

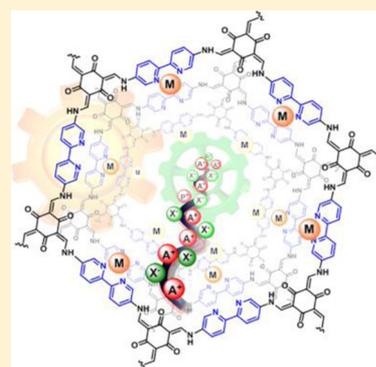
Flexibility Matters: Cooperative Active Sites in Covalent Organic Framework and Threaded Ionic Polymer

Qi Sun, Briana Aguila, Jason Perman,^{1b} Nicholas Nguyen, and Shengqian Ma^{*1b}

Department of Chemistry, University of South Florida, 4202 E. Fowler Avenue, Tampa, Florida 33620, United States

S Supporting Information

ABSTRACT: The combination of two or more reactive centers working in concert on a substrate to facilitate the reaction is now considered state of the art in catalysis, yet there still remains a tremendous challenge. Few heterogeneous systems of this sort have been exploited, as the active sites spatially separated within the rigid framework are usually difficult to cooperate. It is now shown that this roadblock can be surpassed. The underlying principle of the strategy presented here is the integration of catalytic components with excellent flexibility and porous heterogeneous catalysts, as demonstrated by the placement of linear ionic polymers in close proximity to surface Lewis acid active sites anchored on the walls of a covalent organic framework (COF). Using the cycloaddition of the epoxides and CO₂ as a model reaction, dramatic activity improvements have been achieved for the composite catalysts in relation to the individual catalytic component. Furthermore, they also clearly outperform the benchmark catalytic systems formed by the combination of the molecular organocatalysts and heterogeneous Lewis acid catalysts, while affording additional recyclability. The extraordinary flexibility



and enriched concentration of the catalytically active moieties on linear polymers facilitate the concerted catalysis, thus leading to superior catalytic performance. This work therefore uncovers an entirely new strategy for designing bifunctional catalysts with double-activation behavior and opens a new avenue in the design of multicapable systems that mimic biocatalysis.

INTRODUCTION

Enzymes seamlessly integrate multiple and cooperative functionalities in a space-saving manner and serve as models for scientists to design highly efficient catalysts.¹ Challenges nevertheless remain to design and prepare multifunctional catalysts featuring cooperative active sites,² especially for the heterogeneous catalysis, as the active sites spatially separated within the rigid framework are usually difficult to cooperate.³ To counter this, the introduction of molecular catalysts in proximity to surface active sites of heterogeneous supports offers an opportunity to exploit such cooperative effects.⁴ However, the encapsulation of guest molecules by porous hosts are vulnerable to leaching, since the encapsulation/release is a reversible process.⁵ Thus, there is still a need to find alternative guest materials which leverage the benefits of both homogeneous and heterogeneous catalysts. In view of the flexible nature of linear polymers, the functional moieties on them have significant movability thereby exhibiting properties similar to those of their homogeneous counterparts, which makes them promising candidates to be utilized instead of molecular catalysts.⁶ Also, recent studies have shown the feasibility of confining the linear polymers in the porous structure, thus adding to the practical advantages.⁷

Emerging as a promising class of porous materials, covalent organic frameworks (COFs)⁸ have received a great deal of attention due to their potential versatility in applications such as gas adsorption and storage,⁹ catalysis,¹⁰ sensing,¹¹ optoelectronics,¹² and many more.^{13,14} COFs' versatile properties can

be adjusted from a thoughtful selection of building units prior to synthesis. Therefore, scientists can manage the composition and the structural architecture in a crystalline and porous material with precise control over chemical functionality, density, and spatial arrangement of the active sites. This universal control is very attractive to design host materials for guest encapsulation. COFs are thus expected to serve as an auspicious platform for integrating multiple components to effect cooperative functions. Bearing these facts in mind, we postulate that composites of COFs and linear polymers featuring catalytically active components therefore are very promising as they may function as multifunctional catalysts cooperating with each other while simultaneously offering the possibility of facile catalyst recovery and reuse (Figure 1a).

Herein, we contribute an effective strategy to realize heterogeneous concerted catalysis, as illustrated by cooperative action between the catalytically active species from the COF and linear polymers threaded throughout. As a proof of concept, the cycloaddition reaction of CO₂ with epoxides was selected as it has been well-established that nucleophilic attack of halide anions to epoxides is greatly promoted with the assistance of Lewis acid sites, which in turn facilitates the insertion of CO₂ thus leading to dramatically enhanced reaction rates (Scheme 1).¹⁵ In this context, we integrated these active species via placing polymeric ionic polymers with halide anions

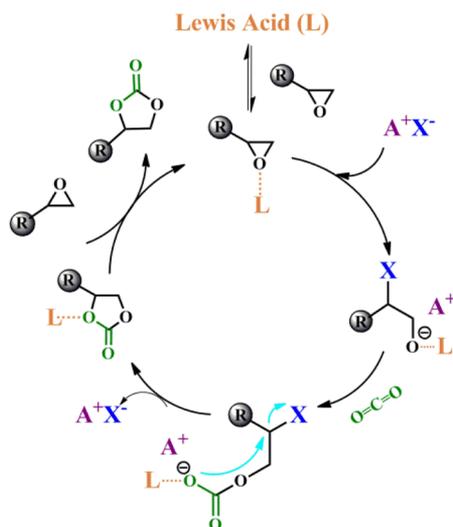
Received: October 11, 2016

Published: November 17, 2016



Figure 1. (a) The concept of heterogeneous concerted catalysis between active sites on the porous materials and highly flexible linear polymers and (b) schematic of PPS-COF-TpBpy-Cu synthesis and structures of COF-TpBpy and PPS-COF-TpBpy-Cu.

