

Accepted Article

Title: Vinylene-Linked Covalent Organic Frameworks by Base-Catalyzed Aldol Condensation

Authors: Amitava Acharjya, Pradip Pachfule, Jerome Roeser, Franz-Josef Schmitt, and Arne Thomas

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201905886 Angew. Chem. 10.1002/ange.201905886

Link to VoR: http://dx.doi.org/10.1002/anie.201905886 http://dx.doi.org/10.1002/ange.201905886

WILEY-VCH

WILEY-VCH

Vinylene-Linked Covalent Organic Frameworks by Base-Catalyzed Aldol Condensation

Amitava Acharjya,^a Pradip Pachfule,^a Jérôme Roeser,^a Franz-Josef Schmitt,^a and Arne Thomas^a*

Abstract: The development of new linkages and synthetic routes for the formation of 2D covalent organic frameworks (COFs) is a challenging task. Herein, we report the synthesis of two vinylene (-CH=CH-) linked COFs (V-COF-1 and V-COF-2), by exploiting the electron deficient nature of the aromatic s-triazine unit of $C_{3^{-}}$ symmetric 2,4,6-trimethyl s-triazine (TMT). The acidic terminal methyl hydrogens of TMT can easily be abstracted by a base, resulting in a stabilized carbanion, which further undergoes aldol condensation with multitopic aryl aldehydes to be reticulated into extended crystalline frameworks (V-COFs). Both V-COF-1 (with terepthalaldehyde (TA)) and V-COF-2 (with 1,3,5-tris(pformylphenyl)benzene (TFPB)) are polycrystalline and exhibit permanent porosity and BET surface areas of 1341 m².g⁻¹ and 627 m².g⁻¹ respectively. Due to the close proximity (3.52 Å) of the pre-organized vinylene linkages within adjacent 2D layers stacked in eclipsed fashion, [2+2] photo-cycloadditon in V-COF-1 was observed to form covalent crosslinks between the COF layers.

The discovery of Covalent Organic Frameworks (COFs) demonstrated that organic building blocks could be reticulated via strong covalent bonds into well-ordered 2D and 3D extended crystalline frameworks.^[1-6] These ordered crystalline materials feature defined porosities and functionalities and have consequently garnered increasing attention in various applications such as gas storage and separation,^[7,8] energy storage,^[9,10] photovoltaics,^[9,11] opto-electronics,^[12,13] proton and ion conduction^[14-19] and heterogeneous catalysis.^[20-26] The formation of such extended crystalline frameworks is generally achieved by implementing reversible condensation reactions in order to polymerize rigid building blocks. Careful control over the rate of reversible bond formation allow the construction of the desired crystalline framework by applying the principles of reticular chemistry.^[27-29] Until recently, linkages (i.e. bonds formed to reticulate the building blocks) reported for COF synthesis were mostly based on reversible B-O, [1,2,16,30,31] B-N, [32] Si-O^[33,34] and C-N bond formation^[35-39]. The reversible nature of those linkages affected by the insertion-deletion of water molecules, allow the formation of the desired extended crystalline frameworks, but was also identified to be detrimental in terms of chemical stability, especially in aqueous media.^[28,40] Indeed, although thermally robust, many COFs are prone to hydrolysis and structural collapse in aqueous/acidic media or even in contact with moisture. Several strategies, including ketoenol tautomerization,^[35] interlayer stacking optimization^[36] or post-functionalization^[41,42] have been applied to circumvent these limitations, yielding COFs featuring high chemical and thermal stability.

