Universidad Autónoma de Madrid

Biblos-e Archivo
Repositorio Institucional UAM

Repositorio Institucional de la Universidad Autónoma de Madrid
https://repositorio.uam.es

Esta es la **versión de autor** del artículo publicado en:
This is an **author produced version** of a paper published in:

Chemistry – A European Journal 26.29 (2020): 6495-6498

DOI: https://doi.org/10.1002/chem.202000224

Copyright: © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

El acceso a la versión del editor puede requerir la suscripción del recurso
Access to the published version may require subscription

10.1002/chem.202000224

WILEY-VCH

COMMUNICATION

Gas-Solid Heterogeneous Post-Synthetic Modification of Imine-based Covalent Organic Frameworks

Jesús A. Martín-Illán,[a] Sergio Royuela,[b,c] M. Mar Ramos,[c] José L. Segura*[b] and Félix Zamora*[a,d,e]

[a] J. A. Martín-Illán, Prof. F. Zamora
Departamento de Inorgánica
Facultad de Ciencias
Universidad Autónoma de Madrid
Madrid 28049, Spain
E-mail: felix.zamora@uam.es

[b] S. Royuela, Prof. J. L. Segura
Departamento de Química Orgánica
Facultad de CC. Químicas
Universidad Complutense de Madrid
Madrid 28040, Spain
E-mail: segura@quim.ucm.es

[c] S. Royuela, Prof. M. Mar Ramos
Departamento de Tecnología Química y Ambiental
Universidad Rey Juan Carlos
Madrid 28933, Spain

[d] Prof. F. Zamora
Institute for Advanced Research in Chemical Sciences (IAdChem)
Universidad Autónoma de Madrid
Madrid 28049, Spain

[e] Prof. F. Zamora
Condensed Matter Physics Center (IFIMAC)
Universidad Autónoma de Madrid
Madrid 28049, Spain

Supporting information for this article is given via a link at the end of the document.

Abstract: The copper-catalyzed azide–alkyne cycloaddition (CuAAC) click reaction is among the most extensively used strategies for the post-polymerization modification of COFs. This work shows a novel procedure for the post-synthetic functionalization of imine based-COFs using a heterogeneous solid–gas reaction between alkyne-functionalized COFs and azides in the absence of copper catalyst. This novel alternative represents a step forward towards a greener post-synthetic modification of COFs opening a high potential for the development of new applications.

Covalent Organic Frameworks (COFs) are crystalline and porous polymers built up based on modular chemistry criteria using dynamic covalent bonds.[1] The precise linkage of molecular organic building blocks can give rise to three-dimensional (3D) or two-dimensional (2D) layered COF structures. In fact, COFs have been recently considered as a source of chemically designed 2D materials.[2] Indeed, nanolayers of COFs, the so-called CONs, have shown interesting properties and applications.[3] Therefore, there is a growing interest in developing new synthetic strategies for COF synthesis, such as formal transimination reactions[4] or the self-condensation of bifunctional monomers.[5] Moreover, COFs are versatile platforms, allowing the uniform incorporation and organization of molecular building blocks into their pores. The most typical procedure to do so is by post-synthetic reactions of functionalized COFs, with click chemistry reactions being among the most widely used. Thus, click chemistry has enabled the incorporation of a wide variety of functional groups in COFs such as aliphatic, aromatic, acid, ester, amine, alcohol, thiol, fullerene or radical groups.[6] Jiang and co-workers reported on the first post-synthetic modification in COFs by click chemistry using the copper catalysed azide–alkyne cycloaddition (CuAAC) click reaction.[7] Subsequently, a variety of CuAAC reactions have been successfully used for the post-synthetic modification of COFs, producing efficiently functional materials with applications in different areas including energy storage, catalysis, water remediation or molecular recognition among others.[8] Therefore, post-synthetic modification of COFs using click chemistry can pave the way for the efficient synthesis of novel materials with high potential for the development of new applications.