Scheme 1. Proposed Mechanism for the Lewis Acid-Catalyzed CO₂ Insertion into Epoxide in the Presence of Halide Anions



in a COF bearing Lewis acid sites. The resultant composites still retain the crystallinity and high surface area, thereby enabling ready access of the reactants to the active sites. We demonstrate that the composites exhibit significantly improved catalytic efficiency compared to individual components and outperform the combination of the organic ionic compounds and metalated COF catalyst. The flexibility and locally enriched active species enhance the cooperation activation. In addition, the composite is robust and can be readily recycled. These findings suggest the basis for a new design concept for achieving cooperativity acting multifunctional catalysis.

RESULTS AND DISCUSSION

Materials Preparation, Physicochemical Characterization, and Local Structure Analysis. To carry out this study, we chose a COF bearing 2,2'-bipyridine synthesized by the condensation of 1,3,5-triformylphloroglucinol and 5,5'-diamino-2,2'-bipyridine as the COF component (COF-TpBpy) for composites because of its excellent chemical stability, large pore size (~2.1 nm, Figure 1), and open, accessible coordination sites for potential metalation.^{10c} Phosphonium salts [PS,

ethylidiphenyl(4-vinylphenyl)phosphonium bromide] were chosen as a representative ionic monomer to illustrate thoroughly. To accommodate the linear polymers in COF channels, in situ radical polymerization of ionic monomers in COF-TpBpy was performed at 80 °C for 3 days. The resultant product was washed thoroughly with DMF to remove unincorporated polymers and unreacted monomers, affording the product denoted as PPS-COF-TpBpy.

Chemical confirmation of polymeric phosphonium salts (PPS) confined in COF-TpBpy was given by IR spectroscopy, solid state NMR, thermogravimetric analysis (TGA), and EDX mapping attached to a SEM. Figure S1 shows the IR spectra of PPS-COF-TpBpy and COF-TpBpy. Additional peaks appeared at 1106, 725, and 690 cm⁻¹ in the PPS-COF-TpBpy spectrum, arising from the peaks of the phosphonium salt moieties. Since both of the PS and PPS contain these peaks, the IR spectra thus are not sufficient for verifying the polymerization. To provide additional proof, ¹³C MAS NMR analysis was employed. As shown in the Figure 2a, the emergence of an obvious peak at 40.3 ppm attributed to the polymerized vinyl groups confirms the polymer formation. ³¹P MAS NMR

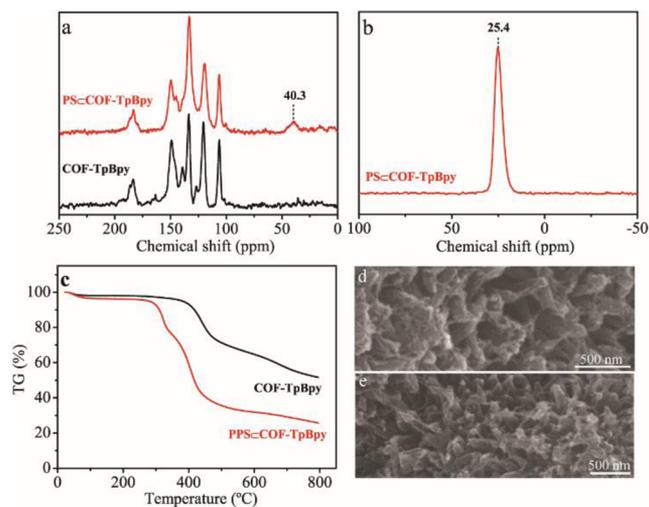


Figure 2. (a) ¹³C MAS NMR spectra, (b) ³¹P MAS NMR spectrum, (c) TG curves, and SEM images of (d) COF-TpBpy and (e) PPS-COF-TpBpy.

spectrum of PPSCCOF-TpBpy (Figure 2b) gives just one signal at 25.4 ppm and the chemical shift is similar to that observed in the monomer, revealing the retained quaternary phosphonium salt structure during the polymerization process. The TGA profile of PPSCCOF-TpBpy reveals that apart from the weight loss ascribed to the degradation of the COF host at the temperature of 360 °C, there is only one other sharp step of weight loss at 290 °C observed, which is attributed to the degradation of the guest material (Figure 2c and Figure S2). These behaviors suggest the uniform accommodation of PPS in the COF host. The EDX mapping via SEM further confirms the homogeneously distributed P, N, and O elements (Figure S3). The loading amount of PPS is estimated to be ca. 24.3 wt % by Br element analysis. In the SEM measurements, it is of interest that the overall morphology of the COF-TpBpy remained unchanged after the introduction of guest polymers (Figure 2d and 2e). This is a clear demonstration that polymerization occurs entirely within the crystalline framework. In order to understand the possible status of PPS polymer in the PPSCCOF-TpBpy, we isolated the PPS polymer by digesting COF-TpBpy using HBr. The structure of the obtained PPS was characterized ¹H NMR (Figure S4) and the polymerization degree was analyzed by gel permeation chromatography (GPC) to have a molecular weight of around $M_n = 7230$ (Figure S5). This molecular weight is equivalent to ca. 18 phosphonium salt units. Therefore, PPS is calculated to be penetrated through around 50 COF layers. Undulating forces of the PPS chain are suggested and contribute to the entropy that is localized within the COF-TpBpy, which highlights the advantage of in situ polymerization, considering that the monomers can freely diffuse while the resultant polymers are restricted.