In this context, recently reported 2D COFs based on

 Mr. A. Acharjya, Dr. P. Pachfule, Dr. J. Roeser, Dr. F-J. Schmitt, Prof. Dr. A. Thomas.
Department of Chemistry-Functional Meterials Technische Universität Berlin Hardenbergstr. 40, BA2, 10623 Berlin (Germany) E-mail: arne.thomas@tu-berlin.de cyanovinylene [-CH=C(CN)-] linkages hold the promise for the generation of chemically stable COFs as the cyanovinylene linkage is significantly less prone to hydrolysis compared to boroxine, boronate ester or imine linkages, mostly used for the synthesis of COFs.^[10,43] The challenge to crystallize a COF by reversible [-CH=C(CN)-] bond formation was overcome by implementing reversible Knoevenagel condensation of 1,4 phenylenediacetonitrile (PDAN) with multitopic aldehyde-functionalized building blocks. Such COFs featuring fully conjugated backbones are also promising materials in terms of optoelectronic or photovoltaic applications.^[44]

Herein, we report the synthesis of two purely vinylene (-CH=CH-) linked 2D COFs (V-COF-1 and V-COF-2) achieved by base-catalyzed reversible aldol condensation, exploiting the highly electron deficient s-triazine core of 2,4,6-trimethyl striazine (TMT). The methyl protons of TMT are acidic and undergo base catalyzed aldol condensation with benzaldehyde to yield 2,4,6 tri-styryl triazine quantitatively (Scheme 1a).[45,46] V-COF-1 and V-COF-2 were obtained by extending this model reaction to terepthalaldehyde (TA) and 1,3,5-tris(4-formyl)phenyl benzene (TFPB) (Scheme 1b). During our investigation on the base-catalyzed pathway, Yaghi et. al. reported the acidcatalyzed synthesis of a biphenyl analogue of V-COF-1, which however could not be synthesized after extensive trials employing basic conditions.^[47] On the other hand, we were so far also unable to synthesize crystalline V-COF-1 and -2 using the reported acid-catalyzed pathway, showing that the choice of catalytic pathway and solvent can be crucial to obtain V-COFs with varying backbone structure. V-COF-1 and V-COF-2, possess surface areas (SA_BET) of 1341 $m^2 \cdot g^{\text{-1}}$ and 627 $m^2 \cdot g^{\text{-1}},$ respectively. Although chemically and thermally stable, we identified that V-COF-1 is photo-responsive, as the preorganized vinylene groups of adjacent 2D layers offer a platform for [2+2] cycloaddition upon UV-Vis irradiation fulfilling Schmidt's criteria for photo-cyclization.[48]



Scheme 1. V-COF synthesis. (a) Illustration of the base catalyzed aldol condensation of 2,4,6 trimethyl s-triazine (TMT) and Terepthalaldehyde (TD) to yield 2,4,6 tristylryl s-triazine (TST). (b) Schematic representation of reticulation of the crystalline V-COFs by the condensation of 2,4,6 trimethyl s-triazine with ditopic or tritopic aldehydes respectively.

WILEY-VCH



Figure 1. Synthesis and structural characterization of V-COFs (a) Synthetic conditions for the reticulation of V-COF-1 and V-COF-2, (b) PXRD pattern of the V-COF-1 and V-COF-2 experimental pattern (black), Pawley refined profile curve (red), Bragg diffractions (brown), difference (orange), simulated pattern from eclipsed (green) and (c) Structural models of both V-COF-1 and V-COF-2 with their respective stacking patterns.

Syntheses of V-COF-1 and V-COF-2 were performed by solvothermal condensation of 2,4,6 trimethyl *s*-triazine (TMT) with terepthalaldehyde (TA) and 1,3,5-tris(4-formyl)phenyl benzene (TFB), in 7:1 and 1:1 (methanol: mesitylene) solvent mixtures respectively, for 4 days at 180 °C in presence of NaOH as base (Figure 1a). Both the COFs were collected as light-yellow polycrystalline solids by filtration and further washed with methanol, water and acetone before being dried under vacuum at 100 °C overnight.

