



Tetrazine-Based Metal-Organic Frameworks as Scaffolds for Post-Synthetic Modification by Click Reaction

Madhan Vinu,*^[a,b,c] Kulandaivel Sivasankar,^[c] Samikannu Prabu,^[c] Jeng-Liang Han,^[c] Chia-Her Lin,*^[c] Chun-Chuen Yang,^[d] and Jan Demel*^[a]

Abstract: Metal-organic frameworks are one of the most active research fields today. Despite the progress in recent years, synthesis of highly porous structures bearing functional groups for specific applications remains a challenge. Here, we describe synthesis of Zr(IV) and Hf(IV)-based tetrazine containing metal-organic frameworks, ZrTz-68 and HfTz-68 with pore size of 2.1 nm, specific surface area up to 4217 m² g⁻¹, and a UiO-68 topology. The synthesis can be done on a multi-gram scale from inexpensive linker 4,4'-(1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid (H₂TzDB). Moreover, because of the *n*-conjugated tetrazine groups these MOFs can be easily post-synthetically modified by a "click" reaction maintaining the crystallinity of the framework. Due to the diversity of "clickable" substituents, this strategy represents highly versatile tool for a wide range of applications.

Introduction

Metal-organic frameworks (MOFs) are crystalline porous materials formed by organic multi-dentate ligands with metal centers or metal oxide clusters.^[1,2] Because of the high variability of porosity, surface area, topology, and tunable chemical nature, this class of materials is a rapidly growing area of research.^[3-5] As a result, MOFs are investigated for a variety of potential applications including, gas storage^[6] and separations,^[7] heterogeneous catalysis,^[8-10] sensing,^[11] and drug delivery.^[12] It has been shown, that for certain catalyzed reactions the catalytic centers need to be isolated in order to achieve high catalytic activity.^[13,14] It is very difficult to obtain MOFs equipped with large functional groups in their pore structures by direct solvothermal reactions. However, post-synthetic modification of MOFs have proved to enable addition of functional groups.^[15,16] increasing the hydrophobicity of the pore structure, or the stability.[17]

[d] Prof. C.-C. Yang, Department of Physics, Chung-Yuan Christian University, Chung Pei Road, Chungli, Taoyuan City, 32023, Taiwan

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

Post-synthetic modification (PSM) is a powerful tool that converts as-synthetized MOFs to topologically identical materials with diverse functionalities or enhanced stability.^[18,19] In recent years, PSM evolved so that it allows metal-to-metal exchange in SBUs,^[20] covalent modifications on linker molecules,^[21] exchange of linker molecules, or exchange of terminal ligands at the SBUs.^[22]

Alternatively, the modification can be done through chemical modification of the linker by "click chemistry" to introduce large reactive species into MOFs.^[23-27] In this respect [4+2] cycloaddition of 1,2,4,5-tetrazines and various dienophiles, referred as inverse electron demand Diels-Alder (IEDDA) reaction, represent an attractive reaction that allows reaction of tetraazines with wide range of unsaturated compounds.^[28] Surprisingly, only few tetrazine based MOFs have been described in the literature: Calahorro and co-workers developed tetrazine functionalized potassium 3D MOF for luminescence and cytotoxicity studies,^[29] alternatively Nickerl *et al.* synthetized dihydro-1,2,4,5-tetrazine-3,6-dicarboxylate Zr-MOF by ligand exchange reaction to create an optical sensor for the detection of oxidative agents such as nitrous gases.

