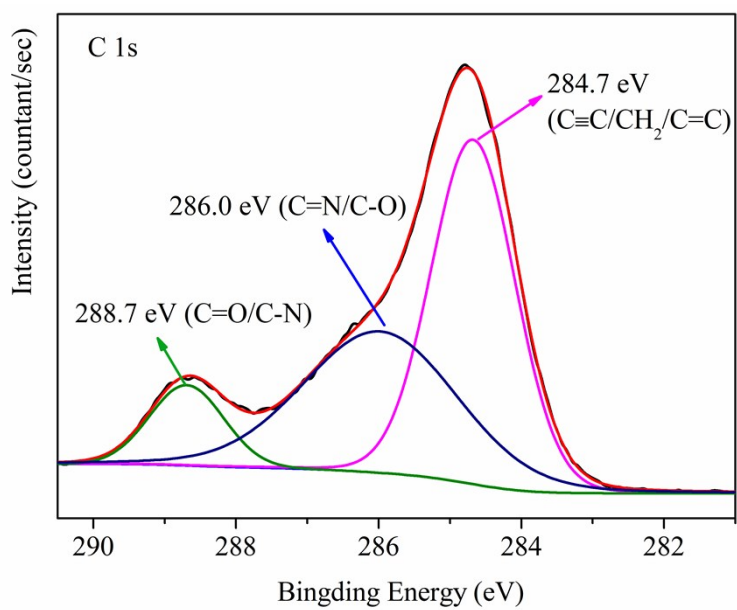


Fig. S3 XPS spectrum of C 1s for TCD-AO.

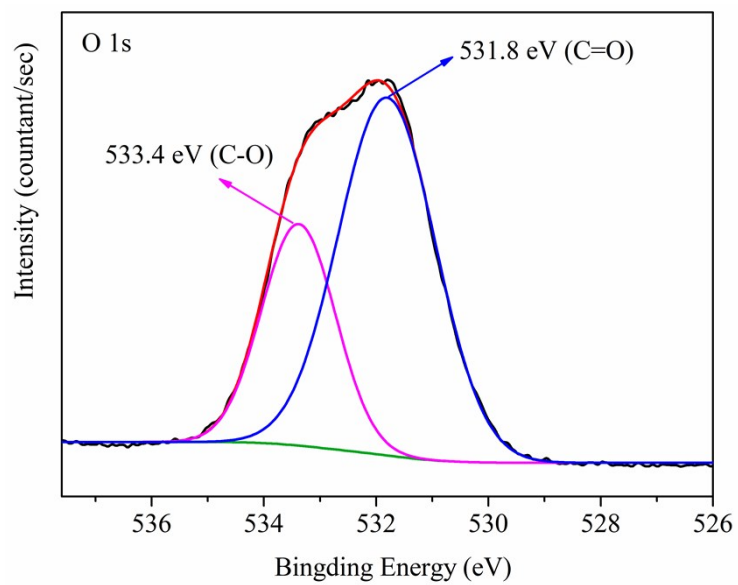


Fig. S4 XPS spectrum of O 1s for TCD-AO.