Given that the residing PPS is not chemically bonded to the host COF-TpBpy, it should remain flexible and movable within the COF channels. To this end, the degree of freedom of confined PPS in the COF host was investigated by static solid-state ³¹P NMR spectroscopy due to the uniform chemical environment and the high natural abundance of ³¹P nuclei. The spectra of PPSCCOF-TpBpy in its solid form and as a suspension in THF are shown in Figure 3. The static spectrum of the dry solid sample exhibits an asymmetric and broad pattern because of the chemical-shift anisotropy of the ³¹P nucleus. Upon introducing of THF solvent to the solids, the peak is sharpened and centered around 24 ppm. Considering

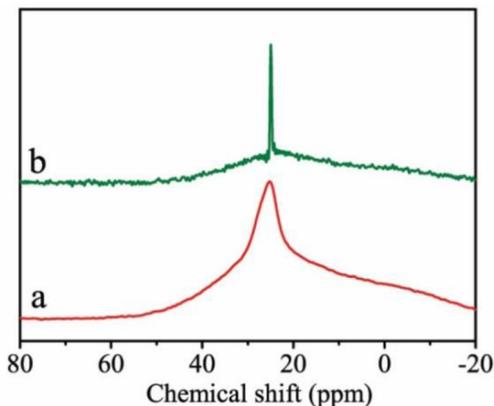


Figure 3. Solid-state ³¹P NMR spectra under static conditions of (a) dried PPSCCOF-TpBpy and (b) PPSCCOF-TpBpy upon introducing THF.

that both of the PS and PPS are insoluble in the THF solvent, it is thus indicated that PPS confined in the COF host does have a high flexibility and movability.¹⁶ This observation suggests that PPS could act as a quasi-homogeneous catalyst after introducing a solvent or liquid reagent into the COF.

Considering that Cu salts are inexpensive and combine the advantages of high activity and selectivity in cycloaddition of epoxides with CO₂,¹⁷ we therefore treated PPSCCOF-TpBpy with Cu(OAc)₂ to afford PPSCCOF-TpBpy-Cu. X-ray photoelectron spectroscopy (XPS) spectrum of the PPSCCOF-TpBpy-Cu demonstrates the binding energies of Cu 2p_{5/2} and Cu 2p_{3/2} at 952.1 and 932.4 eV, respectively, which are obviously lower than those of Cu(OAc)₂ (954.3 and 934.5 eV, respectively). Meanwhile, the N 1s binding energy of the PPSCCOF-TpBpy-Cu (399.4 eV) exhibits a higher value than that of the parent PPSCCOF-TpBpy (398.6 eV, Figure S6). These results suggest that strong interactions exist between the Cu species and bipyridine moieties in the PPSCCOF-TpBpy-Cu. ICP-OES results reveal that the Cu loading amount in the PPSCCOF-TpBpy-Cu is 4.6 wt %.¹⁸

Powder X-ray diffraction (PXRD) patterns verified that the crystalline structure of COF-TpBpy is retained in the PPSCCOF-TpBpy and PPSCCOF-TpBpy-Cu. However, the resultant peaks are broad and the relative intensity of the first peak corresponding to the (100) peak decreased during the step by step post synthetic modification. This can be presumably attributed to the presence of large numbers of flexible chains in the pores of COF-TpBpy which weakens the diffractions.¹⁹

Nitrogen sorption at 77 K was measured to investigate the porosity. As expected, a decrease in BET surface area from 1497 m²/g for pristine COF-TpBpy to 789 m²/g and 496 m²/g for PPSCCOF-TpBpy and PPSCCOF-TpBpy-Cu was observed, respectively. Although the pores of the COF are partially filled by polymer chains and Cu species, the surface area of the composite is still significant, and the open structure of the COF enables ready access of the reactants to the functional groups on the polymer chains and Cu species situated on the pore surfaces (Figure 4).

Catalytic Performance Investigation. Given the mobility of the catalytically active sites on the highly flexible PPS and their great potential cooperation with the Lewis acid sites (Cu species) anchored on the COF walls, we set out to evaluate its performance in the cycloaddition of epoxides with CO₂ to form cyclic carbonates. It is also based on the following considerations: (1) employing CO₂ as an abundant, inexpensive, and nontoxic C1 source could contribute to a more sustainable use of resources; (2) this transformation is highly atom-economical and the yielded cyclic organic carbonates have many important industrial applications. The initial reactions were conducted under atmospheric CO₂ and solvent-free conditions.²⁰ A set of control experiments were conducted to illustrate the advantages of the PPSCCOF-TpBpy-Cu catalytic system. As presented in Table 1, the PPSCCOF-TpBpy-Cu shows exceptional catalytic activity in the conversion of epichlorohydrin to the corresponding carbonate, outperforming all other catalytic systems tested under same reaction conditions. A carbonate yield of 95% can be achieved for PPSCCOF-TpBpy-Cu, which compares far more favorably to the corresponding value for COF-TpBpy-Cu (5%, entry 2) and PPS (12%, entry 3) used individually. The observed high catalytic activity of PPSCCOF-TpBpy-Cu is attributed to the cooperation between two different catalytic

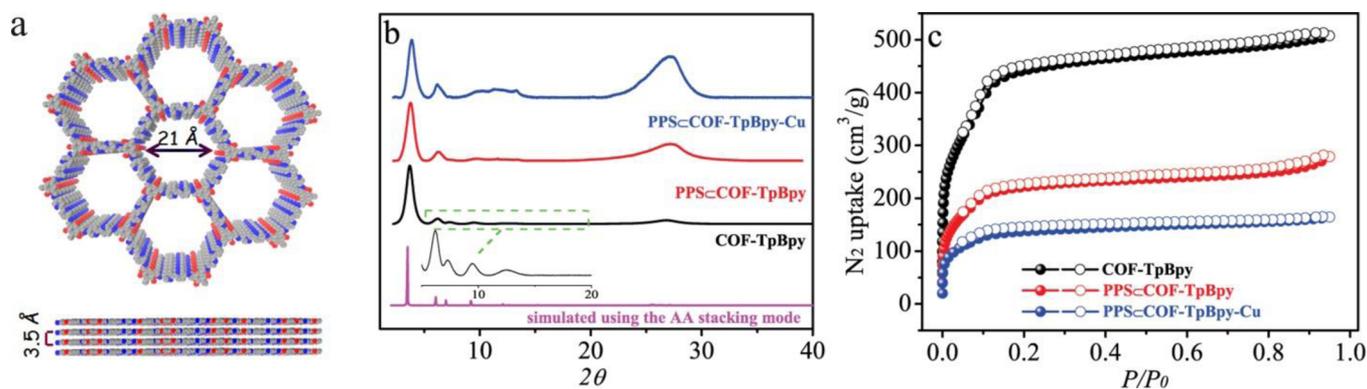


Figure 4. (a) View of the slipped AA stacking structure of COF-TpBpy (O, red; N, blue; C, gray), (b) simulated and experimental PXRD patterns, and (c) N₂ sorption isotherms collected at 77 K.

