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Synthesis of Vinylene-Linked Covalent Organic Frameworks from Acetonitrile: Combining Cyclotrimerization and Aldol Condensation in One Pot

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Supporting Information Placeholder

ABSTRACT: Combining two or more consecutive reactions in one pot is a common approach for process development, as such a method involves cheap starting materials and allows in-situ generation of a reactive intermediate, to undergo further reaction, without isolation. Herein, we report the synthesis of a vinylenelinked (-CH=CH-) covalent organic framework (COF-701) directly from acetonitrile, a cheap commodity solvent, by combining/telescoping two consecutive reactions, cyclotrimerization of nitrile and subsequent aldol condensation with aldehydes, in one pot. Acetonitrile is trimerized to generate protonated 2,4,6-trimethyl s-triazine tautomers in-situ, which undergo Aldol condensation with 4,4'-biphenyldicarbaldehyde in one pot to form crystalline COF-701. COF-701 is obtained as polycrystalline powder and possesses permanent microporosity and a BET surface area (SA_{BET}) of 736 m².g⁻¹. This strategy can be further extended to generate other porous vinylene-linked frameworks.

Covalent organic frameworks (COFs) are extended 2D and 3D crystalline porous solids constructed solely from organic building blocks linked by covalent bonds.¹ An abundant toolkit of covalent bond formation reactions have been reported for the crystallization of such fully organic frameworks.¹⁻⁵ Nevertheless, the inherent lower chemical stability of commonly used linkages based on reversible B-O,6-10 B-N,11 Si-O12,13 and C-N14-17 bond formation remains an issue that drives the further development of such materials. Different synthetic strategies such as keto-enol tautomerization,¹⁸⁻²⁰ post-synthetic modification (PSM)^{21,22} or interlayer stacking optimization²³ have been applied to generate chemically stable COFs in acidic and basic media. It was generally believed that reticulating COFs with strong C-C covalent bonds would address the stability issues of COF linkages while also leading to materials with improved properties notably due to the formation of frameworks with extended π -conjugated domains.24,25 Indeed the recent discovery of cyanovinylene (-C(CN)=CH-)²⁵⁻²⁹ and vinylene-linked (-CH=CH-) COFs,³⁰⁻³³ showed that a new class of chemically stable C-C linked COFs can be developed. Vinylene-linked COFs³⁰⁻³⁵, in particular, are desirable due to their high stability³⁰ and structural resemblance to poly-phenylene vinylenes (PPVs)³², used in light emitting diodes (LEDs) and organic photovoltaics. Interestingly, vinylene-linked COFs can be synthesized by both acid^{30,36} and base catalyzed^{31,32,35} condensation reactions between active aryl-methyl group-containing monomers and multitopic aryl aldehydes, imparting flexibility and diversity over the choice of synthetic conditions to be used.

A simple retrosynthetic analysis reveals that the vinylenelinked frameworks bearing an s-triazine core should be accessible directly from acetonitrile in two consecutive steps under appropriate synthetic conditions (Figure 1a). While multicomponent reactions have been reported for the generation of crystalline frameworks,^{37–39} one pot syntheses by combining two successive reactions have never been reported for COF synthesis. Multistep sequential reactions are sometimes used for the industrial synthesis of fine chemicals and drug development,40 as such a procedure, due to the dispensability of intermediate isolation steps, allow for cheaper and safer production processes. Here, we report a strategy for preparing vinylene-linked COFs by a multistep synthesis approach directly from the cheap commodity solvent acetonitrile. In particular, COF-701,30 the first reported vinylene-linked COF prepared under acidic condition, attracted our attention since it was reported to form by acid-catalyzed aldol condensation involving 2,4,6-trimethyl s-triazine (TMT). We show that the trimerization of acetonitrile catalyzed by the Brønsted acid, trifluoromethanesulphonic acid (TfOH), generates in-situ protonated tautomers of TMT which further undergo aldol condensation with aryl aldehydes in one pot (Figure 1b).