In this paper, we report on the direct synthesis of threedimensional tetrazine based zirconium and hafnium MOFs that can be subject to "click reaction" to introduce bulky functional molecules into the pore structure, see Scheme 1. The linear tetrazine dicarboxylate linker forms with $Zr_6O_4(OH)_4^{12+}$ and Hf₆O₄(OH)₄¹²⁺ SBUs MOFs denoted ZrTz-68 and HfTz-68, their structures contain mesoporous channels with 2.1 nm in diameter and specific surface area up to 4217 and 2773 m² g⁻¹ for ZrTz-68 and HfTz-68, respectively. First, we optimized the synthetic procedures in terms of modulator,^[30] time, temperature, activation solvent, and concentration of different modulators. Then, to demonstrate the versatility of postsynthetic modification by "click" reaction we modified the MOFs by three alkene containing organic molecules: Quinine (QV), thioquinine (QVS),^[31-34] and organometallic copper complex CuNONO, see Scheme 1.[35,36] Finally, on the basis of the original synthetic procedures, with only subtle modifications, we demonstrate that both the organic linker and the MOFs can be synthesized on multi-gram scale.

Results and Discussion

Two new zirconium and hafnium MOFs (denoted ZrTz-68 and HfTz-68) were synthesized using novel linear dicarboxylate

 [[]a] Dr. M. Vinu, Dr. J. Demel Department of Materials Science, Institute of Inorganic Chemistry of the Czech Academy of Sciences, v.v.i. Husinec-Řež 1001, Řež, 25068 (Czech Republic)
E-mail: vinuchem06@gmail.com, demel@iic.cas.cz
Homepage: https://demel.iic.cas.cz/

[[]b] Dr. M. Vinu, Department of Chemistry, Karunya Institute of Technology and Sciences (Deemed-to-be University), Karunya Nagar, Coimbatore – 641 114, India

[[]c] Dr. K. Sivasankar, Dr. S. Prabu, Prof. J.-L. Han, Prof. C.-H. Lin, Department of Chemistry, Chung-Yuan Christian University, Chung Pei Road, Chungli, Taoyuan City, 32023, Taiwan

linker 4,4'-(1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid (H₂TzDB), the synthetic procedure of the linker is given in Scheme S1. The MOFs were prepared by solvothermal reactions of H₂TzDB and ZrCl₄ or HfCl₄. In order to obtain good crystallinity, modulators have to be employed, for the list of used modulators and the resulting powder X-ray diffraction patterns (PXRD) see Figure S1. The optimal synthetic conditions found were using N,Ndimethylformamide (DMF) and trifluoroacetic acid as a modulator at 120 °C for 48 h. By this procedure we obtained octahedron-shaped crystalline powders, see Figure 1. Interestingly, when the as-synthetized MOFs were soaked in DMF for 2-30 days the one-month soaked samples show better resolved particles (see Figure 1) with 1-2 µm in size and keeping the PXRD intact. This is probably due to slow recrystallization that takes place in DMF even at RT. The synthesis of the MOF can be readily scaled-up by a factor of 10 and so one batch can yield 3.5 g of ZrTz-68 and 3.6 g of HfTz-68, respectively.



Scheme 1. Synthesis and Post-synthetic modification of ZrTz-68, HfTz-68 MOFs with QV, QVS and CuNONO.





Figure 2. Rietveld fit of ZrTz-68, black dots represent measured data, red curve is a calculated profile, blue line is a difference curve and magenta vertical bars are Bragg's positions of the *hkl* reflections.

The ZrTz-68 crystalize in the space group *Fm-3m*, with a=32.447 Å (Figure-2 & Tables S1, SI) and **fcu** net topology in which the inner $M_6O_4(OH)_4(CO_2)_{12}$ SBU cores are capped by μ_3 -O and μ_3 -OH groups to form the triangular faces, see Figure 3. This SBUs are connected together by twelve carboxylate groups from H_2 TzDB linker to form three-dimensional (3D) structure with tetrahedral and octahedral cages with sizes of 0.9 and 2.2 nm, respectively (Figure 3 and 4). The total solvent-accessible volume for ZrTz-68 is 69% (determined by PLATON).



Figure 1. SEM images of (a), as-synthesized ZrTz-68, (b), one month DMF soaked ZrTz-68, (c), as-synthesized HfTz-68, and (d), one month DMF soaked HfTz-68.