Table 1. Catalytic Data of Cycloaddition of Epichlorohydrin and CO₂ Catalyzed over Various Catalytic Systems^a

entry	catalyst	yield (%)
1 ^b	PPSCOF-TpBpy-Cu	95
2 ^c	COF-TpBpy-Cu	5
3 ^d	PPS	12
4 ^e	COF-TpBpy-Cu + PPS	16
5 ^f	COF-TpBpy-Cu + PPh ₃ EtBr	73
6 ^g	PPS and DVBCOF-TpBpy-Cu	49

^aReaction conditions: epichlorohydrin (1.0 g, 10.9 mmol), CO₂ (1 atm), 40 °C, and 24 h. ^bPPSCOF-TpBpy-Cu catalyst (25 mg, containing 0.018 mmol of Cu²⁺ and 0.015 mmol of Br⁻). ^cCOF-TpBpy-Cu catalyst (17.7 mg, containing 0.018 mmol of Cu²⁺; Cu loading amount in the catalyst is 6.5 wt %). ^dPPS (6 mg, containing 0.015 mmol of Br⁻). ^eThe mixture of COF-TpBpy-Cu (17.7 mg) and PPS (6 mg). ^fThe mixture of COF-TpBpy-Cu (17.7 mg) and PPh₃EtBr (6 mg). ^gPPS and DVBCOF-TpBpy-Cu (27 mg, containing 0.018 mmol of Cu²⁺ and 0.017 mmol of Br⁻).

components, namely Br⁻ anions from PPS and Cu²⁺ from the COF. This is further supported by the fact that PPSCOF-TpBpy-Cu can catalyze the cycloaddition of epichlorohydrin and CO₂ about five times more efficiently than the mixture of COF-TpBpy-Cu and PPS (95% vs 16%). In the last scenario, the active Cu²⁺ and Br⁻ species are spatially isolated, as PPS is entangled into a bulk material in the catalytic system, thereby leading to their incompetent cooperation. This observation suggests the superiority of in situ polymerization, which renders the polymers homogeneously distributed in the COF channels. To further substantiate the cooperative effect, a soluble ionic compound (PPh₃EtBr) analogue to the monomer of PPS was introduced into the COF-TpBpy-Cu system. An enhanced activity was observed, giving rise to the carbonate yield as high as 73%; nonetheless, it is still lower than the yield obtained by PPSCOF-TpBpy-Cu (95%). The free mobility of the molecular catalyst enables their cooperation with COF-TpBpy-Cu, thus facilitating the reaction. On the other hand, as molecular catalysts homogeneously distribute in the solution, a portion of them are dissolved in the reactant and do not participate in the cooperative catalytic reaction, thus resulting in the relatively lower utilization efficiency. In contrast, all of the ionic components in the PPSCOF-TpBpy-Cu are enriched in the vicinity of the Cu species in the confined COF channels,

which therefore dramatically increases the chances of concerted catalysis between the two different types of catalytic components thereby affording exceedingly high activity. In order to gain better insight into the role of flexibility played in the cooperation between two catalytic components, a catalyst with less flexibility was synthesized. In that case, the polymer chains threading through the pores of the COF are locked in place by introducing covalent cross-linker (divinylbenzene, DVB) during the in situ polymerization process. After metalation with Cu(OAc)₂, the resultant catalyst (PPS and DVBCOF-TpBpy-Cu, BET: 764 m²/g, Figure S7) affords the carbonate yield at 49%, nearly half as much achieved by employing PPSCOF-TpBpy-Cu. It is therefore indicated that the restricted flexibility of cross-linked PPS significantly reduces the catalytic components cooperation.

Catalyst recyclability and long-term stability are essential features of any catalysts considered for potential use in industrial applications. Since there is an absence of covalent bonds between COF and PPS, this freedom could allow PPS to escape from the COF during the reactions. Remarkably, in our case, this concern of leaching is dispelled, given the fact that there are no observable signals of PPS in the supernatant after reaction in liquid NMR spectrum (Figure S8). Also, no detectable leaching of Cu species can be found as revealed by the ICP-OES results. Moreover, PPSCOF-TpBpy-Cu can readily be recycled with negligible loss of its catalytic performance for at least ten cycles, further highlighting its heterogeneous in nature (Figure 5).

To further demonstrate the robustness of the catalyst, large-scale catalysis by experiments operated under relatively harsh reaction conditions at an initial CO₂ pressure of 2.0 MPa and 120 °C employing epichlorohydrin (10 g) and PPSCOF-TpBpy-Cu (5 mg) was carried out. After 48 h, a 95% yield of chloropropene carbonate and a TON value as high as 28 764 was achieved. Outstandingly, similar values (94% and TON at 28 461) can be afforded by the recycled catalyst, thus indicating the robustness of the catalyst. It is worth mentioning that such a high value of TON (over 20 000) suggests that the PPSCOF-TpBpy-Cu has broad prospects for practical applications.

Furthermore, the scope of the PPSCOF-TpBpy-Cu catalyst for the cycloaddition of various epoxides with atmospheric CO₂ was studied (Table 2). It is found that this catalytic system is broadly applicable. All of the tested epoxides were converted into corresponding carbonates in excellent yields under mild conditions.