The common features of CuAAC reactions are the use of Cu^{I} as catalyst and reactions taking place in a liquid medium (solvent). The problems associated with this procedure are *i*) the use of toxic species of Cu^{I}[9] and *ii*) the large amount of solvent needed to wash up the so-formed COF materials. However, the use of a copper catalyst can be avoided, thus going back to the original Huisgen [3+2] azide-alkyne cycloaddition reaction first described over half a century ago.[10] Naturally, in the absence of catalyst the reaction needs higher temperatures and longer times to proceed effectively. In other fields different alternatives have been proposed to avoid the use of copper in azide-alkyne cycloaddition reactions such as electron-deficient alkynes[11] or strain-promoted cycloadditions.[12]

To circumvent the second problem, we have explored the use of reagents in the gas phase as a means to avoid the use of solvents. This strategy has been previously investigated to functionalize the surface of some inorganic materials *via* copper-free solid-gas azide-alkyne cycloaddition reactions.[13] However, the application of this approach for the post-synthetic modification of COFs is still unexplored. Thus, in this work we report the post-

Accepted Manuscript

This article is protected by copyright. All rights reserved.

10.1002/chem.202000224

synthetic functionalization of an imine based-COF using a heterogeneous solid (COF) – gas (azides) procedure without the use of any solvent or catalyst.

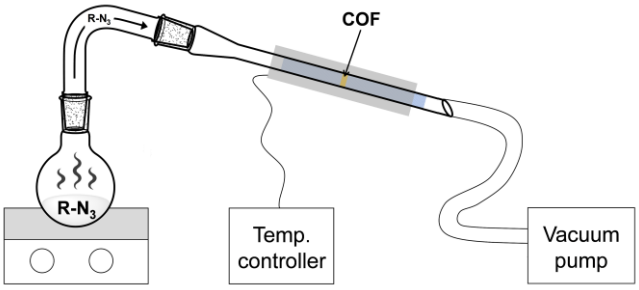
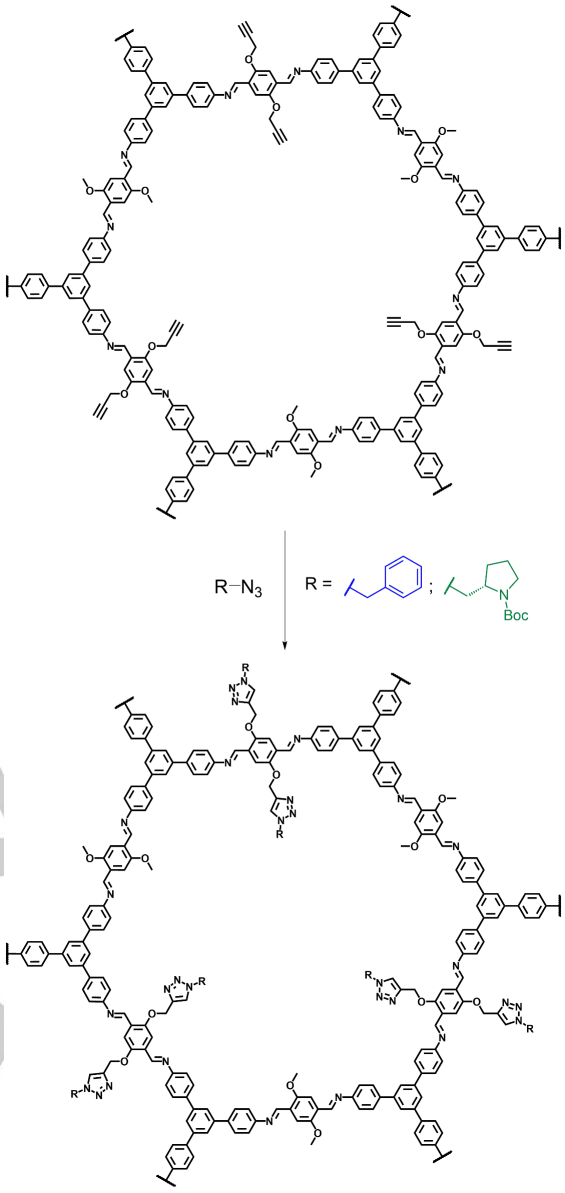


Figure 1. Schematic representation of the experimental setup developed for the heterogeneous solid-gas click reaction.

