OL Organic Letters

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Synthesis and Catalytic Properties of Metal–*N*-Heterocyclic-Carbene-Decorated Covalent Organic Framework

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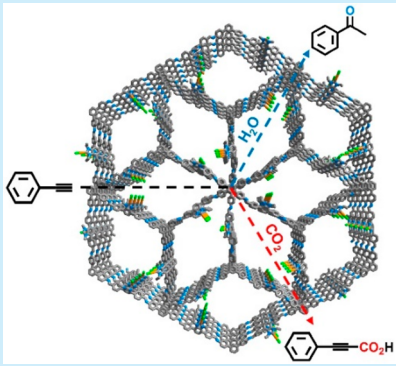
Cite This: https://dx.doi.org/10.1021/acs.orglett.0c02721 Read Online

ABSTRACT: We demonstrate herein that the *N*-heterocyclic-carbene (NHC)–metal complex (NHC–M)-involved covalent organic framework (COF) can be prepared by the direct polymerization of the NHC–M monomer with its counterpart under solvothermal conditions. The NHC–M–COF with different counterions is readily achieved via solid-state anion exchange. The obtained **NHC–AuX–COF** (X = Cl^- and SbF_6^-) can be a highly active reusable catalyst to separately promote the carboxylation of the terminal alkyne with CO_2 and alkyne hydration under mild conditions.



Since Arduengo et al. reported the first stable and isolable *N*-heterocyclic carbene (NHC),[1] NHC–metal (NHC–M) complexes have been recognized as an important class of organometallic catalysts.[2] However, the recycling and reuse of NHC–M catalysts remains challenging because the molecular NHC–M complexes are typically of single use in catalysis.[3] To meet the multifaceted requirements of low-cost, resource-saving, and environment-friendly synthesis, molecular NHC–M complexes are intelligently loaded on solid supports, such as metal–organic frameworks (MOFs)[4] and organic polymers,[5] by chemists to realize the catalysis in a heterogeneous way.

Since Yaghi et al. reported the first example of a covalent organic framework (COF),[6] COF-based chemistry has experienced rapid development.[7−11] It is of note that COFs possess capacious and expedite channels that can not only facilitate the transport of reactants and products but also provide efficient access to catalytic sites within the COFs. These inborn features could endow COFs with more advantages for their applications in heterogeneous catalysis.[9]

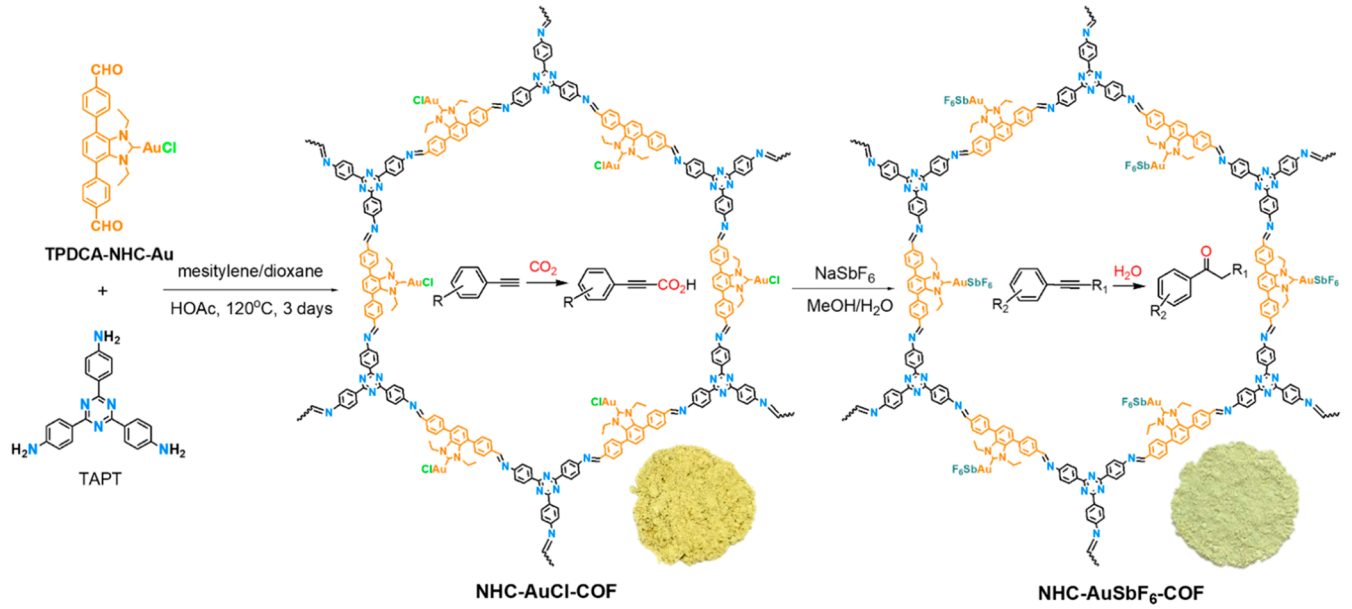
As we know, COF catalysts can be prepared by introducing the catalytic species into COFs via direct polymerization or postsynthetic modifications (PSMs).[9] Compared with direct polymerization, the PSM approach might sometimes result in less loading of the catalytic moieties with relatively uneven distributions because not all PSM reactions are quantitative, especially for those large-sized substrates under solid-state conditions.[12] We wonder if the NHC–M–COFs could be prepared by the direct polymerization of NHC–M organometallic monomers with their counterparts. In doing so, both the high catalyst loading and their uniform distribution in the COF would be realized; furthermore, the catalyst leaching during the catalytic process could be effectively avoided. Compared with the reported organocatalysts and metal-nanoparticle-loaded COF catalysts,[12] the synthesis of NHC–M–COFs in this way is unprecedented thus far.