As for the development of any new COF synthetic strategy, investigating a model reaction can give precious indication on the framework formation. In order to control the stoichiometry of the reaction, a time dependent proton (1H) NMR study was performed to determine the yield of protonated TMT formed by trimerization of acetonitrile with TfOH (Supporting Information (SI), Section S2, Figure S1). Protonated tautomeric TMT species⁴¹ were directly detected upon addition of TfOH and a 20% yield was calculated (after 1 hour) from the relative integral of TMT species and acetonitrile as well as by isolation of diprotonated TMTtriflate salt^{42,43} from solution (SI, Section S2, Figure S2 and S3). The model compound 2.4.6-tristyryl s-triazine (TST) was isolated in 80% yield in presence of benzaldehyde (based on 20%) trimerization yield after 1 hour) and thus confirmed the viability of our strategy for vinylene-linked COF formation directly from acetonitrile (Figure 1b, SI, Section S2).

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a. Retrosynthetic analysis of vinylene-linked COF-701 framework:



Figure 1: a. Schematic Illustration of retrosynthetic steps to form a vinylene-linked framework (COF-701) from acetonitrile b. Synthetic scheme of 2,4,6-tristyryl *s*-triazine (model compound) directly from acetonitrile by combining two consecutive reactions.

The first attempts to crystallize COF-701 from acetonitrile under the solvothermal reaction conditions reported initially (mesitylene/dioxane/acetonitrile) proved to be unsuccessful, as only black amorphous solids were collected (Table S1, entry COF-701-1). Since TfOH can catalyze unwanted radical reaction pathways with common solvents⁴⁴,⁴⁵ the choice of suitable solvent for the synthesis of crystalline COF-701 is fundamental. A thorough screening of different solvents and temperature provided a comprehensive idea of suitable solvents for the synthesis of COF-701 directly from acetonitrile (Table S1). COF-701 could be successfully crystallized under solvothermal conditions in a methanol and acetonitrile (1:1) mixture at 120 °C (SI, Section S2). COF-701 was collected as dark red powder by filtration and further washed with methanol, water and acetone, before being neutralized with dilute-ammonia solution. After Soxhlet extraction with methanol overnight and vacuum drving at 100 °C. COF-701 was obtained as light-yellow powder. Notably, the of isolated TMT-triflate salt and 4, 4'reaction biphenyldicarboxaldehyde (BPDA) under COF-701 formation condition did not yield any solid product. Therefore, the presence of excess amount of acid in the reaction is deemed necessary for the subsequent aldol condensation step.

Fourier transform infrared (FT-IR) spectroscopy analyses were applied to assess the structural features of the crystalline framework (Figure 2a). Complete disappearance of -C=Ostretching frequency of starting aldehyde monomers at 1689 cm⁻¹ and appearance of a new band at 1627 cm⁻¹ attributed to -CH=CH- stretching indicated complete condensation of the starting building blocks and the successful formation of the vinylene linkage in COF-701. Moreover, presence of the *s*triazine ring was also confirmed by characteristic C-N (aromatic) stretching frequencies of *s*-triazine heterocycle at 1366 cm⁻¹ and 1507 cm^{-1.46} Elemental analysis of COF-701 powders also matched the reported values (SI, Section S2)

Formation of vinylene (-HC=CH-) linkages as well as *s*triazine cores were confirmed by ¹³C cross-polarization Totalsideband-suppression (CP-TOSS) NMR spectroscopy analysis of polycrystalline COF-701 powders (Figure 2b). Vinylene carbon signals located at $\delta \sim 138.1$ ppm and 132.1 ppm were unambiguously assigned within the aromatic carbon signals. Moreover, two distinct aromatic s-triazine carbon-signals at $\delta \sim 170$ ppm and 176 ppm reveals the formation of triazine cores within the COF. That two signals can be differentiated furthermore points to a partial [2+2]-cycloaddition of vinylene linkages within the 2D-layers of COF-701, further corroborated by the presence of a broad signal at $\delta \sim 43$ ppm attributed to the cyclobutane moieties.^{31,47}

The crystallinity of COF-701 was analyzed by powder X-ray diffraction (PXRD) analyses. A good match was found between the experimentally obtained PXRD patterns and the proposed 2D layered model with **hcb** topology reported for COF-701 (Figure 3, SI, Figure S5). Final lattice parameters were extracted after Pawley refinement and COF-701 synthesized from acetonitrile was found to crystallize in a hexagonal unit cell (*P6/m*, a = b = 29.7405 Å, c = 3.4456 Å, $R_p = 2.47$ % and $R_{wp} = 3.22$ %). The stacking mode of the layers could not be derived from the PXRD pattern alone, nevertheless an eclipsed stacking arrangement can be concluded from the main pore size derived from porosity analysis (*vide infra*), further supported by the partial cycloaddition of vinylene-linkages (favorable in eclipsed stacking arrangement) as revealed by the ¹³C CP-TOSS NMR analysis.