To perform the solid-gas reaction an experimental setup was designed *ad-hoc* (Figure 1). Our aim was to have a flow of the gaseous azide passing through a plug of the alkyne-bearing COF. This way, the reaction would take place directly in the COF pores as the azide passes through them, in the absence of solvent and catalyst. Thus, a glass tube is first half-filled with cotton and a nylon filter placed on top. The starting COF material is added taking care that it is evenly distributed across the tube's circumference. Another nylon filter and more cotton are located on top of the COF to hold it in place and to avoid accumulation on one side of the tube. Then, the system is connected to a vacuum pump and, on the other side, a bent connecting tube (*e.g.* a distillation adapter) joins the main tube to a round-bottom flask containing the desired azide. The flask is placed on an oil bath to gently heat the azide and facilitate the liquid to gas phase transition. Finally, the tube holding the COF is wrapped with a heating tape connected to a temperature controller and covered with aluminium foil (see SI for pictures of the experimental setup). To carry out the reaction, the heating tape is set to the desired temperature, the vacuum pump started, and the azide gentle heated. The system is let to run overnight and then the cotton is removed and the COF taken out and analysed.

As the starting materials for the reaction we selected **[HC≡C]$_{0.5}$-TPB-DMTP-COF**[7] and two azides previously unreported in the post-synthetic modification of COFs: benzyl azide and (*S*)-2-(azidomethyl)-1-Boc-pyrrolidine (Scheme 1). **[HC≡C]$_{0.5}$-TPB-DMTP-COF** has been extensively used in the literature as a platform for post-synthetic modification due to its high crystallinity, porosity and chemical stability.[7, 8f-k] Before the cycloaddition reaction, the material was characterized by Fourier transform infrared spectroscopy (FTIR), ^{13}C cross-polarized magic angle spinning solid-state NMR (^{13}C CP-MAS-NMR), powder X-ray diffraction (PXRD) and nitrogen adsorption/desorption isotherms at 77 K. All the data are in accordance with those already reported (Figure 2 and Figure S3).



Scheme 1. Heterogeneous phase reaction between solid **[HC≡C]$_{0.5}$-TPB-DMTP-COF** and gaseous benzyl azide or (*S*)-2-(azidomethyl)-1-Boc-pyrrolidine. a) **TPB-DMTP-COF-PhTrz**. b) **TPB-DMTP-COF-(*S*)-Py-Boc.**

On the other hand, benzyl azide is a simple and readily available azide that does not undergo side reactions. Unfortunately, the absence of other functional groups also complicates the analysis due to the lack of characteristics bands on its FTIR or ^{13}C CP-MAS-NMR spectra. Therefore, we decided to extend the scope of our approach with (*S*)-2-(azidomethyl)-1-Boc-pyrrolidine. The Boc protecting group present in this azide can act as a probe both in the FTIR spectrum, through the carbonyl group stretching band, and in the ^{13}C CP-MAS-NMR spectrum, through the tert-butyl group. Furthermore, the deprotected (*S*)-2-(azidomethyl)pyrrolidine has been reported to act as an efficient chiral organocatalyst once anchored in COF's channel walls,[7, 8j] indicating the interest of this material.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

