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Accepted Article

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

To be cited as: ChemSusChem 10.1002/cssc.201601570

Link to VoR: http://dx.doi.org/10.1002/cssc.201601570



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Orderly layered Zr-benzylphosphonate nanohybrids for efficient acid/base-mediated bifunctional/cascade catalysis

Hu Li,^[a,b] Zhen Fang,*^[a] Jian He,^[b] Song Yang^[b]

Abstract: The development of functional metal-organic materials being robust and active for bifunctional/cascade catalysis is of great significance. Herein, a series of mesoporous and orderly layered nanohybrids were synthesized for the first time via simple and of ortho-, template-free assembly meta-. or paraxylylenediphosphonates (o-, p-, or m-PhP) with zirconium. It was found that m-PhPZr nanoparticles (20-50 nm) with mesopores centered at 7.9 nm and high Lewis acid/base site ratio (1:0.7) showed prominent performance under mild conditions (as low as 82 °C) in transfer hydrogenation of carbonyl compounds including bioaldehydes to alcohols with near quantative yields and little Zr leaching. Isotopic labeling study indicated the occurrence of direct hydrogen transfer rather than metal hydride route via bifunctional catalysis. Lewis acidic (Zr) and basic (PO3) centers of the heterogeneous catalyst were further revealed to play a synergistic role in one-pot cascade transformations, e.g., of ethyl levulinate to yvalerolactone and glucose to 5-hydroxymethylfurfural.

Carboxylate-based metal-organic frameworks (MOFs), a class of porous coordination polymers, have been demonstrated to exhibit a wide range of potential applications such as gas storage, adsorption and separation, drug delivery, and luminescence ^[1]. As a promising candidate to conventional heterogeneous catalysts, crystalline MOFs with flexible organic ligands, functional organic sites, embedded metal nanoparticles, and coordinatively unsaturated metal sites are active for solar fuel production and organic synthesis via photocatalysis ^[2]. In chemocatalytic reactions, the microporous cavities of MOFs typically offer substrate-size selectivity [3], which on the other hand may hinder the access of bulk molecules (e.g., highly branched- and long-chain organics) to the active sites of MOFs, thus possibly lowering the reaction rate and performance. To alleviate the mass diffusion and transfer obstacle of large molecules, microwave- and surfactant-assisted strategies are thus adopted to synthesize MOFs with mesoscale domains of 2-50 nm [4]. However, the cost and stability of the resulting mesoporous materials are rarely taken into account ^[5]. Unlike typical MOFs, trivalent/tetravalent metal phosphonate-based unconventional MOFs (UMOFs) are rarely crystalline, but tend to precipitate as irregularly layered hybrids and are highly insoluble as well as stable even in acidic system Owing to phosphonates capable of segregating hydrophobic moieties from hydrophilic groups ^[7], the surfactant-free self-assembly of homogeneous metal and R-PO₃H compositions render the possibility of creating mesoporous hybrid materials with robust structure^[8].

Lignocellulosic biomass, the most abundant organic carbon source in the nature, has been deemed as a prospective alternative to fossil fuel-based industry ^[9]. Catalytic

 [a] Dr. H. Li, Prof. Z. Fang Biomass Group, College of Engineering, Nanjing Agricultural University, 40 Dianjiangtai Road, Nanjing, Jiangsu 210031, China. E-mail: zhen.fang@mail.mcgill.ca, zhenfang@njau.edu.cn. URL: http://biomass-group.njau.edu.cn/
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[b] Dr. H. Li, J. He, Prof. S. Yang State-Local Joint Engineering Laboratory for Comprehensive Utilization of Biomass, State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering (Ministry of Education), Center for R&D of Fine Chemicals, Guizhou University, Guiyang 550025, China hydrogenation and dehydration processes are often used for the efficient removal of oxygen to increase C and H contents for the production of value-added chemicals and biofuels ^[10]. However, noble metals (e.g., Au, Pd, and Ru), high molecular hydrogen pressure, and mordant acids are generally required to achieve the desirable selectivity of biomass-derived products [11]. In contrast, catalytic transfer hydrogenation (CTH) using liquid organic hydrogen donors (e.g., alcohols and formic acid) can enhance the degree of control in selective hydrogenation, alleviate the safety concern of handling flammable H_2 , and reduce the cost and complexity of reaction units ^[12]. Besides noble and transition metal nanoparticles ^[13], cheap Zr-based catalysts (e.g., ZrO₂, ZrO(OH)₂ and ZrFeO_x) are active for CTH carbonyl compounds (e.g., levulinates, of 5hydroxymethylfurfural (HMF) and furfural) ^[14], but, some drawbacks including harsh reaction conditions and deactivation of them are always encountered. Hence, there is still a high demand to develop stable and effective Zr-containing materials for CTH reactions. To our knowledge, rare studies have been made on the structural optimization and use of zirconium phosphonate-based UMOFs for biomass valorization via bifunctional catalysis ^[14f,14g]. Herein, a series of novel zirconium benzylphosphonate nanohybrids were prepared by simply assembling ortho-, para-, and meta-xylylenediphosphonic acids with ZrCl₄ (denoted as o-, p-, and m-PhPZr) for CTH and selected cascade reactions in high efficiency.