Figure 2: a. FT-IR spectra of COF-701 (red), model compound TST (black) and BPDA (blue). b. ¹³C CP-TOSS NMR spectra of COF-701 (red) and model compound 2,4,6-tristyryl *s*-triazine (TST) (black).

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Figure 3: Synthesis and structural characterization of COF-701. a. Synthesis of COF-701 from acetonitrile by combining cyclotrimerization of nitrile and Aldol condensation in one pot. b. PXRD pattern of COF-701: Pawley refined pattern (black), experimental pattern (red), Simulated eclipsed (AA) stacking pattern (blue), difference (orange), Bragg diffraction positions (green) and simulated eclipsed (AA) model (inset). c. N₂ sorption isotherm of COF-701.

The permanent porosity of the COF-701 framework was evaluated by low-pressure nitrogen (N₂) sorption studies on evacuated samples, at 77 K. A steep gas uptake in the low relative pressure range (p/p₀ < 0.05) of the N₂ adsorption branch shows the microporous nature of the framework (Figure 2c). The Brunauer-Emmett-Teller surface area (SA_{BET}) calculated from the N₂ adsorption was found to be 736 m².g⁻¹, which is lower compared to the reported value (1366 m².g⁻¹) and could be attributed to the lower degree of crystallinity. The corresponding pore size distribution was found to be centered at 1.81 nm (SI, Section S4, Figure S6), derived by fitting the Ar adsorption branch data at 87 K with quenched-solid density functional theory (QSDFT) cylindrical pore model,⁴⁸ which closely matched well with the calculated pore size of 2.1 nm of the proposed eclipsed structural model.

Architectural stability of COF-701 was investigated by thermogravimetric analysis (TGA) under N₂ atmosphere. After an initial weight loss of ~2 wt% due to desorption of adsorbed solvents below 100 °C, the frameworks remained stable until 400 °C (SI, Section S5, Figure S7). Scanning electron microscopy analysis revealed the formation of spherical particles of ~1 μ m (SI, section S6, Figure S8).

While synthesis of several vinylene-linked COFs were reported by base-catalyzed aldol condensation, acid-catalyzed pathway remains largely unexplored. We therefore attempted to verify the versatility of our methodology and targeted several other frameworks. First, we performed the synthesis of V-COF-1³¹ from acetonitrile and terepthalaldehyde (TA) (SI, Section S2). Similar to COF-701, a light-yellow polymer was obtained upon neutralization of the bright red solid collected from the one pot reaction with acetonitrile and TA. FT-IR and solid state ¹³C CP-TOSS NMR spectra of V-COF-1 confirmed the formation of vinylene-linkages as well as the presence of the s-triazine heterocycle (SI, Section S7, Figure S9, S10). Powder XRD measurements confirmed the crystallinity of V-COF-1, however the broad peaks also show a lower structural order than for COF-701. (Figure 4). Permanent microporosity of V-COF-1 was confirmed by the low-pressure nitrogen (N₂) sorption studies at 77 K (SI, Section S8, Figure S11) as V-COF-1 exhibited a SABET of 790 m².g⁻¹. The corresponding pore size distribution maximum located at 1.48 nm (SI, Section S8, Figure S12) matched well with the calculated pore size of 1.6 nm of the proposed eclipsed structural model.31



Figure 4: a. Synthetic scheme of V-COF-1 b. PXRD pattern of V-COF-1: experimental pattern (black), simulated eclipsed stacking pattern (red).