To verify that ZrTz-68 adopts the expected structure of UiO-68 with the exception of the four nitrogen atoms in the tetrazine linker, we employed theoretical modelling using the Materials Studio 5.5, for details see ESI. The unit cell was elongated according to the experimental lattice constants and the atoms of the H₂TzDB linker without hydrogen atoms were inserted. Then, we performed the geometry optimizations which converged to



10.1002/ejic.201901230

WILEY-VCH

Figure 3. View of the ZrTz-68 structure (a), the coordination of twelve linkers around the SBU (b), the formation of tetrahedral cage (c), and octahedral cage (d). Blue polyhedra are Zr_6 SBU, yellow spheres are void spaces, carbon atoms are black, nitrogen atoms are blue, and hydrogen atoms were omitted for clarity.

UiO-67 and 68 are known to be susceptible to hydrolysis on air,^[36] similarly the newly prepared MOFs ZrTz-68 and HfTz-68 have limited stability on humid air. In Figures S2 & S3 is shown that after 6 days there is distinguishable decrease in crystallinity. We also studied the thermal stability by PXRD measured at varied temperature. Interestingly the stability of HfTz-68 is 300°C whereas for ZrTz-68 it is only 200°C, see Figure S4.



Figure 4. The BET isotherm (left) and DFT pore size curve (left) of ZrTz-68(Blue), ZrTz-68(Red).

The porosity of the prepared MOFs was probed by N₂ adsorption at 77 K, both samples exhibit type I(b) isotherm (see Figure 4), which is characteristic for materials containing small mesopores. The Brunauer-Emmett-Teller (BET) specific surface areas, Non-Localized Density Functional Theory (NLDFT) calculated pore sizes, and pore volumes are summarized in Table 1. The specific surface area of ZrTz-68 (4217 m²g⁻¹) is in good agreement with the specific surface area reported for UiO-68 (4170 m²g⁻¹).^[37] The specific surface area of HfTz-68 is lower by ca. 35% in comparison with the Zr analogue which is similar to value of 36 % reported earlier for Zr and Hf analogues of UiO-66.^[38] The pore size distribution shows single pore channel diameter with the maxima at 2.1 nm. Additionally, we measured CO₂ adsorption isotherm at 273 and 298 K for both ZrTz-68 and HfTz-68, see Figure S5.

Click reactions were developed in 1998 by K. Barry Sharpless and since then these reactions have gained tremendous interest due to the simplicity, versatility, and quantitative yield. In this work, we use the cycloaddition of 1,2,4,5-tetrazines with alkene, referred as inverse electron demand Diels-Alder (IEDDA) reaction.^[39] The use of the click reaction allows the introduction of large functional groups into the structure of mesoporous MOFs. Here we selected bulky alkene molecules, specifically quinine, thioquinine, and copper complex CuNONO. We selected benign conditions: 70 °C for 12 h in diethyl ether without any catalyst (Scheme 1). After PSM the powder samples were washed and centrifuged with fresh diethyl ether three times and activated at 120 °C for 12 h. After the click reaction of MTz-68@PSM samples were characterized by FTIR, PXRD, SEM and N₂ adsorption. The PXRD patterns of ZrTz-68@QV, ZrTz-68@QVS, HfTz-68@QV, HfTz-68@QVS, ZrTz-68@CuNONO,

and HfTz-68@CuNONO confirm that the samples after PSM retain the original structure. The small decrease in intensities of diffraction can be caused by the disorder of the newly introduced functional groups, see Figure 5. In Table 1 are compared the specific surface areas, pore volumes, and pore diameters of PSM modified samples with the parent MOFs. It is clear that the PSM modification led to decrease of the specific surface area and pore volume while keeping the pore diameter intact, see Figure 8 and S9(SI). The post-synthetic modification of samples was accompanied by a significant color change from bright pink (ZrTz-68 and HfTz-68) to light brown (MOF@PSM), see Figure 7.