The prepared o-, p-, and m-PhPZr hybrids were initially characterized by transmission electron microscopy (TEM). In Fig 1A-C, all the samples with disordered particle dimension are in nano scale (< 100 nm), which can be ascribed to the amorphous structure of zirconium phosphonates illustrated by X-ray diffraction (XRD, Fig. S1). Notably, m-PhPZr shows highly ordered interlayers, while a larger amount of platelike particles are bonded together in the cases of o- and p-PhPZr, thus exhibiting no regular layer distribution (Fig. S2). Inductively coupled plasma-optical emission spectrometer (ICP-OES) analysis shows an approximately 1:2 of Zr/P molar ratio for o-, pand *m*-PhPZr nanohybrids (Table S1), and the possible connectivity patterns between Zr⁴⁺ and different connectivity patterns different benzylphosphonates are provided in Fig. S3. The broad and strong absorptions ranging from 900 to 1200 cm⁻¹ in Fourier transform infrared (FT-IR) spectra of o-, p-, and m-PhPZr nanohybrids (Fig. S4) are assigned to P-O stretching vibrations ^[15], from the characteristic of α -type ZrP materials ^[16].



Fig. 1. TEM images of (A) o-PhPZr, (B) p-PhPZr, and (C) m-PhPZr

Thermogravimetric (TG) analysis demonstrates the thermostability of *m*-PhPZr (up to ~300 °C) is superior to that of *o*- and *p*-PhPZr nanohybrids (Fig. 2A). Despite the presence of micropores in these nanohybrids (Fig. 2B), the average pore diameter of *m*-PhPZr is centered at 7.9 nm (Fig. 2C), showing more regular pore-size distribution to others (Fig. S5). Moreover, a good spatial correspondence of Zr, P and O elemental maps in

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m-PhPZr is observed by scanning transmission electron microscope and high-angle annular dark-field (STEM-HAADF) (Fig. 2D-G), indicating the even connectivity and dispersion of – PO_3^{2-} and Zr^{4+} moieties. The presence of O^{2-} and Zr species in the bonding mode of -P-O-Zr- was most likely to be responsible for forming basic and acidic sites of the hybrids, respectively^[14f]. For comparison, other Zr-containing hybrids were also prepared with similar structural and textural properties (Figs. S1, S4-S9, Tables S2-S3). It should be noted that the difference in basicity and acidity of these Zr-based catalysts (Table S3), determined separately by CO_2 -TPD (temperature programmed desorption, Fig. S8) and pyridine adsorbed FT-IR (Fig. S9), could be ascribed to the discrepant types of acid radicals (i.e., phosphonate and carboxylate)^[14f] and their different substitution positions (i.e., *ortho-*, *meta-*, and *para*) in the aromatic ring^[17] that possibly affected the binding strength of the acid radical and Zr^{4+} .

Catalytic transformation of levulinic acid and its esters to yvalerolactone (GVL) is one of the important reactions for producing biofuel additives from biomass ^[18], which generally involves cascade reduction of carbonyl groups and intramolecular transesterification (i.e., cyclization). Hereby, CTH of ethyl levulinate (EL) to GVL in isopropanol (i-PrOH) was thus selected to study the performance of o-, p-, and m-PhPZr nanohybrids (Table 1). Pristine ZrO2 gave a high EL conversion of 97%, but a moderate GVL yield of 76% with isopropyl levulinate (IPL) as the major byproduct (entry 1), which may be ascribed to the occurrence of intermolecular transesterification facilitated by more base sites (Table S3, Fig. S8). In contrast, o-, p-, and m-PhPZr hybrids having relatively low molar ratios of base/acid sites and moderate Lewis acidity (Table S3, Fig. S9) were likely to impede the formation of IPL (1-6% yields), showing improved GVL yields of 89-98% (entries 2-4). In addition to the superior GVL yield, m-PhPZr also exhibited the highest GVL formation rate (38.9 μ mol g⁻¹ min⁻¹) and turnover frequency (TOF; 8.6 h⁻¹). The promotional and synergistic effect of Lewis acid-base sites on increasing GVL selectivity and EL conversion are clearly confirmed by the active sites-poisoned experiments (entries 5-6), wherein, GVL yield is significantly decreased by poisoning either Lewis acid or base sites.