Continuing with our research on the synthesis of COFs and their catalytic applications,[13] we report herein, for the first time, **NHC–AuCl–COF**, which was generated from an NHC–AuCl-decorated 4,4′′-*p*-terphenyldicarboxaldehyde monomer (**TPDCA–NHC–Au**) and 1,3,5-tris(4-aminophenyl)triazine (TAPT) via direct polymerization under solvothermal conditions. By anion exchange, **NHC–AuSbF$_6$–COF** with different counterions was also synthesized. The obtained NHC–AuX–COF (X = Cl^-, SbF_6^-) can be a highly active heterogeneous catalyst to promote terminal alkyne carboxylation with CO_2 and alkyne hydration under mild conditions, respectively (Scheme 1).

The NHC–Au-decorated monomer **TPDCA–NHC–Au** was prepared from 4,7-dibromo-1-ethyl-1*H*-benzo[*d*]imidazole via multiple synthetic steps (Supporting Information). **NHC–AuCl–COF** was synthesized as yellow solids through Schiff base condensation between **TPDCA–NHC–Au** and TAPT under solvothermal conditions (Scheme 1, Supporting Information). IR and ^{13}C CP-MAS (Figure S1) were used to establish the connectivity of the COF, and the existence of

Received: August 14, 2020

Scheme 1. Synthesis of NHC−AuX−COF (X = Cl^-, SbF_6^-) and Its Catalytic Reactions[a]



[a]Photographs of COF samples are inserted.

TPDCA−NHC−Au and TAPT monomers was directly evidenced.

Inductively coupled plasma (ICP) analysis showed that the Au content in **NHC−AuCl−COF** was 23.40 wt % (calcd. 24.13 wt %). The oxidation state of Au was determined by X-ray photoelectron spectroscopy (XPS) measurement, and the binding energies for Au 4f7/2 and 4f5/2 were 85.38 and 88.92 eV, respectively, indicating that the Au in **NHC−AuCl−COF** is monovalent (Figure 1a).[5b] **NHC−AuCl−COF** is highly crystalline, and no Au NP was detected, which was well supported by its TEM image (Figure 1b). SEM showed that **NHC−AuCl−COF** features micrometer-scale lamellar morphology (Figure 1c), and the mappings of C, N, Cl, and Au indicate that their distributions are uniform (Figure S2). TGA showed no weight loss up to ∼400 °C, indicating that **NHC−AuCl−COF** possesses excellent thermal stability (Figure 1d).

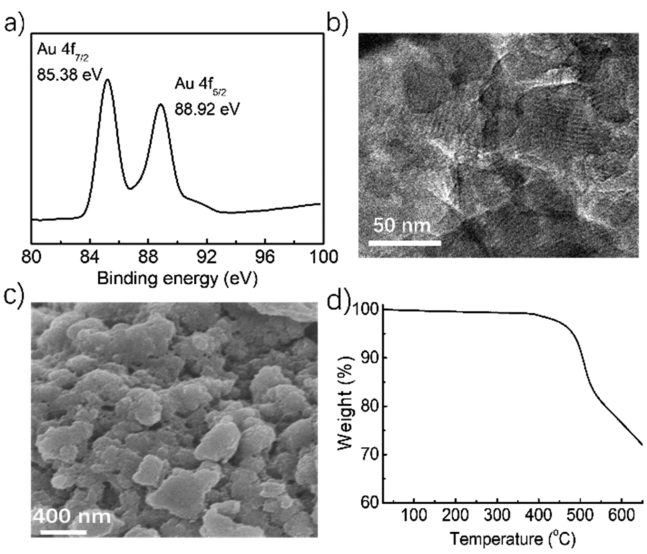


Figure 1. (a) XPS spectrum, (b) TEM image, (c) SEM image, and (d) TGA trace of **NHC−AuCl−COF**.

The structural modeling of **NHC−AuCl−COF** was conducted with the Materials Studio (ver. 5.0) software based on the collected powder X-ray diffraction (PXRD) data (Figure 2).[14] Its most probable structure was a 2D staggered AB-stacking mode, and the observed diffraction peaks at 2.0, 3.4, 4.0, 6.9, and 8.9° were, respectively, assignable to the (100), (110), (200), (220), and (140) facets. The Pawley