Crystallinity of V-COF-1 and V-COF-2 was assessed by powder X-ray diffraction (PXRD) analyses. The experimental PXRD pattern of V-COF-1 and V-COF-2 confirmed the formation of a crystalline framework with no evidence of remaining starting material (Figure S2). Given the connectivity of the building blocks, several models with different stacking modes were generated in hexagonal 2D nets with hcb topology (Section S4). A good match was found between the experimentally obtained PXRD patterns and the calculated patterns of a fully eclipsed model (Figure 1, Figure S3, S5). The final lattice parameters were extracted after Pawley refinement and V-COF-1 was found to crystallize in a hexagonal unit cell (P6/m, a = b = 21.6934 Å, c = 3.5232 Å, $R_P = 2.66$ %; $R_{WP} = 3.40$ %) with similar unit cell parameters as the isoreticular LZU-1 constructed from benzene nodes and imine linkages.^[49] V-COF-2 was poorly crystalline as evidenced by the broad diffraction peaks observed experimentally, but was found to crystallize in a similar hexagonal unit cell (space group: $P\overline{6}$, a = b = 17.5632 Å, c=3.4544 Å, $R_p = 2.82\%$; $R_{wp} = 3.58\%$) (Figure 1, Figure S4, S6).

Fourier transform infrared (FT-IR) spectroscopy analyses were applied to assess the structural integrity of the crystalline framework (Figure 2a). Complete disappearance of -C=O- stretching frequency of starting aldehyde monomers at 1690 cm⁻¹ and appearance of a new band at 1631 cm⁻¹ attributed to - C=C- stretching indicated complete condensation of the starting building blocks and the successful formation of the vinylene linkage in V-COF-1 and V-COF-2.

¹³C cross-polarization magic angle spinning nuclear magnetic resonance (CP-MAS NMR) spectroscopy confirmed the full conversion of starting monomers as no residual carbonyl resonance located at δ~190 ppm could be detected. The two expected signals for the vinylene (-C=C-) carbons at ~138.1 ppm and ~132.1 ppm in COFs could be unambiguously assigned within the aromatic carbon signals (figure 2b, Figure S7). V-COF-1 and V-COF-2 surprisingly exhibited two distinct signals for the aromatic triazine carbon atoms at ~172.9 and ~166.4 ppm in the ¹³C CP-MAS NMR spectra, respectively, while just one peak, as expected, was observed for the molecular model compounds. Splitting of the triazine signals has been also observed in the solid state ¹³C NMR spectrum of Melamine and was attributed to different H-bonding environment leading to two chemically inequivalent carbon atoms.[50,51] However, this explanation could be ruled out here, since there is no electron deficient hydrogen donor within the building blocks. Instead, the second triazine environment is caused by a [2+2] cycloaddition between vinylene groups.^[52-54] This is corroborated by the presence of a broad signal in the aliphatic region (δ ~38.1 ppm) indicating the formation of cyclobutane moieties in the COFs (see below).

The permanent porosity of the V-COF-1 and V-COF-2 frameworks was evaluated by low-pressure nitrogen (N_2) and argon (Ar) sorption studies on evacuated samples, at 77 K and 87 K, respectively. A steep gas uptake in the low relative

WILEY-VCH



Figure 2. Structural characterization of V-COFs (a) FT-IR analyses of V-COFs with the starting materials (TMT and TD) and model compound (TST). (b) ¹³C CP-MAS NMR spectra of V-COF-1 and V-COF-2 and model compound (TST). (c) N₂ sorption measurements of V-COF-1 and V-COF-2 powders.

pressure range (p/p₀ < 0.05) of the N2 adsorption branch shows the microporosity of the samples (Figure 2c). The Brunauer-Emmett-Teller surface areas (SA_{BET}) calculated from the N₂ adsorption were found to be 1341 m².g⁻¹ and 627 m².g⁻¹, respectively. The SA_{BET} of V-COF-1 is almost twice as high as the SA_{BET} reported for the isoreticular LZU-1 COF (729 m².g⁻¹).^[55,56] The corresponding pore size distribution of 1.69 nm was derived by fitting the Ar adsorption branch data at 87 K with a cylindrical quenched-solid density functional theory (QSDFT) model, and matched well with the theoretically calculated pore size of 1.6 nm of the proposed eclipsed structural model (Figure S8). The pore size distribution of V-COF-2 was found to be centered at 0.82 nm, derived by fitting the N₂ adsorption branch data at 77K with the QSDFT model and again matched well with theoretically calculated pore size of 0.8 nm (Figure S9).