Subsequently, framework formation with 1,3,5-tris(4-(TFPB) 1,3,5-tris(4formylphenyl)benzene and formylphenyl)triazine (TFPT) was investigated (SI section S2). Both frameworks, coined V-COF-2 and V-COF-3, were predominantly amorphous featuring small crystalline domains, as revealed by PXRD analyses (SI, Section S9, Figure S13), FT-IR analyses also confirmed the formation of vinylene linkages as well as the presence of triazine heterocycle (SI, Section S10, Figure S14). Despite being predominantly amorphous, both the frameworks exhibited permanent microporosity and SABET values of 760 m².g⁻¹ and 350 m².g⁻¹, respectively (SI, section S11, Figure S15). The corresponding pore size distribution maxima of 1.41 nm and 1.52 nm (SI, Section S11, Figure S16) closely matched with the calculated pore size of proposed eclipsed structural model.³¹ It should be noted that the preparation of welldefined COFs is highly dependent on the used reaction conditions, which need to achieve the right balance between monomer/oligomer solubility and reversibility of the COF forming reactions. An upstream reaction before COF formation, like the here presented trimerization reaction (see Scheme S1), demand even more control on the reaction conditions to finally obtain the COFs with high crystallinity. Moreover, unlike the imine- or boroxine-linked COFs, where often a binary solvent mixture of mesitylene and 1,4 dioxane is required to yield crystalline frameworks, synthesis of vinylene-linked frameworks seem to be more delicate and strongly depends on the choice of solvent mixtures and temperature used for the solvethermal reaction. Therefore, further optimization of the reaction conditions are necessary to achieve highly porous and well crystalline V-COF frameworks.

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In conclusion, we have demonstrated the one-pot synthesis of vinvlene-linked framework COF-701 by combining cyclotrimerization of acetonitrile and a subsequent Aldol condensation with BPDA. We believe, this is not only the first report of a telescoping synthesis combining cyclotrimerization of nitrile and aldol condensation, but also the first application of such a two step-one pot reaction for COF synthesis. Furthermore, general applicability of our method was established by extending the reactions with other multitopic aryl-aldehyde building units (TA, TFPB and TFPT) to generate microporous frameworks (V-COF-1, V-COF-2 and V-COF-3 respectively). 2,4,6-trimethyl striazine, (TMT), the starting monomer for vinylene-linked COF syntheses, is an expensive chemical (1 g cost nearly 1000 \$), which is usually prepared from ethyl acitimidate hydrochloride in a rigorous and time-consuming two-step reaction involving several isolation and purification steps. The here shown approach applying directly the commodity chemical acetonitrile therefore enables significant cost and time savings and thus a scalable COF synthesis. Moreover, our approach provides a complete account on the acid catalyzed synthetic pathway of vinylene-linked COFs and avoids the side reactions (Cannizzaro reaction of aldehydes) otherwise associated with the base catalyzed synthesis of V-COFs. This method will thus serve as a cheap and scalable alternative for the synthesis of vinylene-linked frameworks directly from acetonitrile.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications

Full synthetic procedures and characterization data, PXRD analysis (PDF)

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REFERENCES

(1) Yaghi, O.M., Kalmutzki, M.J. and Dierks, C. S. Historical Perspective on the Discovery of Covalent Organic Frameworks. *Introduction to Reticular Chemistry*. Wiley-VCH: Weinheim 2019, pp 177–195.

(2) Lyle, S. J.; Waller, P. J.; Yaghi, O. M. Covalent Organic Frameworks: Organic Chemistry Extended into Two and Three Dimensions. *Trends Chem.* **2019**, *1* (2), 172–184.

(3) Geng, K.; He, T.; Liu, R.; Dalapati, S.; Tan, K. T.; Li, Z.; Tao, S.; Gong, Y.; Jiang, Q.; Jiang, D. Covalent Organic Frameworks: Design, Synthesis, and Functions. *Chem. Rev.* **2020**, acs.chemrev.9b00550.

(4) Diercks, C. S.; Yaghi, O. M. The Atom, the Molecule, and the Covalent Organic Framework. *Science (80-.).* **2017**, *355* (6328), eaal1585.

(5) Lohse, M. S.; Bein, T. Covalent Organic Frameworks: Structures, Synthesis, and Applications. *Adv. Funct. Mater.* **2018**, *28* (33), 1705553.

(6) Cote, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. Porous, Crystalline, Covalent Organic Frameworks. *Science (80-.).* **2005**, *310* (5751), 1166–1170.

(7) El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortés, J. L.; Côté, A. P.; Taylor, R. E.; O'Keeffe, M.; Yaghi, O. M. Designed Synthesis of 3D Covalent Organic Frameworks. *Science (80-.).* **2007**, *316* (5822), 268–272.

(8) Du, Y.; Yang, H.; Whiteley, J. M.; Wan, S.; Jin, Y.; Lee, S.-H.; Zhang, W. Ionic Covalent Organic Frameworks with Spiroborate Linkage. *Angew. Chemie - Int. Ed.* **2016**, *55* (5), 1737–1741.