Figure 5. The PXRD patterns of the MTz-68, MTz-68@QV, MTz-68@QVS and MTz-68@CuNONO.

Direct evidence of the PSM can be obtained from the IR-spectra. In Figure 6 are compared spectra of parent MOFs and MOF@QVS. The FTIR spectrum of the parent MOFs display several characteristic absorptions that are weakened after PSM, namely 1414 cm⁻¹ from N=N and 1345 cm⁻¹ from C–N=N–C,^[40] simultaneously new C-H stretching vibrations at 2800-3000 cm⁻¹ arise from the alkene molecules. The FTIR spectra of the MOF@QV and MOF@CuNONO are given in the SI (Figure S6-S8). After post-synthetic modified samples morphology of particles were characterized using SEM images given in the SI (Figure S-10).

The PSM is also accompanied by increased stability of the resulting MOFs. As discussed above, the as-synthesized MOF samples lose their crystallinity at room temperature on humid air in one week, on the other hand, the PSM modified MOF samples are stable in humid air, see Figure S3 (SI).





Figure 6. FT-IR spectra of QVS compared with before and after post-synthetic modified ZrTz-68 and HfTz-68.



Figure 7. The color changes of MOFs compared with PSM samples of first (a) ZrTz-68, (b)ZrTz-68@QV, (c)ZrTz-68@QVS, (d)ZrTz-68@CuNONO and second HfTz-68.



1200

Figure 8. The BET isotherm of (a) ZrTz-68(Black), ZrTz-68@QV(Blue), ZrTz-68@QVS(Red), ZrTz-68@CuNONO(Green), (b) HfTz-68(Black), HfTz-68@QV(Blue), HfTz-68@QVS(Red), and HfTz-68@CuNONO(Green).

Table 1. BET specific surface areas of MOFs compared before and after post-synthetic modification derived from $N_{\rm 2}$ isotherm.

No.	MOF	BET Surface Area (m² g ⁻¹)	Pore Volume (cm³ g ⁻¹)	Pore Diameter (nm)
1	ZrTz-68	4217	1.72	2.1
2	HfTz-68	2773	1.24	2.1
3	ZrTz-68@QV	1348	0.69	2.0
4	ZrTz- 68@QVS	746	0.67	2.2
5	HfTz-68@QV	1224	0.59	2.1
6	HfTz- 68@QVS	757	0.27	2.0
7	ZrTz- 68@CuNONO	1005	0.46	2.1
8	HfTz-	909	0.48	2.0



68@CuNONO

Conclusions

We have demonstrated that tetrazine based linkers are suitable for the preparation of UiO-68 analogues ZrTz-68 and HfTz-68. The MOFs display high porosity with specific surface area up to 4217 m² g⁻¹ and pore diameter of 2.1 nm. The synthesis was done using simple solvothermal method which can be easily scaled up. The main advantage of the tetrazine linker is the possibility of post-synthetic modification via click reaction. We have demonstrated that it is possible to introduce bulky functional groups without compromising the structure, crystallinity, and morphology of MOFs. We believe that postsynthetic modification of MOFs by click reactions is better suited for the introduction of bulky organic molecules than other postsynthetic modification strategies such as ligand exchange. The main advantages are nonnecessity to synthetize new linker molecule bearing carboxylic acid groups and overcoming solubility issues of such bulky molecule.