Architectural stability of the V-COF-1 and V-COF-2 was investigated by thermogravimetric analysis (TGA) under N₂ atmosphere (Figure S10, S11). After an initial weight loss of ~2 wt% due to desorption of adsorbed solvents below 100 °C, the frameworks remained stable until 400 °C. Chemical stability of crystalline V-COF-1 and V-COF-2 was further investigated in harsh acidic and basic conditions (Figure S12, S13). Both V-COF-1 and V-COF-2 were found to be stable in concentrated acidic and basic medium for at least 4 days. V-COF-1 was also found to be stable in common organic solvents such as THF, acetone and DMF, for 4 days, with no signs of decomposition (Figure S14).

Considering the high crystallinity and conjugated structure, we investigated the optical properties of V-COF-1. The diffuse reflectance UV-Vis (UV-DRS) spectrum of V-COF-1 shows a distinct red shift in absorbance with respect to the monomers (TD and TMT), indicating a higher degree of conjugation (Figure S15). V-COF-1 shows an absorbance edge at ~410 nm, whereas the absorbance tail is extended up to ~535 nm. Interestingly, V-COF-1 was found to be photosensitive, as the light yellow colour of pristine COF powders slowly faded with time upon sunlight irradiation, indicating a structural change within V-COF-1 (Figure 3a). To further elucidate the effect of light irradiation, V-COF-1 powder was irradiated directly with UV-Vis light (λ ~320-500 nm) considering that the maximum absorbance of the COF lies within this wavelength range

(Section S10). ¹³C CP-MAS NMR spectra of the irradiated (48h) sample revealed the formation of cyclobutane moieties between the COF layers. At the same time, the vinylene carbon signal (δ ~138.1, 132.4 ppm) intensity significantly decreased and the ratio of the triazine carbon signals (at δ ~172.9 and ~166.4) reversed compared to the pristine COF (Figure 3b). A broad signal at (δ ~ 38.1 ppm) at the aliphatic region of the ¹³C CP-MAS NMR spectra proved the formation of cyclobutane moieties unambiguously.

Solid-state supramolecular photochemistry offers an efficient way to engineer new functional polymers by taking advantage of the preorganization of reactive moieties in the crystalline matrix.^[57-59] In general, different strategies such as hydrogen bonding interaction, $\pi \cdots \pi$ stacking and metal ligand interactions have been explored to control the topochemical arrangement of the reactive modules. Efficient $\pi \cdots \pi$ stacking of 2D layers within 2D COFs offer a suitable platform for the preorganization of photo-reactive moieties in a particular fashion to undergo photochemical reaction.[60] Topochemical [2+2] photocycloaddition in solid state requires parallel orientation of two double bonds within a distance of 3.5-4.2Å, entailed by Schmidt's criteria.^[48] Thus, preorganization of the vinylene based templates are necessary for controlled synthesis of new 2D or 3D polymers. Schlüter et. al. reported the synthesis of a 2D polymer by topochemical [2+2] photocycloaddition of a trivinyleneic monomer, whereas numerous vinyleneic building units inside metal organic frameworks (MOFs) or coordination polymers are also reported to undergo [2+2] cycloaddition.[61,62] Considering the high crystallinity and eclipsed stacking of 2D layers, V-COF-1 offers a suitable platform for [2+2] photocycloaddition within the vinylene linkages of adjacent layers. Still, this is the first report where parallel oriented vinylene moieties of adjacent layers undergo [2+2] cycloaddition within the 2D layers of a covalent organic framework.