(9) Spitler, E. L.; Dichtel, W. R. Lewis Acid-Catalysed Formation of Two-Dimensional Phthalocyanine Covalent Organic Frameworks. *Nat. Chem.* **2010**, *2* (8), 672–677.

(10) Hunt, J. R.; Doonan, C. J.; Levangie, J. D.; Côté, A. P.; Yaghi, O. M. Reticular Synthesis of Covalent Organic Borosilicate Frameworks. *J. Am. Chem. Soc.* **2008**, *130* (36), 11872–11873.

(11) Jackson, K. T.; Reich, T. E.; El-Kaderi, H. M. Targeted Synthesis of a Porous Borazine-Linked Covalent Organic Framework. *Chem. Commun.* **2012**, *48* (70), 8823.

(12) Roeser, J.; Prill, D.; Bojdys, M. J.; Fayon, P.; Trewin, A.; Fitch, A. N.; Schmidt, M. U.; Thomas, A. Anionic Silicate Organic Frameworks Constructed from Hexacoordinate Silicon Centres. *Nat. Chem.* **2017**, *9* (10), 977–982.

(13) Yahiaoui, O.; Fitch, A. N.; Hoffmann, F.; Fröba, M.; Thomas, A.; Roeser, J. 3D Anionic Silicate Covalent Organic Framework with Srs Topology. *J. Am. Chem. Soc.* **2018**, *140* (16), 5330–5333.

(14) Uribe-Romo, F. J.; Hunt, J. R.; Furukawa, H.; Klöck, C.; O'Keeffe, M.; Yaghi, O. M. A Crystalline Imine-Linked 3-D Porous Covalent Organic Framework. *J. Am. Chem. Soc.* **2009**, *131* (13), 4570– 4571.

(15) Uribe-Romo, F. J.; Doonan, C. J.; Furukawa, H.; Oisaki, K.; Yaghi, O. M. Crystalline Covalent Organic Frameworks with Hydrazone Linkages. *J. Am. Chem. Soc.* **2011**, *133* (30), 11478–11481.

(16) Ding, S. Y.; Gao, J.; Wang, Q.; Zhang, Y.; Song, W. G.; Su, C. Y.; Wang, W. Construction of Covalent Organic Framework for Catalysis: Pd/COF-LZU1 in Suzuki-Miyaura Coupling Reaction. J. Am. Chem. Soc. 2011, 133 (49), 19816–19822.

(17) Calik, M.; Sick, T.; Dogru, M.; Döblinger, M.; Datz, S.; Budde, H.; Hartschuh, A.; Auras, F.; Bein, T. From Highly Crystalline to Outer Surface-Functionalized Covalent Organic Frameworks-A Modulation Approach. *J. Am. Chem. Soc.* **2016**, *138* (4), 1234–1239.

(18) Kandambeth, S.; Mallick, A.; Lukose, B.; Mane, M. V.; Heine, T.; Banerjee, R. Construction of Crystalline 2D Covalent Organic Frameworks with Remarkable Chemical (Acid/Base) Stability via a Combined Reversible and Irreversible Route. *J. Am. Chem. Soc.* **2012**, *134* (48), 19524–19527.

(19) Pachfule, P.; Acharjya, A.; Roeser, J.; Langenhahn, T.; Schwarze, M.; Schomäcker, R.; Thomas, A.; Schmidt, J. Diacetylene Functionalized Covalent Organic Framework (COF) for Photocatalytic Hydrogen Generation. *J. Am. Chem. Soc.* **2018**, *140* (4), 1423–1427.

(20) Biswal, B. P.; Chandra, S.; Kandambeth, S.; Lukose, B.; Heine, T.; Banerjee, R. Mechanochemical Synthesis of Chemically Stable Isoreticular Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2013**, *135* (14), 5328–5331.

(21) Haase, F.; Troschke, E.; Savasci, G.; Banerjee, T.; Duppel, V.; Dörfler, S.; Grundei, M. M. J.; Burow, A. M.; Ochsenfeld, C.; Kaskel, S.; Lotsch, B. V. Topochemical Conversion of an Imine- into a Thiazole-Linked Covalent Organic Framework Enabling Real Structure Analysis.

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Nat. Commun. 2018, 9 (1), 2600.