Experimental Section

1. Materials and Methods

Chemicals of reagent grade or better were used as received. The conventional (glass vial) or heat and stirring (round bottom flask; RB) reactions were carried out at 120 °C for 2 day. Elemental analyses were carried out to confirm the composition of the organic part of the prepared samples. FTIR spectra were recorded in the range of 400-4000 cm⁻¹ on a JASCO FTIR-460 spectrophotometer using KBr pellets. Thermal gravimetric analyses (TGA) using a DuPont TA Q50 analyzer were performed on powder samples under flow of N2 with a heating rate of 10 °C min⁻¹. The gas sorption isotherms were measured at 77 K for $N_{2},\,$ and 273 and 298 K for CO2 using 3flex system of Micromeritics. Ultrahigh purity grade N_2 and He gas were used as received. Before the gas sorption measurements, the sample was initially dehydrated at 453 K for 12 h under vacuum. Field-emission scanning electron microscopy images (SEM) were collected using a JEOL JSM-7600F. Dried powder samples were deposited on carbon tape and coated with platinum prior to the measurement.

2. Synthesis of Linker

Synthesis of 4,4'-(1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid):

The 4-cyanobenzoic acid (6.0 g, 40 mmol) was added to a 100 mL RB flask followed by addition of 35% hydrazine solution (40.0 mL). Then the solution was heated to 80-85 °C under reflux for 4 h with stirring. After cooling to room temperature, the yellow colored solid was collected by filtration and washed with water (2×50 mL). The solid was added to

acetic acid (60 mL) followed by an aqueous solution of 30 mL NaNO₂ (8.2 g, 120 mmol) at 0 °C for 3 h under stirring. The purple colored tetrazine compound was collected by filtration and washed with water (2×50 mL). The solid was collected and dried in an oven at 90 °C to give a purple product (yield = 3.0 g, 46.88% based on 4-cyanobenzoic acid).

3. MOF Synthesis

Synthesis of $[M_6O_4(OH)_4(C_{16}N_4H_8O_4)]$, (M= Zr, Hf) (ZrTz-68 and HfTz-68)

The preparation of both ZrTz-68 and HfTz-68 was done by solvothermal method:0.105 g of ZrCl₄ or 0.144 g of HfCl₄ (both 0.45 mmol), 0.145 g of H₂TzDB (0.45 mmol) and 0.2 mL of trifluoroacetic acid were mixed in 25 mL of DMF in a 100 mL RB flask by 10 min ultra-sonication. The solution was heated with stirring in oil bath at 120 °C for 2 days. After cooling to room temperature the powder was centrifuged and washed with fresh DMF three times. After that, the sample was immersed in DMF and CHCl₃ for 2 days respectively. Then dried under vacuum at 120 °C for 2-12 h, and collected with the yield of 350 mg. The large scale synthesis of both MOFs was done by increasing the amount of all components 10 times yielding 3.5 g from one batch. The resulting MOF exhibited identical PXRD and sorption of N₂ as MOF produced by the standard procedure.

3. Post-Synthetic Modification

Synthesis of MTz-68@QV, MTz-68@QVS and MTz-68@CuNONO

To 0.01 mmol of the as-synthesized ZrTz-68 (0.0275 g, 0.01 mmol) or HfTz-68 (0.0312 g, 0.01 mmol) was added QV (0.05 mmol), QVS (0.05 mmol), or CuNONO (0.01 mmol) followed by 5 mL of diethyl ether in a 25 mL glass vial. The mixture was stirred at 70 °C for 12 h. After cooling to room temperature the resulting powder was centrifuged and washed there times with fresh diethyl ether and dried under vacuum at 120 °C to give samples denoted: ZrTz-68@QV, ZrTz-68@QVS, HfTz-68@QV, HfTz-68@QVS, HfTz-68@QVS,

Acknowledgments

Financial support from Ministry of Science and Technology, Taiwan and Chung Yuan Christian University are gratefully acknowledged.