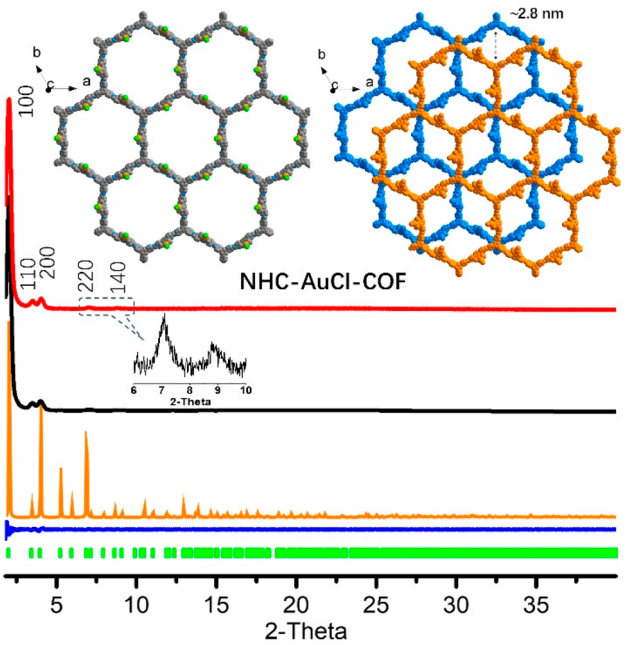


Figure 2. PXRD pattern of **NHC−AuCl−COF**: experimental (red line) and Pawley-refined (black) profiles and the simulated pattern (orange) for the AB stacking mode. The refinement differences (blue) and the observed reflections (green) are also shown. Insets are the single and AB stacking layers in **NHC−AuCl−COF**.

https://dx.doi.org/10.1021/acs.orglett.0c02721
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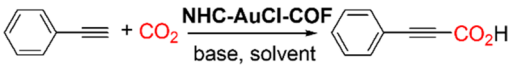
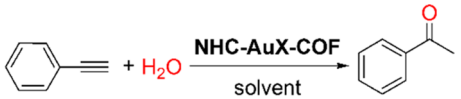
Table 1. Optimization of the NHC−AuCl−COF-Catalyzed Carboxylation of Phenylacetylene with CO_2[a]



entry	cat. (mol % Au)	base	t (h)	solv.	T (°C)	yield (%)[b]
1	**NHC−AuCl−COF** (0.5)	Cs_2CO_3	16	DMSO	50	96
2	**NHC−AuCl−COF** (0.5)	Cs_2CO_3	16	DMF	50	96
3	**NHC−AuCl−COF** (0.5)	Cs_2CO_3	16	DMSO	80	96
4	**NHC−AuCl−COF** (0.5)	Cs_2CO_3	16	DMSO	20	11
5	**NHC−AuCl−COF** (0.5)	K_2CO_3	16	DMSO	50	43
6	**NHC−AuCl−COF** (0.3)	Cs_2CO_3	16	DMSO	50	78
7	**NHC−AuCl−COF** (1.0)	Cs_2CO_3	16	DMSO	50	96
8[c]	**NHC−AuCl−COF** (0.5)	Cs_2CO_3	16	DMSO	50	
9		Cs_2CO_3	16	DMSO	50	

[a]CO_2 (1 atm), phenylacetylene (1 mmol), base (1.1 mmol), solvent (4 mL). [b]Isolated yields. [c]Without CO_2. The products are determined by ^{1}H NMR, ^{13}C NMR, and MS spectra (Supporting Information).

Table 2. Optimization of the NHC−AuX−COF-Catalyzed (X = Cl^-, SbF_6^-) Model Alkyne Hydration Reaction[a]



entry	cat. (mol % Au)	t (h)	solv.	T (°C)	yield (%)[b]
1	**NHC−AuCl−COF** (0.5)	20	H_2O	60	20
2	**NHC−AuSbF$_6$−COF** (0.5)	20	H_2O	60	99
3	**NHC−AuSbF$_6$−COF** (0.5)	20	H_2O	90	99
4	**NHC−AuSbF$_6$−COF** (1.0)	20	H_2O	60	99
5	**NHC−AuSbF$_6$−COF** (0.5)	20	H_2O	30	48
6	**NHC−AuSbF$_6$−COF** (0.3)	20	H_2O	60	73
7		20	H_2O	60	

[a]Phenylacetylene (1 mmol), solvent (1 mL). [b]Isolated yields. The products are determined by ^{1}H NMR, ^{13}C NMR, and MS spectra (Supporting Information).

refinement (black) showed a negligible difference between the simulated (orange) and experimental PXRD pattern (red) (Figure 2). **NHC−AuCl−COF** was assigned to the space group $P3$ with optimized parameters of $a = b = 52.0050$ Å, $c = 8.0140$ Å, $\alpha = \beta = 90°$, and $\gamma = 120°$ and residuals wRp = 5.88% and Rp = 4.11% (Table S1). Notably, **NHC−AuCl−COF** herein, with other types of possible stacking modes, gave a PXRD pattern that significantly deviated from the measured profiles (Figure S3 and Table S1).

The porosity of **NHC−AuCl−COF** was demonstrated by the gas adsorption−desorption measurement (Figure S4). The N_2 absorption amount of **NHC−AuCl−COF** at 77 K is 148 $cm^3\ g^{-1}$, and the corresponding surface area on the basis of the BET model is 139 $m^2\ g^{-1}$. The pore-size distribution by nonlocal density functional theory (NLDFT) analysis indicates that it possesses a narrow pore diameter distribution centered at ∼2.7 nm (Figure S4).