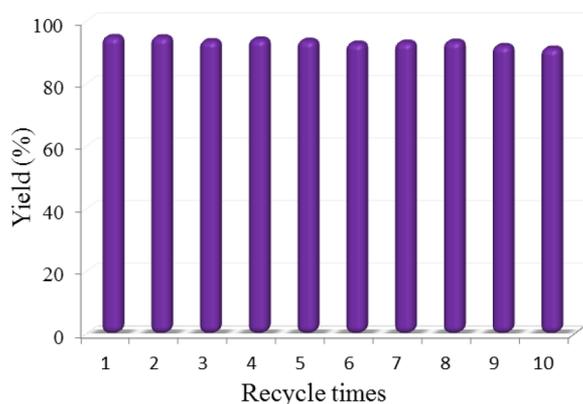


Figure 5. Recycling tests of the PPS-COF-TpBpy-Cu. Reaction conditions: epichlorohydrin (1.0 g, 10.9 mmol), CO₂ (1 atm), PPS-COF-TpBpy-Cu catalyst (25 mg), 40 °C, and 24 h.

Table 2. PPS-COF-TpBpy-Cu Catalyzed Cycloaddition Reactions of Epoxides with Atmospheric CO₂ to Cyclic Carbonates^a

Entry	Epoxides	Products	T (°C)	Time (h)	Yields (%) ^b
1			25	72	94
2			40	24	94
3			40	36	93
4			40	36	94
5			80	36	98

^aReaction conditions: epoxide (1.0 g), CO₂ (1 atm), and PPS-COF-TpBpy-Cu (25 mg). ^bThe yields were determined by NMR.

CONCLUSION

In summary, a new strategy is realized for concerted heterogeneous catalysis as demonstrated by encapsulating a catalytically active linear ionic polymer within the channels of a COF-TpBpy bearing Lewis acid. The flexibility and mobility of the catalytic moieties on the linear polymer enables them to cooperate with the active sites anchored on the COF pore walls. In addition, the essential catalytic components enriched in the confined space are beneficial to boosting the cooperation and promoting the catalytic efficiency. As a result, the composite exhibited significantly improved catalytic efficiency compared to the individual catalytic component. This proof-of-concept study is important because it affords an amenable route to bridge natural and artificial systems. Given that the strategy presented herein is applicable to a variety of porous materials

and linear polymers, our approach thus offers a general approach for preparing broad classes of multifunctional materials with significantly enhanced performance for various applications. For example, similar cooperation effect was observed when an imidazole type of linear ionic polymer (polymeric 1-ethyl-3-vinyl-1*H*-imidazol-3-ium bromide, PIS) was introduced into the COF catalyst (Figure 6 and Figures

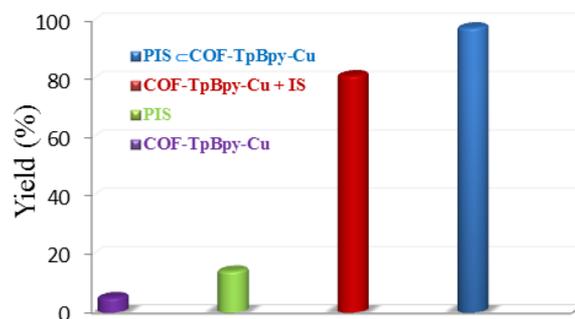


Figure 6. Catalytic performance of cycloaddition of epichlorohydrin with CO₂ over various catalytic systems. Reaction conditions: epichlorohydrin (1.0 g, 10.9 mmol), CO₂ (1 atm), 40 °C, and 24 h. PIS-COF-TpBpy-Cu catalyst (25 mg, containing 0.017 mmol of Cu²⁺ and 0.023 mmol of Br⁻); COF-TpBpy-Cu catalyst (17.7 mg); PIS (4.7 mg, containing 0.023 mmol of Br⁻); The mixture of COF-TpBpy-Cu (17.7 mg) and IS (1-ethyl-3-vinyl-1*H*-imidazol-3-ium bromide, 4.7 mg).

S9–S12). Studies aimed at extending this strategy to the encapsulation of other types of linear polymers into COFs for advanced catalysis applications are currently underway in our laboratory.

EXPERIMENTAL SECTION

Synthesis of COF-TpBpy. A Pyrex tube measuring o.d. × i.d. = 9.5 × 7.5 mm² was charged with trimethylphloroglucinol (21 mg, 0.10 mmol) and 5,5'-diamino-2,2'-bipyridine (27.9 mg, 0.15 mmol) in 1.1 mL of a 5:5:1 v:v solution of 1,4-dioxane: mesitylene: 6 M aqueous acetic acid. The tube was flash frozen at 77 K (liquid N₂ bath), evacuated and flame-sealed. Upon sealing the length of the tube was reduced to ca. 15 cm. The reaction mixture was heated at 120 °C for 5 days to afford an orange-red precipitate which was isolated by filtration and washed with anhydrous tetrahydrofuran using Soxhlet extraction for 2 days. The product was dried under vacuum at 50 °C to afford COF-TpBpy (38.1 mg, 78%).

Synthesis of PPS-COF-TpBpy. To the mixture of COF-TpBpy (100 mg), ethyldiphenyl(4-vinylphenyl)phosphonium bromide (100.0 mg), and azobis(isobutyronitrile) (5.0 mg) in a 25 mL Schlenk flask, degassed DMF (2.0 mL) was introduced under N₂ atmosphere. After stirring at room temperature for 24 h, the mixture was heated at 80 °C for another 3 days to afford the product which was isolated by filtration, washed by DMF and acetone and dried under vacuum at 50 °C. Br elemental analysis result reveals that the weight present of PPS in the PPS-COF-TpBpy is 24.3%.

Synthesis of PPS-COF-TpBpy-Cu. The mixture of Cu(OAc)₂·H₂O (20 mg) and PPS-COF-TpBpy (100 mg) in DMF (5 mL) were stirred at room temperature overnight. After that, the solid was filtrated, washed with an excess of DMF and acetone, and dried at 50 °C under vacuum to afford the PPS-COF-TpBpy-Cu. ICP-OES results reveal that the Cu loading amount in the PPS-COF-TpBpy-Cu was 4.6 wt %.