10.1002/chem.202000224

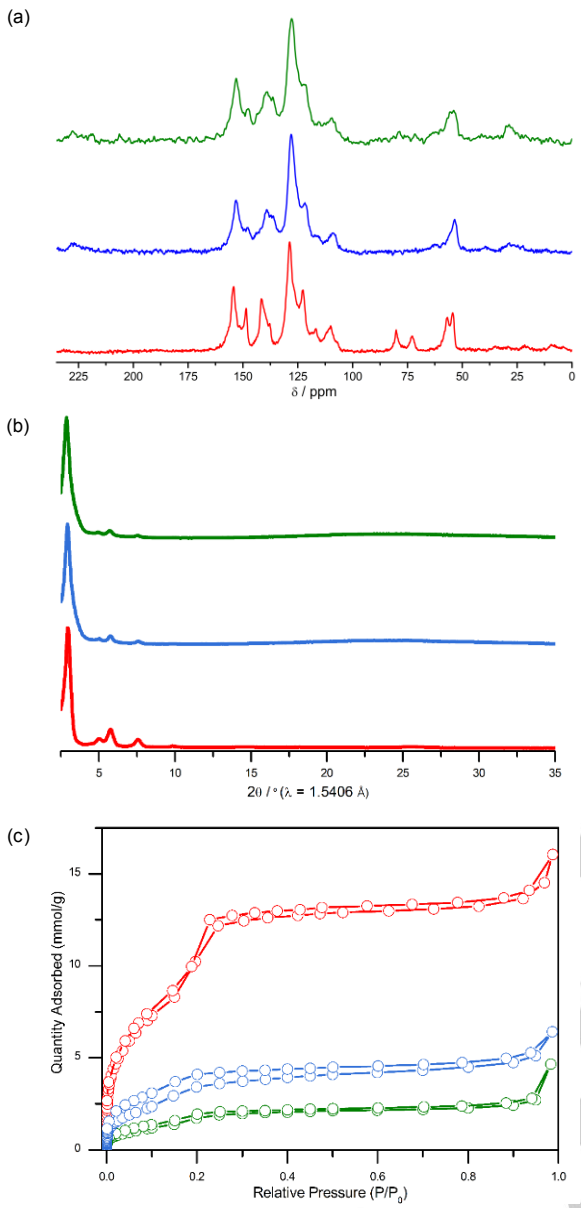


Figure 2. ^{13}C CP-MAS solid-state NMR (a), experimental PXRD patterns (b) and N_2 adsorption–desorption isotherms (c) of **[HC≡C]$_{0.5}$-TPB-DMTP-COF** (red), **TPB-DMTP-COF-PhTrz** (blue) and **TPB-DMTP-COF-(*S*)-Py-Boc** (green).

Thus, reaction of **[HC≡C]$_{0.5}$-TPB-DMTP-COF** with benzyl azide or (*S*)-2-(azidomethyl)-1-Boc-pyrrolidine at 135-140 ºC for 24-48 h yields the new **TPB-DMTP-COF-PhTrz** or **TPB-DMTP-COF-(*S*)-Py-Boc**, respectively. In the case of **TPB-DMTP-COF-(*S*)-Py-Boc,** a prolongation of time reaction (48h) was required to increase yield (Figure S7). The solids were washed up with tetrahydrofuran (THF) and ethanol, to remove unreacted azide, and then dried at 150 ºC under vacuum for 12 h, affording the corresponding products (Scheme 1).

The completeness of the reaction between the alkyne and the azides was confirmed by FTIR and ^{13}C CP-MAS-NMR spectroscopies. Thus, the FTIR spectrum of **TPB-DMTP-COF-PhTrz** (Figure S3) shows the absence of the υ(C≡C) stretching band at 3291 cm^{-1}, whereas maintaining the imine vibration band at 1591 cm^{-1}. Meanwhile, for **TPB-DMTP-COF-(*S*)-Py-Boc** the intensity of the υ(C≡C) stretching band was significantly reduced (Figure S4). In agreement, the ^{13}C CP-MAS-NMR spectrum of **TPB-DMTP-COF-PhTrz** (Figure 2a) also shows the disappearance of the alkyne signals at 80.2 and 72.9 ppm and no change in the signals between 160-100 ppm, assignable to C sp^2, and the signal at 53.5 ppm, corresponding to the methoxy groups (Figure 2a). On the other hand, the **TPB-DMTP-COF-(*S*)-Py-Boc** spectrum clearly presents the characteristic tert-butyl signal at 29.8 ppm from the Boc moiety while the signals corresponding to the alkyne moieties are reduced but still observable (Figure 2a).

These spectroscopic data, together with the elemental analysis (SI), suggest the completeness of the reaction between the **[HC≡C]$_{0.5}$-TPB-DMTP-COF** and benzyl azide, while only around 50 % of the alkynes have reacted with (*S*)-2-(azidomethyl)-1-Boc-pyrrolidine. These observations can be rationalized taking into account the large volume required by the (*S*)-2-(azidomethyl)-1-Boc moiety.

To verify that the crystallinity of the materials was not affected by the experimental setup PXRD patterns were collected after the reaction (Figure 2b). Experimental diffractograms of both **TPB-DMTP-COF-PhTrz** and **TPB-DMTP-COF-(*S*)-Py-Boc** are almost identical to that of the parent COF, revealing no mayor structural defects in the frameworks after the post-synthetic reaction.