Next, we examined the catalytic activity of **NHC−AuCl−COF** for the direct carboxylation of terminal alkynes with CO_2, which is an economical approach for the synthesis of carboxylic acids.[15] On the contrary, the rational utilization of CO_2 is an attractive and straightforward method to reduce the greenhouse effect.[16]

As shown in Table 1 (entries 1−8), catalytic reactions were performed under different conditions, including different possible solvents, bases, and catalyst amounts at different temperatures. The best result was observed when the reaction was conducted in DMSO or DMF at 50 °C for 16 h (entries 1 and 2) with **NHC−AuCl−COF** (0.5 mol % Au equiv) and Cs_2CO_3 to give the carboxylation product in 96% yield (TON = 192, TOF = 12 h^{-1}). A reaction temperature >50 °C was not conducive to increase the product yield (entry 3); meanwhile, a lower temperature (20 °C) would lead to a very low 11% yield (entry 4). In addition, when the reaction was performed in the presence of K_2CO_3, the product was obtained in a decreased 43% yield (entry 5). With the aid of less catalyst loading, 0.3 mol % instead of 0.5 mol %, the product was isolated in a slightly lower 78% yield (entry 6). Also, more catalyst loading could not enhance the yield (entry 7). It is of note that no desired carboxylation product was detected in the absence of CO_2, indicating that the formed carboxyl group indeed came from CO_2 (entry 8). In addition, no product was detected without **NHC−AuCl−COF** (entry 9).

As a heterogeneous catalyst, **NHC−AuCl−COF** can be reused, and the yield of alkyne carboxylation is still up to 94%, even after five catalytic cycles, without a loss of its crystallinity or structural integrity (Figure S5). The leaching amount of Au in **NHC−AuCl−COF** is only ∼1% (Au, 23.08 wt %), as determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the oxidation state of Au is intact based on the XPS (Figure S5). The postulated mechanism is believed to be the same as that of the molecular NHC−M-catalyzed alkyne carboxylation (Figure S6).[16,17]

The scope of **NHC−AuCl−COF**-catalyzed carboxylation was investigated utilizing various substrates. Besides phenylacetylene, the substituted phenylacetylenes with either electron-donating (−CH_3, −C_2H_5, −OCH_3, and −Ph) or electron-withdrawing groups (−Cl, −NO_2, and −Br) at

https://dx.doi.org/10.1021/acs.orglett.0c02721
Org. Lett. XXXX, XXX, XXX−XXX

different substituted positions furnished the excellent 95−99% yields (Table S2), implying that **NHC−AuCl−COF** could tolerate various functional groups under the given reaction conditions. It is of note that almost no desired products were detected from the protic functional-group-substituted (−OH) substrate or an aliphatic alkyne.

To demonstrate the generality of NHC−Au−COF in catalysis, we also evaluated its activity for alkyne hydration, which is an important reaction for the syntheses of aldehydes and ketones.[18] To meet the requirement of green synthesis, we performed the reaction in water. Table 2 reveals that **NHC−AuCl−COF** is unsatisfactory for the phenylacetylene hydration, and the acetophenone yield obtained from this model reaction is only 20% under the given conditions (0.5 mol % Au, H_2O, 60 °C, 20 h). Nolan et al. reported that the molecular NHC−AuCl can effectively promote alkyne hydration but with the aid of SbF_6^-.[19] Relying on these findings, together with our own results (entry 1), we then prepared **NHC−AuSbF$_6$−COF** from **NHC−AuCl−COF** by replacing Cl^- with SbF_6^- (MeOH/H_2O, 30 min, r.t., 96% yield, Supporting Information). Besides a visual color change (Scheme 1), ICP analysis showed that the Au/Sb ratio is 1:0.97 after anion exchange, implying that almost all of the Cl^- in **NHC−AuCl−COF** has been replaced with SbF_6^-. The Au content in **NHC−AuSbF$_6$−COF** is 18.99 wt % based on the ICP-AES measurement. The PXRD pattern and SEM and TEM images after anion exchange are identical to those of **NHC−AuCl−COF**, suggesting that the COF structure and morphology are well maintained upon anion exchange (Figure S7). In addition, the existence of SbF_6^- was further evidenced by the scanning electron microscopy−energy-dispersive X-ray (SEM-EDX) spectrum (Figure S7). Its corresponding surface area calculated on the basis of the BET model is 112.7 m^2g^{-1}, which is slightly less than that of **NHC−AuCl−COF** (Figure S8).

As expected, **NHC−AuSbF$_6$−COF** exhibited excellent activity. As indicated in Table 2, the treatment of phenylacetylene with water at 60 °C afforded acetophenone in quantitative yield after 20 h (TON = 198, TOF = 9.9 h^{-1}, entry 2) in the presence of **NHC−AuSbF$_6$−COF** (0.5 mol % Au equiv). Higher temperature (90 °C, entry 3) or higher catalyst loading (1.0 mol % Au equiv, entry 4) could not enhance the hydration yield, whereas lower temperature (30 °C, entry 5) or lower catalyst loading (0.3 mol % Au equiv, entry 6) led to a modest 48 or 73% yield. Again, no product was observed without the gold catalyst (entry 7).