(22) Segura, J. L.; Royuela, S.; Mar Ramos, M. Post-Synthetic Modification of Covalent Organic Frameworks. *Chem. Soc. Rev.* **2019**, *48* (14), 3903–3945.

(23) Xu, H.; Gao, J.; Jiang, D. Stable, Crystalline, Porous, Covalent Organic Frameworks as a Platform for Chiral Organocatalysts. *Nat. Chem.* **2015**, *7* (11), 1–50.

(24) Waller, P. J.; Gándara, F.; Yaghi, O. M. Chemistry of Covalent Organic Frameworks. *Acc. Chem. Res.* **2015**, *48* (12), 3053–3063.

(25) Jin, E.; Asada, M.; Xu, Q.; Dalapati, S.; Addicoat, M. A.; Brady,
M. A.; Xu, H.; Nakamura, T.; Heine, T.; Chen, Q.; Jiang, D. Two-Dimensional Sp2 Carbon–Conjugated Covalent Organic Frameworks. *Science* (80-.). 2017, 357 (6352), 673–676.

(26) Zhuang, X.; Zhao, W.; Zhang, F.; Cao, Y.; Liu, F.; Bi, S.; Feng, X. A Two-Dimensional Conjugated Polymer Framework with Fully Sp² - Bonded Carbon Skeleton. *Polym. Chem.* **2016**, *7* (25), 4176–4181.

(27) Jin, E.; Li, J.; Geng, K.; Jiang, Q.; Xu, Q.; Jiang, D. Designed Synthesis of Stable Light-Emitting Two-Dimensional Sp 2 Carbon-Conjugated Covalent Organic Frameworks. *Nat. Commun.* **2018**, *9* (1), 1– 10.

(28) Chen, R.; Shi, J. L.; Ma, Y.; Lin, G.; Lang, X.; Wang, C. Designed Synthesis of a 2D Porphyrin-Based Sp 2 Carbon-Conjugated Covalent Organic Framework for Heterogeneous Photocatalysis. *Angew. Chemie - Int. Ed.* **2019**, *58* (19), 6430–6434.

(29) Becker, D.; Biswal, B. P.; Kaleńczuk, P.; Chandrasekhar, N.; Giebeler, L.; Addicoat, M.; Paasch, S.; Brunner, E.; Leo, K.; Dianat, A.; Cuniberti, G.; Berger, R.; Feng, X. Fully Sp2-Carbon-Linked Crystalline Two-Dimensional Conjugated Polymers: Insight into 2D Poly(Phenylenecyanovinylene) Formation and Its Optoelectronic Properties. *Chem. - A Eur. J.* **2019**, *25* (26), 6562–6568.

(30) Lyu, H.; Diercks, C. S.; Zhu, C.; Yaghi, O. M. Porous Crystalline Olefin-Linked Covalent Organic Frameworks. J. Am. Chem. Soc. 2019, 141 (17), 6848–6852.

(31) Acharjya, A.; Pachfule, P.; Roeser, J.; Schmitt, F.-J.; Thomas, A. Vinylene-Linked Covalent Organic Frameworks by Base-Catalyzed Aldol Condensation. *Angew. Chemie Int. Ed.* **2019**, *58* (42), 14865–14870.

(32) Jadhav, T.; Fang, Y.; Patterson, W.; Liu, C.; Hamzehpoor, E.; Perepichka, D. F. 2D Poly(Arylene Vinylene) Covalent Organic Frameworks via Aldol Condensation of Trimethyltriazine. *Angew. Chemie Int. Ed.* **2019**, *58* (39), 13753–13757.

(33) Bi, S.; Yang, C.; Zhang, W.; Xu, J.; Liu, L.; Wu, D.; Wang, X.; Han, Y.; Liang, Q.; Zhang, F. Two-Dimensional Semiconducting Covalent Organic Frameworks via Condensation at Arylmethyl Carbon Atoms. *Nat. Commun.* **2019**, *10* (1), 1–10.

(34) Xu, J.; He, Y.; Bi, S.; Wang, M.; Yang, P.; Wu, D.; Wang, J.; Zhang, F. An Olefin-Linked Covalent Organic Framework as a Flexible Thin-Film Electrode for a High-Performance Micro-Supercapacitor. *Angew. Chemie - Int. Ed.* **2019**, *58* (35), 12065–12069.