The effect of formation of cyclobutane from the vinylene linkages was also observed in the fluorescence emission spectrum of the V-COF-1 powders measured over time with light irradiation (Figure 3d). The pristine COF powders dispersed in ethanol was found to be highly fluorescent upon excitation of λ ~365 nm. With light irradiation over time, a fast quenching a of fluorescence emission together with the a blue-shift of the

10.1002/anie.201905886

WILEY-VCH



Figure 3. Effect of light irradiation on V-COF-1. (a) Photographs of powder V-COF-1 before and after light irradiation in dispersion (b) Changes in ¹³C CP-MAS NMR spectrum before and after light irradiation. (c). Change in N2 sorption isotherm of V-COF-1 before (V-COF-1) and after light irradiation (V-COF-1-Light). (d) Fluorescence emission quenching upon irradiation of light with time, monitored by fluorescence emission spectroscopy.

emission maximum was observed and fluorescence emission completely quenched after 10 minutes. This is expected, as the degree of conjugation decreases upon formation of cyclobutane from conjugated vinylenes.^[63]

Crystallinity of V-COF-1 was affected upon the [2+2] photo-cycloaddition, as sp^2 -hybridized vinylene carbons convert to sp^3 -cyclobutane species causing severe strain within the crystalline lattice (Figure 4). To compensate the strain within the 2D layers, V-COF-1 framework renders amorphous (Figure S17). Such a change in crystallinity upon [2+2] photocycloaddition within crystalline lattices is expected and has been widely investigated in vinylene-based monomer single crystals, sometimes with photosalient effect.^[64] Interestingly, the framework remained porous even after exposure to UV-vis irradiation for long time (48h) with a SA_{BET} of 1093 m².g⁻¹ (Figure 3c).



Figure 4. Illustration of the structural changes of V-COF-1 lattice from Side view and change in chemical environment upon [2+2] photocycloaddition. (Note that the partial cycloaddition of vinylenes is represented, corroborating the ¹³C CP-MAS NMR spectrum of V-COF-1 after light irradiation).

In summary, we report the successful crystallization of two vinylene linked 2D COFs (V-COF-1 and V-COF-2), new achieved by base catalyzed aldol condensation of TMT with ditopic terepthalaldehyde (TD) and tritopic 1,3,5-tris(pformylphenyl)benzene (TFPB). This work demonstrates a successful strategy to exploit highly electron deficient s-triazine core for the crystallization of 2D vinylene linked COFs by base catalyzed condition. Both the COFs were found to be chemically stable in concentrated acidic as well as in basic condition. [2+2] photo-cycloaddition within the columnar $\pi \cdots \pi$ stacked 2Dlayers of a COF was observed for the first time upon UV-vis light irradiation on V-COF-1 powders. Loss of crystallinity of V-COF-1 was observed after light irradiation due to formation of highly strained cyclobutane rings within the 2D layers, as confirmed by ¹³C CP-MAS NMR spectrum. However, the framework remains porous with a SABET of 1093 m².g⁻¹ even after exposure to UVvis irradiation for long time (48h). Therefore, our focus is now dedicated towards the cycloreversion of the cyclobutanes, which could lead to a photo-switchable crystalline framework and could be implemented as a rewritable memory storage device. However, such a task is extremely difficult to achieve in solid polycrystalline state, as the [2+2] cycloreversion from cyclobutane to parent vinylenes can follow different pathways. Thus, suitable conditions to photoswitch the framework is currently under investigation.

Acknowledgements

This work is funded by the "Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC 2008/1 (UniSysCat) – 390540038". A.A. thanks the BIG-NSE and Unicat for doctoral fellowship. We thank Mrs. Christina Eichenauer and Mrs. Maria Unterweger for their assistance. Dr. Matthias Trunk, Mr. Nicolas Chaoui and Dr. Johannes Schmidt are acknowledged for the fruitful discussions.