Again, the hot leaching test demonstrated that **NHC−AuSbF$_6$−COF** was a typical heterogeneous catalyst for alkyne hydration, and the hydration yield was up to 94% yield after five catalytic cycles (Figure S9). The analysis of the **NHC−AuSbF$_6$−COF** after multiple recycling by ICP-AES and XPS showed that no Au content (Au content 18.92 wt % after reuse) or valence change was detected (Figure S9). In addition, its PXRD pattern indicated that its crystallinity and structure are well maintained after multiple reuses (Figure S9). Compared with **NHC−AuCl−COF** (water contact angle (WCA) = 123 ± 2°), **NHC−AuSbF$_6$−COF** is much more hydrophilic (WCA = 0°), so it is more suitable to promote organic reactions in aqueous phase under the applied reaction conditions (Figure S10). The mechanism of **NHC−AuSbF$_6$−COF**-catalyzed alkyne hydration was supposed based on the reported molecular NHC−Au catalyst (Figure S11).[20]

To ascertain a scope for this COF-based catalysis, the reactivity of a series of terminal aromatic alkynes was investigated with **NHC−AuSbF$_6$−COF** (Table S3). The substituted terminal aromatic alkynes with both electron-donating (−OCH_3, −Ph, −C_2H_5,) and electron-withdrawing (−Cl, −Br, −NO_2) groups could be highly efficiently converted to their corresponding acetophenones (95−99% yields). However, for the internal aromatic alkyne of 4-phenyldiphenylacetylene, the corresponding hydration product was isolated in only 50% yield, indicating that the internal alkynes are more reluctant participants than their terminal counterparts toward hydration, which is consistent with the results reported by Hayashi and Tanaka.[21] Additionally, 3-hydroxyphenyl acetylene and aliphatic alkyne phenyl propargyl ether could be converted into 3-hydroxyacetophenone and 1-phenoxypropan-2-one in 63 and 76% yields, respectively.

In summary, we have successfully realized the synthesis of NHC−M-involved covalent organic framework heterogeneous catalysts via a direct polymerization approach. In addition, the type of concomitant counterions in the obtained **NHC−AuX−COF** can be readily changed according to the requirements of different catalytic reactions. It is of note that the metal−NHC−COFs herein indicate that they showed comparable catalytic activity to that of the reported heterogeneous metal-loaded catalysts (Tables S4 and S5). We believe that our synthetic strategy provided herein is general and, moreover, significantly broadens the scope of COF catalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02721.

Instruments and methods; synthesis and additional characterization of **TPDCA−NHC−Au** monomer, **NHC−AuCl−COF**, and **NHC−AuSbF$_6$−COF**; catalytic product characterization; catalyst hot leaching and catalytic cycles; and crystallographic information for COFs (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support from the NSFC (grants 21971153, 21671122, and 21802091), Shandong Provincial Natural Science Foundation (grant ZR2018BB006), a Project of the Shandong Province Higher Educational Science and Technology Program (J18KA066), the Taishan Scholar's Construction Project, and the Changjiang Scholar project of China at SDNU.

■ REFERENCES

(1) Arduengo, A. J., III; Harlow, R. L.; Kline, M. A Stable Crystalline Carbene. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(2) (a) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An overview of N-heterocyclic carbenes. *Nature* **2014**, *510*, 485−496. (b) Peris, E. Smart *N*-Heterocyclic Carbene Ligands in Catalysis. *Chem. Rev.* **2018**, *118*, 9988−10031. (c) de Fremont, P.; Marion, N.; Nolan, S. P. *Coord. Chem. Rev.* **2009**, *253*, 862−892.

(3) Li, Y.; Dong, Y.; Wei, Y.-L.; Jv, J.-J.; Chen, Y.-Q.; Ma, J.-P.; Yao, J.-J.; Dong, Y.-B. Reusable Palladium N-Heterocyclic Tetracarbene for Aqueous Suzuki−Miyaura Cross-Coupling Reaction: Homoge-neous Catalysis and Heterogeneous Recovery. *Organometallics* **2018**, *37*, 1645−1648.

(4) (a) Oisaki, K.; Li, Q.; Furukawa, H.; Czaja, A. U.; Yaghi, O. M. A Metal-Organic Framework with Covalently Bound Organometallic Complexes. *J. Am. Chem. Soc.* **2010**, *132*, 9262−9264. (b) Dong, Y.; Li, Y.; Wei, Y.-L.; Wang, J.-C.; Ma, J.-P.; Ji, J.; Yao, B.-J.; Dong, Y.-B. A N-heterocyclic tetracarbene Pd(II) moiety contain-ing a Pd(II)−Pb(II) bimetallic MOF for three-component cyclotrimerization via benzyne. *Chem. Commun.* **2016**, *52*, 10505−10508. (c) Wei, Y.-L.; Li, Y.; Chen, Y.-Q.; Dong, Y.; Yao, J.-J.; Han, X.-Y.; Dong, Y.-B. Pd(II)-NHDC-Functionalized UiO-67 Type MOF for Catalyzing Heck Cross-Coupling and Intermolecular Benzyne−Benzyne−Alkene In-sertion Reactions. *Inorg. Chem.* **2018**, *57*, 4379−4386.