Catalytic Tests. Typical procedure for the cycloaddition reactions with atmospheric CO₂: the reactions were carried out in a 50 mL Schlenk flask with magnetic stirrer. As a typical run, epoxide (1.0 g) and catalyst listed in Table 1 was transferred into the reactor. After sealing and purging with CO₂ using a balloon, the tube was placed to a

preheated oil bath and stirred for a desired time. After the reaction, the catalyst was separated from the system by centrifugation and the product was analyzed by ^1H NMR.

Typical procedure for the cycloaddition reactions with high CO_2 pressure: the reactions were carried out in a stainless steel autoclave with magnetic stirrer. In a typical run, epichlorohydrin (10 g) and PPSCCOF-TpBpy-Cu (5 mg) were transferred into the autoclave. After sealing and purging with CO_2 to 2.0 MPa, the autoclave was placed in a preheated oil bath and stirred for a certain time. During the reaction, the pressure of the system was maintained at 1.0 to 3.0 MPa by adding CO_2 . After the reaction, the autoclave was cooled using ice water and CO_2 was released. The product was analyzed by ^1H NMR.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10629.

Material synthesis; Characterization details; IR, SEM, XPS, and NMR; and Supporting Figures (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*sqma@usf.edu

ORCID

Jason Perman: 0000-0003-4894-3561

Shengqian Ma: 0000-0002-1897-7069

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the University of South Florida for financial support of this work.

■ REFERENCES

- (1) (a) Breslow, R. *Acc. Chem. Res.* **1995**, *28*, 146–153. (b) Benkovic, S. J.; Hammes-Schiffer, S. *Science* **2003**, *301*, 1196–1202. (c) Wulff, G. *Chem. Rev.* **2002**, *102*, 1–28. (d) Sträter, N.; Lipscomb, W. N.; Klambunde, T.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1996**, *36*, 2024–2055.
- (2) (a) Paull, D. H.; Abraham, C. J.; Scerba, M. T.; Alden-Danforth, E.; Lectka, T. *Acc. Chem. Res.* **2008**, *41*, 655–663. (b) Shi, J. *Chem. Rev.* **2013**, *113*, 2139–2181. (c) Diaz, U.; Brunel, D.; Corma, A. *Chem. Soc. Rev.* **2013**, *42*, 4083–4097. (d) Allen, A. E.; MacMillan, D. W. C. *Chem. Sci.* **2012**, *3*, 633–658. (e) Lee, J. M.; Na, Y.; Han, H.; Chang, S. *Chem. Soc. Rev.* **2004**, *33*, 302–312. (f) Mata, J. A.; Hahn, F. E.; Peris, E. *Chem. Sci.* **2014**, *5*, 1723–1732. (g) Buchwalter, P.; Rosé, J.; Braunstein, P. *Chem. Rev.* **2015**, *115*, 28–126.
- (3) (a) Gu, Y.; Leng, X.; Shen, Q. *Nat. Commun.* **2014**, *5*, 5405. (b) Semba, K.; Nakao, Y. *J. Am. Chem. Soc.* **2014**, *136*, 7567–7570. (c) Sabater, S.; Mata, J. A.; Peris, E. *Nat. Commun.* **2013**, *4*, 3553. (d) Senda, Y.; Nakajima, K.; Nishibayashi, Y. *Angew. Chem., Int. Ed.* **2015**, *54*, 4060–4064. (e) Xu, J.; Chen, X.; Wang, M.; Zheng, P.; Song, B.-A.; Chi, Y. R. *Angew. Chem., Int. Ed.* **2015**, *54*, 5161–5165. (f) Liu, S.; Motta, A.; Mouat, A. R.; Delferro, M.; Marks, T. J. *J. Am. Chem. Soc.* **2014**, *136*, 10460–10469.
- (4) (a) Chen, Z.; Guan, Z.; Li, M.; Yang, Q.; Li, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 4913–4917. (b) Wang, J.; Zhao, L.; Shi, H.; He, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 9171–9176.
- (5) (a) Wang, H.; Xu, J.; Zhang, D.-S.; Chen, Q.; Wen, R.-M.; Chang, Z.; Bu, X.-H. *Angew. Chem., Int. Ed.* **2015**, *54*, 5966–5970. (b) An, J.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc.* **2009**, *131*, 8376–8377. (c) Taylor-Pashow, K. M. L.; Rocca, J. D.; Xie, Z.; Tran, S.; Lin, W. J. *Am. Chem. Soc.* **2009**, *131*, 14261–14263. (d) Demessence, A.; D'Alessandro, D. M.; Foo, M. L.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 8784–8786. (e) Gadzikwa, T.; Farha, O. K.; Malliakas, C. D.;

Kanatzidis, M. G.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2009**, *131*, 13613–13615. (f) Vyas, V. S.; Vishwakarma, M.; Moudrakovski, L.; Haase, F.; Savasci, G.; Ochsenfeld, C.; Spatz, J. P.; Lotsch, B. V. *Adv. Mater.* **2016**, *28*, 8749–8754.

(6) (a) Iwai, T.; Harada, T.; Hara, K.; Sawamura, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 12322–12326. (b) Sun, Q.; Aguila, B.; Verma, G.; Liu, X.; Dai, Z.; Deng, F.; Meng, X.; Xiao, F.-S.; Ma, S. *Chem.* **2016**, *1*, 628–639.

(7) (a) Mulzer, C. R.; Shen, L.; Bisbey, R. P.; McKone, J. R.; Zhang, N.; Abruña, H. D.; Dichtel, W. R. *ACS Cent. Sci.* **2016**, *2*, 667–673. (b) Distefano, G.; Suzuki, H.; Tsujimoto, M.; Isoda, S.; Bracco, S.; Comotti, A.; Sozzani, P.; Uemura, T.; Kitagawa, S. *Nat. Chem.* **2013**, *5*, 335–341. (c) Gao, L.; Li, C. Y. V.; Chan, K. Y.; Chen, Z. N. *J. Am. Chem. Soc.* **2014**, *136*, 7209–7212. (d) Gao, L.; Li, C. V.; Chan, K.-Y. *Chem. Mater.* **2015**, *27*, 3601–3608.