(35) Wei, S.; Zhang, F.; Zhang, W.; Qiang, P.; Yu, K.; Fu, X.; Wu, D.; Bi, S.; Zhang, F. Semiconducting 2D Triazine-Cored Covalent Organic Frameworks with Unsubstituted Olefin Linkages. J. Am. Chem. Soc. 2019, 141 (36), 14272–14279.

(36) Yang, Y.; Niu, H.; Xu, L.; Zhang, H.; Cai, Y. Triazine Functionalized Fully Conjugated Covalent Organic Framework for Efficient Photocatalysis. *Appl. Catal. B Environ.* **2020**, *269*, 118799.

(37) Zeng, Y.; Zou, R.; Luo, Z.; Zhang, H.; Yao, X.; Ma, X.; Zou, R.; Zhao, Y. Covalent Organic Frameworks Formed with Two Types of Covalent Bonds Based on Orthogonal Reactions. J. Am. Chem. Soc. 2015, 137 (3), 1020–1023.

(38) Wang, P. L.; Ding, S. Y.; Zhang, Z. C.; Wang, Z. P.; Wang, W. Constructing Robust Covalent Organic Frameworks via Multicomponent Reactions. *J. Am. Chem. Soc.* **2019**, *141* (45), 18004–18008.

(39) Li, X.-T.; Zou, J.; Wang, T.-H.; Ma, H.-C.; Chen, G.-J.; Dong, Y.-B. Construction of Covalent Organic Frameworks via Three-Component One-Pot Strecker and Povarov Reactions. J. Am. Chem. Soc. 2020, 142 (14), 6521–6526.

(40) Zhao, W.; Chen, F.-E. One-Pot Synthesis and Its Practical Application in Pharmaceutical Industry. *Curr. Org. Synth.* **2013**, *9* (6), 873–897.

(41) Salnikov, G. E.; Genaev, A. M.; Vasiliev, V. G.; Shubin, V. G. Interaction of Acetonitrile with Trifluoromethanesulfonic Acid: Unexpected Formation of a Wide Variety of Structures. *Org. Biomol. Chem.* **2012**, *10* (11), 2282.

(42) Amer, M. I.; Booth, B. L.; Noori, G. F. M.; Proença, M. F. J. R.
P. The Chemistry of Nitrilium Salts. Part 3. The Importance of Triazinium Salts in Houben–Hoesch Reactions Catalyzed by

Trifluoromethanesulphonic Acid. J. Chem. Soc., Perkin Trans. 1 1983, 1075–1082.

(43) Li, W.; Shi, M. Brønsted Acid TfOH-Mediated [3 + 2] Cycloaddition Reactions of Diarylvinylidenecyclopropanes with Nitriles. *J. Org. Chem.* **2008**, *73* (11), 4151–4154.

(44) Sato, Y.; Yato, M.; Ohwada, T.; Saito, S.; Shudo, K. Involvement of Dicationic Species as the Reactive Intermediates in Gattermann, Houben-Hoesch, and Friedel—Crafts Reactions of Nonactivated Benzenes. J. Am. Chem. Soc. **1995**, 117 (11), 3037–3043.

(45) Kobayashi, S.; Morikawa, K.; Saegusa, T. Superacids and Their Derivatives. IX. Selective Cyclodimerization of Etylene Oxide to 1,4-Dioxane Catalyzed by Superacids and Their Derivatives. *Macromolecules* **1975**, *8* (6), 952–954.

(46) Kuhn, P.; Antonietti, M.; Thomas, A. Porous, Covalent Triazine-Based Frameworks Prepared by Ionothermal Synthesis. *Angew. Chemie* -*Int. Ed.* **2008**, *47* (18), 3450–3453.

(47) Jadhav, T.; Fang, Y.; Liu, C.-H.; Dadvand, A.; Hamzehpoor, E.; Patterson, W.; Jonderian, A.; Stein, R. S.; Perepichka, D. F. Transformation between 2D and 3D Covalent Organic Frameworks via Reversible [2 + 2] Cycloaddition. *J. Am. Chem. Soc.* **2020**, *142* (19), 8862–8870.

(48) Neimark, A. V.; Lin, Y.; Ravikovitch, P. I.; Thommes, M. Quenched Solid Density Functional Theory and Pore Size Analysis of Micro-Mesoporous Carbons. *Carbon N. Y.* **2009**, *47* (7), 1617–1628.