Keywords: Covalent Organic Frameworks (COFs)• Vinylene linked• Porous polymer • π ··· π stacking • [2+2] cycloaddition

References:

- [1] A. P. Cote, M. O. Keeffe, N. W. Ockwig, A. J. Matzger, O. M. Yaghi, *Science* **2005**, *310*, 1166–1171.
- [2] H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O'Keeffe, O. M. Yaghi, *Science* 2007, 316, 268–72.
- [3] P. J. Waller, F. Gándara, O. M. Yaghi, Acc. Chem. Res. 2015, 48, 3053–3063.
- [4] C. S. Diercks, O. M. Yaghi, Science 2017, 355, eaal1585.
- [5] X. Feng, X. Ding, D. Jiang, Chem Soc Rev 2012, 41, 6010–22.
- [6] T. Ma, E. A. Kapustin, S. X. Yin, L. Liang, Z. Zhou, J. Niu, L.-H. Li, Y. Wang, J. Su, J. Li, et al., *Science* **2018**, *361*, 48–52.
- [7] S. Zhao, B. Dong, R. Ge, C. Wang, X. Song, W. Ma, Y. Wang, C. Hao, X. Guo, Y. Gao, *RSC Adv.* 2016, *6*, 38774–38781.
- [8] C. J. Doonan, D. J. Tranchemontagne, T. G. Glover, J. R. Hunt, O. M. Yaghi, *Nat. Chem.* 2010, 2, 235–238.
- [9] S. Chandra, D. Roy Chowdhury, M. Addicoat, T. Heine, A. Paul, R. Banerjee, Chem. Mater. 2017, 29, 2074–2080.
- [10] X. Zhuang, W. Zhao, F. Zhang, Y. Cao, F. Liu, S. Bi, X. Feng, Polym.

WILEY-VCH

Chem. 2016, 7, 4176–4181.