(8) (a) Côté, A. P.; Benin, A. J.; Ockwig, N. W.; O'Keefe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310*, 1166–1170. (b) Feng, X.; Ding, X.; Jiang, D. *Chem. Soc. Rev.* **2012**, *41*, 6010–6022. (c) Ding, S.-Y.; Wang, W. *Chem. Soc. Rev.* **2013**, *42*, 548–568. (d) Ascherl, L.; Sick, T.; Margraf, J. T.; Lapidus, S. H.; Calik, M.; Hettstedt, C.; Karaghiosoff, K.; Döblinger, M.; Clark, T.; Chapman, K. W.; Auras, F.; Bein, T. *Nat. Chem.* **2016**, *8*, 310–316. (e) Bunck, D. N.; Dichtel, W. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 1885–1889. (f) Zeng, Y.; Zou, R.; Luo, Z.; Zhang, H.; Yao, X.; Ma, X.; Zou, R.; Zhao, Y. *J. Am. Chem. Soc.* **2015**, *137*, 1020–1023. (g) Pang, Z.-F.; Xu, S.-Q.; Zhou, T.-Y.; Liang, R.-R.; Zhan, T.-G.; Zhao, X. *J. Am. Chem. Soc.* **2016**, *138*, 4710–4713. (h) Beaudoin, D.; Maris, T.; Wuest, J. D. *Nat. Chem.* **2013**, *5*, 830–834. (i) Chandra, S.; Kandambeth, S.; Biswal, B. P.; Lukose, B.; Kunjir, S. M.; Chaudhary, M.; Babarao, R.; Heine, T.; Banerjee, R. *J. Am. Chem. Soc.* **2013**, *135*, 17853–17861. (j) Kandambeth, S.; Mallick, A.; Lukose, B.; Mane, M. V.; Heine, T.; Banerjee, R. *J. Am. Chem. Soc.* **2012**, *134*, 19524–19527. (k) Huang, N.; Wang, P.; Jiang, D. *Nat. Rev. Mater.* **2016**, *1*, 16068.

(9) (a) Ma, H.; Ren, H.; Meng, S.; Yan, Z.; Zhao, H.; Sun, F.; Zhu, G. *Chem. Commun.* **2013**, *49*, 9773–9775. (b) Doonan, C. J.; Tranchemontagne, D. J.; Glover, T. G.; Hunt, J. R.; Yaghi, O. M. *Nat. Chem.* **2010**, *2*, 235–238. (c) Zeng, Y.; Zou, R.; Zhao, Y. *Adv. Mater.* **2016**, *28*, 2855–2873. (d) Stegbauer, L.; Hahn, M. W.; Jentys, A.; Savasci, G.; Ochsenfeld, C.; Lercher, J. A.; Lotsch, B. V. *Chem. Mater.* **2015**, *27*, 7874–7881.

(10) (a) Xu, H.; Gao, J.; Jiang, D. *Nat. Chem.* **2015**, *7*, 905–912. (b) Fang, Q.; Gu, S.; Zheng, J.; Zhuang, Z.; Qiu, S.; Yan, Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 2878–2882. (c) Ding, S.-Y.; Gao, J.; Wang, Q.; Zhang, Y.; Song, W.-G.; Su, C.-Y.; Wang, W. *J. Am. Chem. Soc.* **2011**, *133*, 19816–19822. (d) Peng, Y.; Hu, Z.; Gao, Y.; Yuan, D.; Kang, Z.; Qian, Y.; Yan, N.; Zhao, D. *ChemSusChem* **2015**, *8*, 3208–3212. (e) Aiyappa, H. B.; Thote, J.; Shinde, D. B.; Banerjee, R.; Kurungot, S. *Chem. Mater.* **2016**, *28*, 4375–4379. (f) Vyas, V. S.; Haase, F.; Stegbauer, L.; Savasci, G.; Podjaski, F.; Ochsenfeld, C.; Lotsch, B. V. *Nat. Commun.* **2015**, *6*, 8508. (g) 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. *Science* **2015**, *349*, 1208–1213. (h) Wang, X.; Han, X.; Zhang, J.; Wu, X.; Liu, Y.; Cui, Y. *J. Am. Chem. Soc.* **2016**, *138*, 12332–12335.

(11) (a) Lin, G.; Ding, H.; Yuan, D.; Wang, B.; Wang, C. *J. Am. Chem. Soc.* **2016**, *138*, 3302–3305. (b) Ding, S.-Y.; Dong, M.; Wang, Y.-W.; Chen, Y.-T.; Wang, H.-Z.; Su, C.-Y.; Wang, W. *J. Am. Chem. Soc.* **2016**, *138*, 3031–3027. (c) Campbell, M. G.; Liu, S. F.; Swager, T. M.; Dincă, M. *J. Am. Chem. Soc.* **2015**, *137*, 13780–13783. (d) Dalapati, S.; Jin, E.; Addicoat, M.; Heine, T.; Jiang, D. *J. Am. Chem. Soc.* **2016**, *138*, 5797–5800.

(12) (a) Chen, L.; Furukawa, K.; Gao, J.; Nagai, A.; Nakamura, T.; Dong, Y.; Jiang, D. *J. Am. Chem. Soc.* **2014**, *136*, 9806–9809. (b) Calik, M.; Auras, F.; Salonen, L. M.; Bader, K.; Grill, I.; Handloser, M.; Medina, D. D.; Dogru, M.; Löbermann, F.; Trauner, D.; Hartschuh, A.; Bein, T. *J. Am. Chem. Soc.* **2014**, *136*, 17802–17807. (c) Du, Y.; Yang, H.; Whiteley, J. M.; Wan, S.; Jin, Y.; Lee, S.-H.; Zhang, W. *Angew. Chem., Int. Ed.* **2016**, *55*, 1737–1741. (d) Bertrand, G. H. V.;

Michaelis, V. K.; Ong, T.-C.; Griffin, R. G.; Dincă, M. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 4923–4928.