Likewise, the reaction does not affect the thermal stability of the new functionalized COFs. Thus, after activation at 150 °C under vacuum for 12 h, thermogravimetric analysis (TGA) revealed that **TPB-DMTP-COF-PhTrz** and **TPB-DMTP-COF-(*S*)-Py-Boc** are thermally stable up to 500 °C (Figure S5).

Porosity of **TPB-DMTP-COF-PhTrz** and **TPB-DMTP-COF-(*S*)-Py-Boc** was examined evaluating their nitrogen sorption isotherm at 77 K. The sorption curves consist of typical type IV isotherms characteristic of mesoporous materials (Figure 2c). The BET surface areas, pore volumes and pore sizes calculated by using non-local density functional theory (NLDFT) are represented in Table 1. As expected, when the dimensions of the pending groups increase (alkyne < benzyl < 1-Boc-pyrrolidine) the BET surface area, pore volume and pore size decrease.[8a]

Table 1. BET surface area, pore size distribution and volume of **[HC≡C]$_{0.5}$-TPB-DMTP-COF**, **TPB-DMTP-COF-PhTrz** and **TPB-DMTP-COF-(*S*)-Py-Boc**.

Properties	**[HC≡C]$_{0.5}$-TPB-DMTP-COF**	**TPB-DMTP-COF-PhTrz**	**TPB-DMTP-COF-(*S*)-Py-Boc**
Surface area (m^{2}g^{-1})	1500	458	180
Pore size (Å)	29.5	26.1	14.1
Pore volume (cm^{3}g^{-1})	0.94	0.29	0.05

In summary, imine-based COFs represent a very promising molecular-based source of 2D materials. Their chemical functionalization at the pore sites can be achieved using post-synthetic copper-catalyzed azide–alkyne cycloaddition reactions. However, this procedure has some drawbacks inherent to the use of the copper catalyst. We have developed a novel procedure for the post-synthetic functionalization of imine based-COFs avoiding the use of catalyst and solvent. The reactions are carried out between alkyne-functionalized COFs and volatile azide molecules at the solid–gas phase. This new procedure has allowed the

Accepted Manuscript

This article is protected by copyright. All rights reserved.

successful preparation of two new functionalized imine-based COFs, **TPB-DMTP-COF-R** (R= PhTrz or (*S*)-Py-Boc), in high yield. Moreover, we envision that the utilization of ultra-high vacuum conditions could allow the use of solid azides, as it has been shown that sublimation usually does not cause degradation of these products.[14]

This novel alternative represents a significant advance in a much greener preparation of functional COFs, with an outstanding atom economy, for the post-synthetic modification of functional 2D COFs.

Experimental Section

[HC≡C]$_{0.5}$-TPB-DMTP-COF was prepared according to a reported procedure.[7] In a typical solid-gas synthesis of **TPB-DMTP-COF-R** (R= PhTrz or (*S*)-Py-Boc) **[HC≡C]$_{0.5}$-TPB-DMTP-COF** (25 mg, 0.02 mmol) was placed on a nylon filter (Figure 1). Then, the corresponding azide (0.79 mmol) was heated at 60 ºC, the pressure of the system reduced to 3 Torr and heated at 130-145 °C for 24-48 h. The resulting solids were washed four times with tetrahydrofuran and ethanol giving rise to brown solids.

TPB-DMTP-COF-PhTrz: 24.5 mg, 87 % yield. Elemental Analysis: Calculated for $C_{96}H_{74}N_{12}$×2.5H_2O: C: 75.03 %; H: 5.18 %; N: 10.94 %. Experimental: C: 75.03 %; H: 5.17 %; N: 10.62 %.

TPB-DMTP-COF-(*S*)-Py-Boc: 23 mg, 87 % yield. Elemental Analysis: Calculated for $C_{92}H_{80}N_{10}$×H_2O: C: 74.28 %; H: 5.56 %; N: 9.42 %. Experimental: C: 74.74 %; H: 5.10 %; N: 9.53 %.

Acknowledgements

This work was financially supported by MINECO (MAT2016-77608-C3-1-P and 2-P).

Keywords: Covalent Organic Frameworks • 2D materials • Click Chemistry • Post-Synthetic Modification • Solvent Free Reactions

[1] a) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705-714; b) J. W. Colson, W. R. Dichtel, *Nat. Chem.* **2013**, *5*, 453-465; c) X. Chen, K. Geng, R. Liu, K. T. Tan, Y. Gong, Z. Li, S. Tao, Q. Jiang, D. Jiang, *Angew. Chem., Int. Ed.* **2019**, 10.1002/anie.201904291; d) M. S. Lohse, T. Bein, *Adv. Funct. Mater.* **2018**, *28*, 1705553.