(5) (a) Liu, C.; Kubo, K.; Wang, E.; Han, K.-S.; Yang, F.; Chen, G.; Escobedo, F. A.; Coates, G. W.; Chen, P. Single polymer growth dynamics. *Science* **2017**, *358*, 352−355. (b) Wang, W.; Zheng, A.; Zhao, P.; Xia, C.; Li, F. Au-NHC@Porous Organic Polymers: Synthetic Control and Its Catalytic Application in Alkyne Hydration Reactions. *ACS Catal.* **2014**, *4*, 321−327.

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

(7) (a) Han, S. S.; Furukawa, H.; Yaghi, O. M.; Goddard, W. A. Covalent Organic Frameworks as Exceptional Hydrogen Storage Materials. *J. Am. Chem. Soc.* **2008**, *130*, 11580−11581. (b) Fan, H.; Mundstock, A.; Feldhoff, A.; Knebel, A.; Gu, J.; Meng, H.; Caro, J. Covalent Organic Framework-Covalent Organic Framework Bi-layer Membranes for Highly Selective Gas Separation. *J. Am. Chem. Soc.* **2018**, *140*, 10094−10098. (c) Wang, Z.-F.; Zhang, S.-N.; Chen, Y.; Zhang, Z.-J.; Ma, S.-Q. Covalent Organic Frameworks for Separation Applications. *Chem. Soc. Rev.* **2020**, *49*, 708−735.

(8) (a) Lin, G.; Ding, H.; Yuan, D.; Wang, B.; Wang, C. A Pyrene-Based, Fluorescent Three-Dimensional Covalent Organic Frame-work. *J. Am. Chem. Soc.* **2016**, *138*, 3302−3305. (b) Hao, Q.; Zhao, C.; Sun, B.; Lu, C.; Liu, J.; Liu, M.; Wan, L.-J.; Wang, D. Confined Synthesis of Two-Dimensional Covalent Organic Framework Thin Films within Superspreading Water Layer. *J. Am. Chem. Soc.* **2018**, *140*, 12152−12158. (c) Ascherl, L.; Evans, E. W.; Hennemann, M.; Di Nuzzo, D.; Hufnagel, A. G.; Beetz, M.; Friend, R. H.; Clark, T.; Bein, T.; Auras, F. Solvatochromic Covalent Organic Frameworks. *Nat. Commun.* **2018**, *9*, 3802. (d) Wu, X.; Han, X.; Xu, Q.; Liu, Y.; Yuan, C.; Yang, S.; Liu, Y.; Jiang, J.; Cui, Y. Chiral BINOL-Based Covalent Organic Frameworks for Enantioselective Sensing. *J. Am. Chem. Soc.* **2019**, *141*, 7081−7089. (e) Liu, X.-G.; Huang, D.-L.; Lai, C.; Zeng, G.-M.; Qin, L.; Wang, H.; Yi, H.; Li, B.-S.; Liu, S.-Y.; Zhang, M.-M.; Deng, R.; Fu, Y.-K.; Li, L.; Xue, W.-J.; Chen, S. Recent Advances in Covalent Organic Frameworks (COFs) as a Smart Sensing Material. *Chem. Soc. Rev.* **2019**, *48*, 5266−5302.

(9) (a) 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*, 19816−19822. (b) Vyas, V. S.; Haase, F.; Stegbauer, L.; Savasci, G.; Podjaski, F.; Ochsenfeld, C.; Lotsch, B. V. A Tunable Azine Covalent Organic Framework Platform for Visi-ble Light-Induced Hydrogen Generation. *Nat. Commun.* **2015**, *6*, 8508. (c) Lin, S.; Diercks, C. S.; Zhang, Y.-B.; Kornienko, N.; Nichols, E. M.; Zhao, Y.; Paris, A. R.; Kim, D.; Yang, P.; Yaghi, O. M.; Chang, C. J. Covalent Organic Frameworks Comprising Cobalt Porphyrins for Catalytic CO_2 Reduction in Water. *Science* **2015**, *349*, 1208−1213. (d) Sun, Q.; Aguila, B.; Perman, J.; Nguyen, N.; Ma, S. Q. Flexibility Matters: Cooperative Active Sites in Covalent Organic Framework and Threaded Ionic Polymer. *J. Am. Chem. Soc.* **2016**, *138*, 15790−1596. (e) Li, H.; Pan, Q.; Ma, Y.; Guan, X.; Xue, M.; Fang, Q.; Yan, Y.; Valtchev, V.; Qiu, S. Three-Dimensional Covalent Organic Frameworks with Dual Linkages for Bifunctional Cascade Catalysis. *J. Am. Chem. Soc.* **2016**, *138*, 14783−14788. (f) Lu, S.; Hu, Y.; Wan, S.; McCaffrey, R.; Jin, Y.; Gu, H.; Zhang, W. Synthesis of Ultrafine and Highly Dispersed Metal Nanoparticles Confined in a Thioether-Containing Covalent Organic Framework and Their Catalytic Applications. *J. Am. Chem. Soc.* **2017**, *139*, 17082−17088. (g) Pachfule, P.; Acharjya, A.; Roeser, J.; Langenhahn, T.; Schwarze, M.; Schomäcker, R.; Thomas, A.; Schmidt, J. Diacetylene Functionalized Covalent Organic Frame-work (COF) for Photo-catalytic Hydrogen Generation. *J. Am. Chem. Soc.* **2018**, *140*, 1423−1427. (h) Yang, J.; Wu, Y.; Wu, X.; Liu, W.; Wang, Y.; Wang, J. An N-Heterocyclic Carbene-functionalised Covalent Organic Framework with Atomically Dispersed Palladium for Coupling Reactions under Mild Conditions. *Green Chem.* **2019**, *21*, 5267−5273. (i) Wang, Y.; Liu, H.; Pan, Q.; Wu, C.; Hao, W.; Xu, J.; Chen, R.; Liu, J.; Li, Z.; Zhao, Y. Construction of Fully Conjugated Covalent Organic Frameworks via Facile Linkage Conversion for Efficient Photo-enzymatic Catalysis. *J. Am. Chem. Soc.* **2020**, *142*, 5958−5963. (j) Guo, J.; Jiang, D.-L. Covalent Organic Frameworks for Heterogeneous Catalysis: Principle, Current Status, and Challenges. *ACS Cent. Sci.* **2020**, *6*, 869−879.