COMMUNICATION

- [11] S. Wan, J. Guo, J. Kim, H. Ihee, D. Jiang, Angew. Chem. Int. Ed. 2009, 48, 5439–5442.
- [12] D. D. Medina, T. Sick, T. Bein, D. D. Medina, T. Sick, T. Bein, 2017, 1700387, 1–8.
- [13] J. Guo, Y. Xu, S. Jin, L. Chen, T. Kaji, Y. Honsho, M. A. Addicoat, J. Kim, A. Saeki, H. Ihee, et al., *Nat. Commun.* **2013**, *4*, 1–8.
- [14] Q. Xu, S. Tao, Q. Jiang, D. Jiang, J. Am. Chem. Soc. 2018, 140, 7429– 7432.
- [15] C. Montoro, D. Rodríguez-San-Miguel, E. Polo, R. Escudero-Cid, M. L. Ruiz-González, J. A. R. Navarro, P. Ocón, F. Zamora, J. Am. Chem. Soc. 2017, 139, 10079–10086.
- [16] Y. Du, H. Yang, J. M. Whiteley, S. Wan, Y. Jin, S. H. Lee, W. Zhang, Angew. Chem. Int. Ed. 2016, 55, 1737–1741.
- [17] S. Chandra, T. Kundu, S. Kandambeth, R. Babarao, Y. Marathe, S. M. Kunjir, R. Banerjee, J. Am. Chem. Soc. 2014, 136, 6570–6573.
- [18] D. A. Vazquez-Molina, G. S. Mohammad-Pour, C. Lee, M. W. Logan, X. Duan, J. K. Harper, F. J. Uribe-Romo, *J. Am. Chem. Soc.* **2016**, *138*, 9767–9770.
- [19] H. Xu, S. Tao, D. Jiang, Nat. Mater. 2016, 15, 722–726.
- [20] J. Roeser, K. Kailasam, A. Thomas, ChemSusChem 2012, 5, 1793– 1799.
- [21] H. Xu, X. Chen, J. Gao, J. Lin, M. Addicoat, S. Irle, D. Jiang, Chem. Commun. 2014, 50, 1292–1294.
- [22] V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld, B. V. Lotsch, *Nat. Commun.* 2015, *6*, 8508.
- [23] L. Stegbauer, K. Schwinghammer, B. V. Lotsch, Chem. Sci. 2014, 5, 2789–2793.
- [24] P. Pachfule, A. Acharjya, J. Roeser, T. Langenhahn, M. Schwarze, R. Schomäcker, A. Thomas, J. Schmidt, J. Am. Chem. Soc. 2018, 140, DOI 10.1021/jacs.7b11255.
- [25] S. Lin, C. S. Diercks, Y.-B. Zhang, N. Kornienko, E. M. Nichols, Y. Zhao, A. R. Paris, D. Kim, P. Yang, O. M. Yaghi, et al., *Science* **2015**, *1*, 1–11.
- [26] S. Kuecken, A. Acharjya, L. Zhi, M. Schwarze, R. Schomäcker, A. Thomas, *Chem. Commun.* 2017, 53, 5854.
- [27] M. Calik, T. Sick, M. Dogru, M. Döblinger, S. Datz, H. Budde, A. Hartschuh, F. Auras, T. Bein, *J. Am. Chem. Soc.* **2016**, *138*, 1234– 1239.
- [28] B. J. Smith, W. R. Dichtel, J. Am. Chem. Soc. 2014, 136, 8783–8789.
- [29] B. J. Smith, A. C. Overholts, N. Hwang, W. R. Dichtel, *Chem. Commun.* 2016, *52*, 3690–3693.
- [30] E. L. Spitler, W. R. Dichtel, Nat. Chem. 2010, 2, 672-677.
- [31] J. R. Hunt, C. J. Doonan, J. D. Levangie, A. P. Côté, O. M. Yaghi, J. Am. Chem. Soc. 2008, 130, 11872–11873.
- [32] K. T. Jackson, T. E. Reich, H. M. El-Kaderi, Chem. Commun. 2012, 48, 8823.
- [33] J. Roeser, D. Prill, M. J. Bojdys, P. Fayon, A. Trewin, A. N. Fitch, M. U. Schmidt, A. Thomas, *Nat. Chem.* **2017**, *9*, 977–982.
- [34] O. Yahiaoui, A. N. Fitch, F. Hoffmann, M. Fröba, A. Thomas, J. Roeser, J. Am. Chem. Soc. 2018, jacs.8b01774.
- [35] S. Kandambeth, A. Mallick, B. Lukose, T. Heine, R. Banerjee, M. Mane, 2012, 2–5.
- [36] H. Xu, J. Gao, Nat. Chem. 2015, 7, 1–50.
- [37] F. J. Uribe-Romo, C. J. Doonan, H. Furukawa, K. Oisaki, O. M. Yaghi, J. Am. Chem. Soc. 2011, 133, 11478–11481.