Keywords: Tetrazine • metal-organic framework • functional groups post-synthetic modification • click reaction

- A. J. Howarth, A. W. Peters, N. A. Vermeulen, T. C. Wang, J. T. Hupp, O. K. Farha, *Chem. Mater.* **2016**, *29*, 26-39.
- [2] M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J.T. Hupp, O. K. Farha, *Chem. Commun.* **2013**, *49*, 9449-9451.
- [3] S. Horike, S. Shimomura, S. Kitagawa, *Nature chem.* **2009**, *1*, 695-704.
- [4] M. Kondo, T. Yoshitomi, H. Matsuzaka, S. Kitagawa, K. Seki, Angew. Chem., Int. Ed. 1997, 36, 1725-1727.
- [5] H. Reinsch, M. A. van der Veen, B. Gil, B. Marszalek, T. Verbiest, D. De Vos, N. Stock, *Chem. Mater.* **2012**, *25*, 17-26.
- [6] D. S. Raja, I.-H. Chang, Y.-C. Jiang, H.-T. Chen, C.-H Lin, *Micropor. Mesopor. Mater.* 2015, 216, 20-26.
- [7] M. Vinu, D. S. Raja, Y.-C. Jiang, T.-Y. Liu, Y.-Y. Xie, Y.-F. Lin, C.-C. Yang, C.-H. Lin, S. M. Alshehri, T. Ahamad, R. R. Salunkhe, Y.

Yamauchi, Y.-H. Deng, K. C.-W. Wu J. Taiwan Inst. Chem. Eng. 2018, 83, 143-151.

- [8] M. Vinu, W.-C. Lin, D. S. Raja, J.-L. Han, C.-H. Lin, *Polymers* 2017, 9, 498.
- [9] I. Luz, X.F.L. Xamena, A. Corma, J. Catal. 2010, 276, 134-140.
- [10] Z.-X. Xu, Y.-X. Tan, H.-R. Fu, J. Liu, J. Zhang, *Inorg. Chem.* 2014, 53, 12199-12204.
- [11] S. Shimomura, S. Kitagawa, J. Mater. Chem. 2011, 21, 5537-5546.
- [12] P. Horcajada, C. Serre, M. Vallet-Regí, M. Sebban, F. Taulelle, G. Férey, Angew. Chem. Int. Ed. 2006, 45, 5974-5978.
- [13] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Chem. Commun. 2012, 48, 11275-11288.
- [14] M. Gustafsson, A. Bartoszewicz, B. Martín-Matute, J. Sun, J. Grins, T. Zhao, Z. Li, G. Zhu, X. Zou, *Chem. Mater.* **2010**, *22*, 3316-3322.
- [15] J. Hynek, S. Ondrušová, D. Bůžek, P. Kovář, J. Rathouský, J. Demel, *Chem. Commun.* **2017**, *53*, 8557-8560.
- [16] S. Castellanos, K. B. S. Sankar Gupta, A. Pustovarenko, A. Dikhtiarenko, M. Nasalevich, P. Atienzar, H. García, J. Gascon, F. Kapteijn. *Eur. J. Inorg.* 2015, *28*, 4648-4652.
- [17] P. Deria, Y. G. Chung, R. Q. Snurr, J. T. Hupp, O. K. Farha, *Chem. Sci.* 2015, 6, 5172-5176.
- [18] K.K. Tanabe, S. M. Cohen, Chem. Soc. Rev. 2011, 40, 498-519.
- [19] R. J. Marshall, R. S. Forgan, Eur. J. Inorg. Chem. 2016, 4310-4331.
- [20] S. Yuan, W. Lu, Y.-P. Chen, Q. Zhang, T.-F. Liu, D. Feng, X. Wang, J. Qin, H.-C. Zhou, J. Am. Chem. Soc. 2015, 137, 3177-3180.
- [21] P. Deria, J. E. Mondloch, O. Karagiaridi, W. Bury, J. T. Hupp, O. K. Farha, *Chem. Soc. Rev.* 2014, 43, 5896-5912.
- [22] B. Li, B. Gui, G. Hu, D. Yuan, C. Wang, *Inorg. Chem.* 2015, 54, 5139-5141.
- [23] A.-C. Knall, C. Slugovc, Chem. Soc. Rev. 2013, 42, 5131-5142.
- [24] M. Savonnet, A. Camarata, J. Canivet, D. Bazer-Bachi, N. Bats, V. Lecocq, C. Pinel, D. Farrusseng, *Dalton Trans.* 2012, *41*, 3945-3948.
- [25] H. L. Jiang, D. Feng, T. F. Liu, J. R. Li, H. C. Zhou, J. Am. Chem. Soc. 2012, 134, 14690-14693.