Fig. 2. (A) TG curves and (B) N₂ adsorption-desorption isotherms for o-, p-, and m-PhPZr hybrids, as well as (C) pore-size distribution, (D) STEM-HAADF image, and (E) Zr, (F) P & (G) O elemental mappings for m-PhPZr nanohybrid

Entry	Catal.	Temp. (°C)	Time (h)	Catal./EL mass ratio	Base/acid sites ratio ^[a]	GVL Yield [%] ^[b]	EL Conv. [%] ^[b]	IPL Yield [%] ^[b]	GVL FR (µmol g ⁻¹ min ⁻¹) ^[c]	TOF [h ⁻¹] ^[d]
1	ZrO ₂	160	6	1:2.1	2.6:1	76	97	20	30.2	1.9
2	o-PhPZr	160	6	1:2.1	0.9:1	89	95	6	35.3	6.3
3	<i>p</i> -PhPZr	160	6	1:2.1	0.8:1	91	98	5	36.1	6.1
4	<i>m</i> -PhPZr	160	6	1:2.1	0.7:1	98	100	1	38.9	8.6
5 ^[e]	<i>m</i> -PhPZr	160	6	1:2.1	-	48	65	15	19.0	
6 ^[f]	<i>m</i> -PhPZr	160	6	1:2.1	-	37	40	2	14.7	
7	UiO-66(Zr)	160	6	1:2.1	3.9:1	72	93	19	28.6	3.4
8	m-PhOZr-H	160	6	1:2.1	2.8:1	79	94	13	31.3	3.8
9	<i>m</i> -PhPZr-H	160	6	1:2.1	1.3:1	86	96	8	34.1	6.7
10 ^[g]	Zr-HBA	150	4	1:0.7		94	100		19.6	3.5
11 ^[g]	Zr-Beta	150	6	1:0.7		92	100		12.8	2.4
12 ^[h]	Zr-Beta	82	18	1:0.6		4	6		0.2	0.3
13	<i>m</i> -PhPZr	82	18	1:0.6	0.7:1	85	100	12	3.3	1.2

^[a] The contents of acid and base sites were determined by pyridine-adsorbed FT-IR spectra and CO_2 -TPD (temperature programmed desorption), respectively. ^[b] EL conversion (Conv.), and GVL & IPL (isopropyl levulinate) yields were determined by gas chromatography (GC); Selec.: Selectivity. ^[c] GVL FR (formation rate) = (mole of GVL) / (catalyst amount × time). ^[d] TOF (turnover frequency) is defined as (mole of GVL) / (mole of catalyst acid-base sites × time) at EL conversion of ~15%. ^[e] Pretreatment with 100 mg pyridine to cover Lewis acid sites of *m*-PhPZr ^[14a]. ^[I] Titration with 100 mg benzoic acid to poison Lewis base sites of *m*-PhPZr ^[14a]. ^[I] The data were obtained from ref. [19]. ^[h] The data were obtained from ref. [20].