[2] a) D. Rodríguez-San-Miguel, P. Amo-Ochoa, F. Zamora, *Chem. Commun.* **2016**, *52*, 4113-4127; b) R. Mas-Ballesté, C. Gómez-Navarro, J. Gómez-Herrero, F. Zamora, *Nanoscale* **2011**, *3*, 20-30; c) I. Berlanga, M. L. Ruiz-González, J. M. González-Calbet, J. L. G. Fierro, R. Mas-Ballesté, F. Zamora, *Small* **2011**, *7*, 1207-1211; d) P. Albacete, A. López-Moreno, S. Mena-Hernando, A. E. Platero-Prats, E. M. Pérez, F. Zamora, *Chem. Commun.* **2019**, *55*, 1382-1385.

[3] a) S. Royuela, E. Martínez-Periñán, M. P. Arrieta, J. I. Martínez, M. M. Ramos, F. Zamora, E. Lorenzo, J. L. Segura, *Chem. Commun.* **2020**, *56*, 1267-1270; b) G. Das, B. P. Biswal, S. Kandambeth, V. Venkatesh, G. Kaur, M. Addicoat, T. Heine, S. Verma, R. Banerjee, *Chem. Sci.* **2015**, *6*, 3931-3939; c) H. Chen, H. Tu, C. Hu, Y. Liu, D. Dong, Y. Sun, Y. Dai, S. Wang, H. Qian, Z. Lin, L. Chen, *J. Am. Chem. Soc.* **2018**, *140*, 896-899; d) G. Das, F. Benyettou, S. K. Sharama, T. Prakasam, F. Gándara, V. A. de la Peña-O'Shea, N. i. Saleh, R. Pasricha, R. Jagannathan, M. A. Olson, A. Trabolsi, *Chem. Sci.* **2018**, *9*, 8382-8387; e) S. Wang, Q. Wang, P. Shao, Y. Han, X. Gao, L. Ma, S. Yuan, X. Ma, J. Zhou, X. Feng, B. Wang, *J. Am. Chem. Soc.* **2017**, *139*, 4258-4261.

[4] a) E. Vitaku, W. R. Dichtel, *J. Am. Chem. Soc.* **2017**, *139*, 12911-12914; b) Z. Xie, B. Wang, Z. Yang, X. Yang, X. Yu, G. Xing, Y. Zhang, L. Chen, *Angew. Chem., Int. Ed.* **2019**, *58*, 15742-15746.

[5] a) W. Hao, D. Chen, Y. Li, Z. Yang, G. Xing, J. Li, L. Chen, *Chem. Mater.* **2019**, *31*, 8100-8105; b) Y. Li, Q. Chen, T. Xu, Z. Xie, J. Liu, X. Yu, S. Ma, T. Qin, L. Chen, *J. Am. Chem. Soc.* **2019**, *141*, 13822-13828; c) X. Yan, H. Liu, Y. Li, W. Chen, T. Zhang, Z. Zhao, G. Xing, L. Chen, *Macromolecules* **2019**, *52*, 7977-7983.

[6] a) J. L. Segura, S. Royuela, M. Mar Ramos, *Chem. Soc. Rev.* **2019**, *48*, 3903-3945; b) H. Ding, A. Mal, C. Wang, *Mater. Chem. Front.* **2020**, *4*, 113-127; c) Y. Yusran, Q. Fang, S. Qiu, *Isr. J. Chem.* **2018**, *58*, 971-984.

[7] H. Xu, J. Gao, D. L. Jiang, *Nat. Chem.* **2015**, *7*, 905-912.