(10) (a) Vyas, V. S.; Vishwakarma, M.; Moudrakovski, I.; Haase, F.; Savasci, G.; Ochsenfeld, C.; Spatz, J. P.; Lotsch, B. V. Exploiting Noncovalent Interactions in an Imine-Based Covalent Organic Framework for Quercetin Delivery. *Adv. Mater.* **2016**, *28*, 8749−8754. (b) Zhang, G.; Li, X.; Liao, Q.; Liu, Y.; Xi, K.; Huang, W.; Jia, X. Water-dispersible PEG-curcumin/amine-functionalized covalent organic framework nanocomposites as smart carriers for in vivo drug delivery. *Nat. Commun.* **2018**, *9*, 2785. (c) Guan, Q.; Fu, D.-D.; Li, Y.-A.; Kong, X.-M.; Wei, Z.-Y.; Li, W.-Y.; Zhang, S.-J.; Dong, Y.-B. BODIPY-Decorated Nanoscale Covalent Organic Frameworks for Photodynamic Therapy. *iScience* **2019**, *14*, 180−198. (d) Guan, Q.; Zhou, L.-L.; Li, Y.-A.; Li, W.-Y.; Wang, S.; Song, C.; Dong, Y.-B. Nanoscale Covalent Organic Framework for Combinatorial Anti-tumor Photodynamic and Photothermal Therapy. *ACS Nano* **2019**, *13*, 13304−13316. (e) Guan, Q.; Zhou, L.-L.; Li, W.-Y.; Li, Y.-A.;

Dong, Y.-B. Covalent Organic Frameworks (COFs) for Cancer Therapeutics. *Chem. - Eur. J.* **2020**, *26*, 5583−5591 and references therein. (f) Guan, Q.; Zhou, L.-L.; Lv, F.-H.; Li, W.-Y.; Li, Y.-A.; Dong, Y.-B. Nanoscale covalent organic frameworks as theranostic platforms for oncotherapy: synthesis, functionalization, and applications. *Angew. Chem., Int. Ed.* **2020**, DOI: 10.1002/anie.202008055. (g) Guan, Q.; Wang, G.-B.; Zhou, L.-L.; Li, W.-Y.; Dong, Y.-B. *Nanoscale Adv.* **2020**, DOI: 10.1039/D0NA00537A, and references therein. (h) Bhunia, S.; Deo, K. A.; Gaharwar, A. K. Gaharwar, 2D Covalent Organic Frameworks for Biomedical Applications. *Adv. Funct. Mater.* **2020**, *30*, 2002046.

(11) (a) Wan, S.; Guo, J.; Kim, J.; Ihee, H.; Jiang, D. A Belt-Shaped, Blue Luminescent, and Semiconducting Covalent Organic Framework. *Angew. Chem., Int. Ed.* **2008**, *47*, 8826−8830. (b) Bertrand, G. H. V.; Michaelis, V. K.; Ong, T. C.; Griffin, R. G.; Dinca, M. Thiophene-Based Covalent Organic Frameworks. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 4923−4928. (c) Dogru, M.; Handloser, M.; Auras, F.; Kunz, T.; Medina, D.; Hartschuh, A.; Knochel, P.; Bein, T. A Photoconductive Thienothio-phene-Based Covalent Organic Framework Showing Charge Transfer Towards Included Fullerene. *Angew. Chem., Int. Ed.* **2013**, *52*, 2920−2996. (d) Du, Y.; Yang, H.; Whiteley, J. M.; Wan, S.; Jin, Y.; Lee, S. H.; Zhang, W. Ionic Covalent Organic Frameworks with Spiroborate Linkage. *Angew. Chem., Int. Ed.* **2016**, *55*, 1737−1741. (e) Li, H.; Chang, J.; Li, S.; Guan, X.; Li, D.; Li, C.; Tang, L.; Xue, M.; Yan, Y.; Valtchev, V.; Qiu, S.; Fang, Q. Three-Dimensional Tetrathiafulvalene-Based Covalent Organic Frameworks for Tunable Electrical Conductivity. *J. Am. Chem. Soc.* **2019**, *141*, 13324−13329. (f) Yuan, S.; Li, X.; Zhu, J.; Zhang, G.; Van Puyvelde, P.; Van der Bruggen, B. Peter Van Puyvelde, Bart Van der Bruggen. Covalent Organic Frameworks for Membrane Separation. *Chem. Soc. Rev.* **2019**, *48*, 2665−2681.