- [38] P. Kuhn, M. Antonietti, A. Thomas, Angew. Chem. Int. Ed. 2008, 47, 3450–3453.
- [39] S. Kuecken, J. Schmidt, L. Zhi, A. Thomas, J. Mater. Chem. A 2015, 3, 24422–24427.
- [40] C. Z. Guan, D. Wang, L. J. Wan, Chem. Commun. 2012, 48, 2943– 2945.
- [41] F. Haase, E. Troschke, G. Savasci, T. Banerjee, V. Duppel, S. Dörfler, M. M. J. Grundei, A. M. Burow, C. Ochsenfeld, S. Kaskel, et al., *Nat. Commun.* 2018, 9, DOI 10.1038/s41467-018-04979-y.
- [42] P. J. Waller, Y. S. AlFaraj, C. S. Diercks, N. N. Jarenwattananon, O. M. Yaghi, *J. Am. Chem. Soc.* 2018, *140*, jacs.8b05830.
- [43] E. Jin, M. Asada, Q. Xu, S. Dalapati, M. A. Addicoat, M. A. Brady, H. Xu, T. Nakamura, T. Heine, Q. Chen, et al., *Science* **2017**, *676*, 673–676.
- [44] E. Jin, J. Li, K. Geng, Q. Jiang, Q. Xu, D. Jiang, Nat. Commun. 2018, 9, 1–10.
- [45] Y. Z. Cui, Q. Fang, H. Lei, G. Xue, W. T. Yu, Chem. Phys. Lett. 2003, 377, 507–511.
- [46] H. Meier, H. C. Holst, A. Oehlhof, European J. Org. Chem. 2003, 2003, 4173–4180.
- [47] H. Lyu, C. S. Diercks, C. Zhu, O. M. Yaghi, J. Am. Chem. Soc. 2019, 0, null.
- [48] G. M. J. Schmidt, Pure Appl. Chem. 1971, 27, 647–678.
- [49] S. Y. Ding, J. Gao, Q. Wang, Y. Zhang, W. G. Song, C. Y. Su, W. Wang, J. Am. Chem. Soc. 2011, 133, 19816–19822.
- [50] B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Müller, W. Schnick, J. Am. Chem. Soc. 2003, 125, 10288–10300.
- [51] K. Damodaran, G. J. Sanjayan, P. R. Rajamohanan, S. Ganapathy, K. N. Ganesh, *Org. Lett.* 2001, *3*, 1921–1924.
- [52] T. Nagai, A. Takiguchi, M. Ueda, K. Oda, S. Hiroto, H. Shinokubo, J. Am. Chem. Soc. 2018, 140, 8392–8395.
- [53] A. L. Henne, R. P. Ruh, J. Am. Chem. Soc. **1947**, 69, 279–281.
- [54] E. E. Lewis, M. A. Naylor, J. Am. Chem. Soc. 1947, 69, 1968–1970.
- [55] S. Y. Ding, J. Gao, Q. Wang, Y. Zhang, W. G. Song, C. Y. Su, W. Wang, J. Am. Chem. Soc. 2011, 133, 19816–19822.
- [56] Y. Zhao, L. Guo, F. Gándara, Y. Ma, Z. Liu, C. Zhu, H. Lyu, C. A. Trickett, E. A. Kapustin, O. Terasaki, et al., *J. Am. Chem. Soc.* 2017, 139, 13166–13172.
- [57] C. H. Huang, D. M. Bassani, European J. Org. Chem. 2005, 4041– 4050.
- [58] P. Kissel, D. J. Murray, W. J. Wulftange, V. J. Catalano, B. T. King, *Nat. Chem.* 2014, 6, 774–778.
- [59] M. J. Kory, M. Wörle, T. Weber, P. Payamyar, S. W. Van De Poll, J. Dshemuchadse, N. Trapp, A. D. Schlüter, *Nat. Chem.* **2014**, *6*, 779– 784.
- [60] N. Huang, X. Ding, J. Kim, H. Ihee, D. Jiang, Angew. Chem. Int. Ed. 2015, 54, 8704–8707.
- [61] R. Z. Lange, G. Hofer, T. Weber, A. Dieter Schluter, J. Am. Chem. Soc. 2017, 139, 2053–2059.
- [62] M. Nagarathinam, A. M. P. Peedikakkal, J. J. Vittal, *Chem. Commun.* 2008, 5277–5288.
- [63] Y. Yamaguchi, Y. Matsubara, T. Ochi, T. Wakamiya, Z. I. Yoshida, J. Am. Chem. Soc. 2008, 130, 13867–13869.
- [64] R. Medishetty, A. Husain, Z. Bai, T. Runčevski, R. E. Dinnebier, P. Naumov, J. J. Vittal, Angew. Chem. Int. Ed. 2014, 53, 5907–5911.

WILEY-VCH

COMMUNICATION



The synthesis of two vinylene-linked (-CH=CH-) Covalent Organic Frameworks (COFs) by base-catalyzed aldol condensation has been reported. Structural properties of highly crystalline COF has been investigated.

Amitava Acharjya,^a Pradip Pachfule,^a Jérôme Roeser,^a Franz-Josef Schmitt,^a and Arne Thomas^a*

Page No. – Page No.

Vinylene Linked Covalent Organic Frameworks by Base-Catalyzed Aldol Condensation