(13) (a) Fang, Q.; Wang, J.; Gu, S.; Kaspar, R. B.; Zhuang, Z.; Zheng, J.; Guo, H.; Qiu, S.; Yan, Y. *J. Am. Chem. Soc.* **2015**, *137*, 8352–8355. (b) Mitra, S.; Kandambeth, S.; Biswal, B. P.; Khayum, M. A.; Choudhury, C. K.; Mehta, M.; Kaur, G.; Banerjee, S.; Prabhune, A.; Verma, S.; Roy, S.; Kharul, U. K.; Banerjee, R. *J. Am. Chem. Soc.* **2016**, *138*, 2823–2828.

(14) (a) Kalidindi, S. B.; Yussenko, K.; Fischer, R. A. *Chem. Commun.* **2011**, *47*, 8506–8508. (b) Ma, H.; Liu, B.; Li, B.; Zhang, L.; Li, Y.-G.; Tan, H.-Q.; Zang, H.-Y.; Zhu, G. *J. Am. Chem. Soc.* **2016**, *138*, 5897–5903. (c) Xu, H.; Tao, S.; Jiang, D. *Nat. Mater.* **2016**, *15*, 722–726.

(15) (a) Ema, T.; Miyazaki, Y.; Shimonishi, J.; Maeda, C.; Hasegawa, J. *J. Am. Chem. Soc.* **2014**, *136*, 15270–15279. (b) Xie, Y.; Wang, T.-T.; Liu, X.-H.; Zou, K.; Deng, W.-Q. *Nat. Commun.* **2013**, *4*, 1960. (c) Desens, W.; Kohrt, C.; Frank, M.; Werner, T. *ChemSusChem* **2015**, *8*, 3815–3822. (d) Maeda, C.; Taniguchi, T.; Ogawa, K.; Ema, T. *Angew. Chem., Int. Ed.* **2015**, *54*, 134–138. (e) Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J. A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. *Chem. Rev.* **2013**, *113*, 6621–6658. (f) Whiteoak, C. J.; Kielland, N.; Laserna, V.; Escudero-Adán, E. C.; Martin, E.; Kleij, A. W. *J. Am. Chem. Soc.* **2013**, *135*, 1228–1231. (g) Dai, Z.; Sun, Q.; Liu, X.; Bian, C.; Wu, Q.; Pan, S.; Wang, L.; Meng, X.; Deng, F.; Xiao, F.-S. *J. Catal.* **2016**, *338*, 202–209.

(16) (a) Sun, Q.; Dai, Z.; Liu, X.; Sheng, N.; Deng, F.; Meng, X.; Xiao, F.-S. *J. Am. Chem. Soc.* **2015**, *137*, 5204–5209. (b) Li, B.; Bai, S.; Wang, X.; Zhong, M.; Yang, Q.; Li, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 11517–11521.

(17) Gawande, M. B.; Goswami, A.; Felpin, F.-X.; Asefa, T.; Huang, X.; Silva, R.; Zou, X.; Zboril, R.; Varma, R. S. *Chem. Rev.* **2016**, *116*, 3722–3811.

(18) Sun, Q.; Lv, Z.; Du, Y.; Wu, Q.; Wang, L.; Zhu, L.; Meng, X.; Chen, W.; Xiao, F.-S. *Chem. - Asian J.* **2013**, *8*, 2822–2827.

(19) Xu, F.; Xu, H.; Chen, X.; Wu, D.; Wu, Y.; Liu, H.; Gu, C.; Fu, R.; Jiang, D. *Angew. Chem., Int. Ed.* **2015**, *54*, 6814–6818.

(20) (a) Gao, W.-Y.; Chen, Y.; Niu, Y.; Williams, K.; Cash, L.; Perez, P. J.; Wojtas, L.; Cai, J.; Chen, Y.-S.; Ma, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 2615–2619. (b) Soll, S.; Zhao, Q.; Weber, J.; Yuan, J. *Chem. Mater.* **2013**, *25*, 3003–3010. (c) Dong, J.; Cui, P.; Shi, P.-F.; Cheng, P.; Zhao, B. *J. Am. Chem. Soc.* **2015**, *137*, 15988–15991. (d) Beyzavi, M. H.; Klet, R. C.; Tussupbayev, S.; Borycz, J.; Vermeulen, N. A.; Cramer, C. J.; Stoddart, J. F.; Hupp, J. T.; Farha, O. K. *J. Am. Chem. Soc.* **2014**, *136*, 15861–15864. (e) Li, P.-Z.; Wang, X.-J.; Liu, J.; Lim, J. S.; Zou, R.; Zhao, Y. *J. Am. Chem. Soc.* **2016**, *138*, 2142–2145. (f) Zhou, Z.; He, C.; Xiu, J.; Yang, L.; Duan, C. *J. Am. Chem. Soc.* **2015**, *137*, 15066–15069. (g) Feng, D.; Chung, W.-C.; Wei, Z.; Gu, Z.-Y.; Jiang, H.-L.; Chen, Y.-P.; Darensbourg, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2013**, *135*, 17105–17110. (h) Gao, W.-Y.; Tsai, C.-Y.; Wojtas, L.; Thiounn, T.; Lin, C.-C.; Ma, S. *Inorg. Chem.* **2016**, *55*, 7291–7294. (i) Gao, W.-Y.; Wojtas, L.; Ma, S. *Chem. Commun.* **2014**, *50*, 5316–5318. (j) He, H.; Perman, J. A.; Zhu, G.; Ma, S. *Small* **2016**, DOI: 10.1002/smll.201602711.