[8] a) A. Nagai, Z. Guo, X. Feng, S. Jin, X. Chen, X. Ding, D. Jiang, *Nat. Commun.* **2011**, *2*, 536; b) L. Chen, K. Furukawa, J. Gao, A. Nagai, T. Nakamura, Y. Dong, D. Jiang, *J. Am. Chem. Soc.* **2014**, *136*, 9806-9809; c) H. Xu, X. Chen, J. Gao, J. Lin, M. Addicoat, S. Irle, D. Jiang, *Chem. Commun.* **2014**, *50*, 1292-1294; d) N. Huang, R. Krishna, D. Jiang, *J. Am. Chem. Soc.* **2015**, *137*, 7079-7082; e) F. Xu, H. Xu, X. Chen, D. Wu, Y. Wu, H. Liu, C. Gu, R. Fu, D. Jiang, *Angew. Chem., Int. Ed.* **2015**, *54*, 6814-6818; f) L. Merí-Bofí, S. Royuela, F. Zamora, M. L. Ruiz-González, J. L. Segura, R. Muñoz-Olivas, M. J. Mancheño, *J. Mater. Chem. A* **2017**, *5*, 17973-17981; g) Y. Wu, Z. Zhang, S. Bandow, K. Awaga, *Bull. Chem. Soc. Jpn.* **2017**, *90*, 1382-1387; h) A. M. Rice, E. A. Dolgopolova, B. J. Yarbrough, G. A. Leith, C. R. Martin, K. S. Stephenson, R. A. Heugh, A. J. Brandt, D. A. Chen, S. G. Karakalos, M. D. Smith, K. B. Hatzell, P. J. Pellechia, S. Garashchuk, N. B. Shustova, *Angew. Chem., Int. Ed.* **2018**, *57*, 11310-11315; i) S. Royuela, E. García-Garrido, M. Martín Arroyo, M. J. Mancheño, M. M. Ramos, D. González-Rodríguez, Á. Somoza, F. Zamora, J. L. Segura, *Chem. Commun.* **2018**, *54*, 8729-8732; j) S. Royuela, R. Gil-San Millan, M. J. Mancheno, M. Mar Ramos, J. L. Segura, J. A. R. Navarro, F. Zamora, *Materials* **2019**, *12*, 1974; k) B. K. Hughes, W. A. Braunecker, D. C. Bobela, S. U. Nanayakkara, O. G. Reid, J. C. Johnson, *J. Phys. Chem. Lett.* **2016**, *7*, 3660-3665.

[9] N. J. Agard, J. M. Baskin, J. A. Prescher, A. Lo, C. R. Bertozzi, *ACS Chem. Biol.* **2006**, *1*, 644-648.

[10] R. Huisgen, *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565-598.

[11] Z. Li, T. S. Seo, J. Ju, *Tetrahedron Lett.* **2004**, *45*, 3143-3146.

[12] N. J. Agard, J. A. Prescher, C. R. Bertozzi, *J. Am. Chem. Soc.* **2004**, *126*, 15046-15047.

[13] a) F. Gao, S. Aminane, S. Bai, A. V. Teplyakov, *Chem. Mater.* **2017**, *29*, 4063-4071; b) C. He, R. Janzen, S. Bai, A. V. Teplyakov, *Chem. Mater.* **2019**, *31*, 2068-2077.

[14] F. Bebensee, C. Bombis, S.-R. Vadapoo, J. R. Cramer, F. Besenbacher, K. V. Gothelf, T. R. Linderoth, *J. Am. Chem. Soc.* **2013**, *135*, 2136-2139.

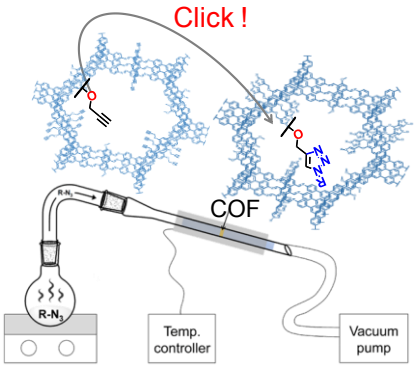
Accepted Manuscript

This article is protected by copyright. All rights reserved.

10.1002/chem.202000224

Entry for the Table of Contents

Graphic for Table of Contents



Text for Table of Contents

Post-synthetic functionalization of imine based-COFs is carried out at solid (COF) – gas (azides) phase, without solvent and catalyst, in high yield. This procedure is a green post-synthetic modification of COFs and a source of 2D materials with high potential for the development of new applications.

WILEY-VCH
Accepted Manuscript

This article is protected by copyright. All rights reserved.