(12) Ma, H.-C.; Zou, J.; Li, X.-T.; Chen, G.-J.; Dong, Y.-B. Homochiral Covalent Organic Frameworks for Asymmetric Catalysis. *Chem. - Eur. J.* **2020**, DOI: 10.1002/chem.202001006, and references therein.

(13) (a) Ma, H.-C.; Kan, J.-L.; Chen, G.-J.; Chen, C.-X.; Dong, Y.-B. Pd NPs-Loaded Homochiral Covalent Organic Framework for Heterogeneous Asymmetric Catalysis. *Chem. Mater.* **2017**, *29*, 6518−6524. (b) Ma, H.-C.; Zhao, C.-C.; Chen, G.-J.; Dong, Y.-B. Photothermal conversion triggered thermal asymmetric catalysis within metal nanoparticles loaded homochiral covalent organic framework. *Nat. Commun.* **2019**, *10*, 3368. (c) 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*, 6521−6526. (d) Ma, H.-C.; Chen, G.-J.; Huang, F.; Dong, Y.-B. Homochiral Covalent Organic Framework for Catalytic Asymmetric Synthesis of a Drug Intermediate. *J. Am. Chem. Soc.* **2020**, *142*, 12574−12578.

(14) *Materials Studio, Release Notes*; Accelrys Software, 2018.

(15) (a) Gooßen, L. J.; Rodriguez, N.; Manjolinho, F.; Lange, P. P. Synthesis of Propiolic Acids via Copper-Catalyzed Insertion of Carbon Dioxide into the C-H Bond of Terminal Alkynes. *Adv. Synth. Catal.* **2010**, *352*, 2913−2917. (b) Yu, D.; Zhang, Y. Copper- and copper-N-heterocyclic carbene-catalyzed C-H activating carboxylation of terminal alkynes with CO_2 at ambient conditions. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 20184−20189. (c) Zhang, X.; Zhang, W.-Z.; Ren, X.; Zhang, L.-L.; Lu, X.-B. Ligand-Free Ag(I)-Catalyzed Carboxylation of Terminal Alkynes with CO_2. *Org. Lett.* **2011**, *13*, 2402−2405.

(16) Bui, M.; Adjiman, C. S.; Bardow, A.; Anthony, E. J.; Boston, A.; Brown, S.; Fennell, P. S.; Fuss, S.; Galindo, A.; Hackett, L. A.; Hallett, J. P.; Herzog, H. J.; Jackson, G.; Kemper, J.; Krevor, S.; Maitland, G. C.; Matuszewski, M.; Metcalfe, I. S.; Petit, C.; Puxty, G.; Reimer, J.; Reiner, D. M.; Rubin, E. S.; Scott, S. A.; Shah, N.; Smit, B.; Trusler, J. P. M.; Webley, P.; Wilcox, J.; Mac Dowell, N. Carbon capture and storage (CCS): the way forward. *Energy Environ. Sci.* **2018**, *11*, 1062−1176.

(17) Manjolinho, F.; Arndt, M.; Gooßen, K.; Gooßen, L. J. Catalytic C−H Carboxylation of Terminal Alkynes with Carbon Dioxide. *ACS Catal.* **2012**, *2*, 2014−2021.

(18) Steinborn, D. In *Fundamentals of Organometallic Catalysis*, 1st ed.; Wiley-VCH: Weinheim, Germany, 2011.

(19) Marion, N.; Ramón, R. S.; Nolan, S. P. [(NHC)AuI]-Catalyzed Acid-Free Alkyne Hydration at Part-per-Million Catalyst Loadings. *J. Am. Chem. Soc.* **2009**, *131*, 448−449.

(20) (a) Ibrahim, H.; de Frémont, P.; Braunstein, P.; Théry, V.; Nauton, L.; Cisnetti, F.; Gautier, A. Water-Soluble Gold-*N*-Heterocyclic Carbene Complexes for the Catalytic Homogeneous Acid- and Silver-Free Hydration of Hydrophilic Alkynes. *Adv. Synth. Catal.* **2015**, *357*, 3893−3900. (b) Casado, R.; Contel, M.; Laguna, M.; Romero, P.; Sanz, S. Organometallic Gold(III) Compounds as Catalysts for the Addition of Water and Methanol to Terminal Alkynes. *J. Am. Chem. Soc.* **2003**, *125*, 11925−11935.

(21) (a) Mizushima, E.; Sato, K.; Hayashi, T.; Tanaka, M. Highly Efficient AuI-Catalyzed Hydration of Alkynes. *Angew. Chem., Int. Ed.* **2002**, *41*, 4563−4565. (b) Mizushima, E.; Cui, D.-M.; Nath, D. C. D.; Hayashi, T.; Tanaka, M. Au(I)-Catalyzed Hydration of Alkynes: 2,8-Nonanedione. *Org. Synth* **2006**, *83*, 55−60.

https://dx.doi.org/10.1021/acs.orglett.0c02721
Org. Lett. XXXX, XXX, XXX−XXX