- [26] C. Liu, T. Li, N. L. Rosi, J. Am. Chem. Soc. 2012, 134, 18886-18888.
- [27] B. Gui, X. Meng, H. Xu, C. Wang, *Chin. J. Chem.* **2015**, *34*, 186-190.
- [28] A. J. Calahorro, B. Fernández, C. García-Gallarín, M. Melguizo, D. Fairen-Jimenez, G. Zaragoza, A. Salinas-Castillo, S. Gómez-Ruiz, A. Rodríguez-Diéguez, *New J. Chem.* **2015**, *39*, 6453-6458.
- [29] C. Wang, J.-L. Wang, W. Lin, J. Am. Chem. Soc. 2012, 134, 19895-19908.
- [30] H. Y. Bae, S. Some, J. S. Oh, Y. S. Lee, C. E. Song, *Chem. Commun.* 2011, 47, 9621-9623.
- [31] J. M. Andrés, J. Losada, A. Maestro, P. Rodríguez-Ferrer, R. Pedrosa, J. Org. Chem. 2017, 82, 8444-8454.
- [32] D. Mailhol, M. d. M. S. Duque, W. Raimondi, D. Bonne, T. Constantieux, Y. Coquerel, J. Rodriguez, Adv. Synth. Catal. 2012, 354, 3523-3532.
- [33] P. Kasaplar, P. Riente, C. Hartmann, M. A. Pericàs, Adv. Synth. Catal. 2012, 354, 2905-2910.
- [34] M. Ulusoy, O. Şahin, A. Kilic, O. Büyükgüngör, Catal. Lett. 2011, 141, 717-725.
- [35] M. Y. Wani, S. Kumar, C. T. Arranja, C. M. F. Dias, A. J. F. N. Sobral, New J. Chem. 2016, 40, 4974-4980.
- [36] M. C. Lawrence, C. Schneider, M. J. Katz, Chem. Commun. 2016, 52, 4971-4974.
- [37] J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud, J. Am. Chem. Soc. 2008, 130, 13850-13851.
- [38] S. Jakobsen, D. Gianolio, D. S. Wragg, M. H. Nilsen, H. Emerich, S. Bordiga, C. Lamberti, U. Olsbye, M. Tilset K. P. Lillerud, *Phy. Rev. B*. 2012, *86*, 125429.
- [39] M. L. Blackman, M. Royzen, J. M. Fox, J. Am. Chem. Soc. 2008, 130, 13518-13519.
- [40] Q. Wang, J. Wu, Y. Gao, Z. Zhang, J. Wang, X. Zhang, X. Yan, A. Umar, Z. Guo, D. O'Hare, *RSC Adv.* 2013, 3, 26017-26024.

WILEY-VCH

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Text for Table of Contents



Post-Synthetic Modified MOF*

Dr. Madhan Vinu, Dr. Kulandaivel Sivasankar, Dr. Samikannu Prabu, Prof. Jeng-Liang Han, Prof. Chia-Her Lin, Prof. Chun-Chuen Yang and Dr. Jan Demel.

Page No. – Page No.

Tetrazine-Based Metal-Organic Frameworks as Scaffolds for Post-Synthetic Modification by Click Reaction

* The π -conjugated tetrazine containing metal-organic frameworks, ZrTz-68 and HfTz-68 with pore size of 2.1 nm, specific surface area up to 4217 m² g⁻¹ MOFs can be easily post-synthetically modified by a "click" reaction maintaining the crystallinity of the framework and stability.