To investigate the universality of the concerted role of acid-base sites on converting EL to GVL, UiO-66(Zr), a typical carboxylatebased metal-organic framework being synthesized from terephthalic acid and ZrCl₄ under hydrothermal treatment, was also used as catalyst but only afforded a GVL yield of 72% (entry 7). The relatively higher content of base sites (0.31 mol g⁻¹) but lower Lewis acidity (0.08 mol g⁻¹; Table S3) in UiO-66(Zr) was more prone to cause IPL (19% yield) being generated from EL. As a counterpart of UiO-66(Zr), *m*-PhOZr-H prepared from isophthalic acid and ZrCl₄ with the same method displayed a reductive molar ratio of base/acid sites (2.8:1 vs 3.9:1), but still could not effectively restrain the generation of IPL (entry 8). By using the identical synthetic approach, the resulting *m*-PhPZr-H hybrid was found to have a comparable content of Lewis acid-base sites to *m*-PhOZr-H (0.36 vs 0.38 mol g⁻¹; Table S3) while an even lower base/acid site ratio of 1.3:1. The enhanced GVL yield (86%) from EL catalyzed by *m*-PhPZr-H (entry 9) revealed the more predominant role of Lewis acid sites than base ones, despite the concerted effect of acid-base couple sites had been evidently demonstrated for this reaction. On the other hand, the method used to prepare zirconium phosphonate-based UMOFs (i.e., *o*-, *p*-, and *m*-PhPZr) in the present study without a long period of hydrothermal treatment process was able to facilitate the formation of Lewis acid sites (Table S3, Figs. S8-S9), thus preferably promoting CTH of EL to GVL. Furthermore, *m*-PhPZr was also manifested to have unprecedented performance to other previously reported Zr-based catalysts even under open refluxing conditions (entries 10-13), demonstrating that *m*-PhPZr was more optimal for producing GVL from EL via the CTH process due to its superior ratio and content of base/acid sites.

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As discussed above, Lewis acid-base sites generated from zirconium and phosphate (P-O-Zr) or carboxylate (C-O-Zr) moieties were crucial for efficient CTH. Therefore, the local environment of Zr and O species was further examined by X-ray photoelectron spectroscopy (XPS; Fig. 3). Fig. 3A shows that the highest Zr 3d binding energy of *m*-PhPZr corresponds to the largest positive charge of Zr atoms, directly leading to the strongest Lewis acidity of Zr centers ^[21]. Moreover, the binding energy of O 1s assigned to P-O-Zr interactions coexistent with P=O species in m-PhPZr was lower than that of C-O-Zr interactions in m-PhOZr-H (Fig. 3B), illustrating a higher negative charge on oxygen and more enhanced basicity of the m-PhPZr catalyst. The superior strength of Lewis acid sites (Zr^{4+}) in *m*-PhPZr was beneficial to activate carbonyl groups of EL while a relatively higher basicity (O2-) was favorable for dissociating the hydroxy groups in *i*-PrOH (Scheme S1), both of which contributed to increase the selectivity and reaction rate towards GVL. However, too much higher basicity (e.g., ZrO₂) resulted in the rapid formation of IPL via intermolecular transesterification ^[22] Further two biomass-based transesterification Further, two biomass-based transformations promoted by acid-base couple sites including cascade isomerization-dehydration of glucose to HMF $^{\scriptscriptstyle [23]}$ and simultaneous esterification-transesterification of acidic seed oil to biodiesel ^[24] were conducted (Tables S4-S5). As expected, *m*-PhPZr exhibited better performance than *m*-PhOZr-H and ZrO₂ for both reactions, which confirmed the better compatibility and more concerted catalytic effect of acid-base sites in m-PhPZr during reactions, compared to *m*-PhOZr-H and ZrO₂.





Reaction time and catalyst dosage were also found to significantly affect the performance of *m*-PhPZr in CTH of EL to GVL (Fig. S10). With the increase of catalyst/EL mass ratio from 1:2.1 to 1:1, a comparable GVL yield of 97% at almost complete EL conversion was obtained in a shorter time of 4 h at 160 °C (Fig. S10 A-B). However, more IPL was generated in the early stage of the reaction when less *m*-PhPZr was used (Fig. S10 C-D), as illustrated by GC-MS spectra in Fig. S11. Likewise, a lower reaction temperature (100-140 °C) was favorable for forming IPL (up to 18%) at a relatively decreased EL conversion of 43-87% (Fig. S12). To our delight, the *in situ* generated IPL along with unreacted EL could be further converted to GVL by

prolonging reaction duration, even though a much lower catalyst/EL mass ratio of 1:6.3 was utilized (Fig. S10 D). These results are well consistent with the good activity of *m*-PhPZr in the open sytem for CTH of EL at the boiling point of *i*-PrOH (82 °C) after 18 h (Table 1, entry 13).

To examine the catalytic behavior of *m*-PhPZr in CTH of EL to GVL, the catalyst was filtered out from the reaction mixture after 2 h at 160 °C (Fig. S13). No obvious reaction was observed to occur for another 2-4 h, which clearly verified the heterogeneous catalysis of *m*-PhPZr. ICP-OES analysis shows an extremely low concentration of Zr (~0.2 ppm) leached into the reaction solution, indicating the robust structure of active species in *m*-PhPZr. Moreover, *m*-PhPZr was cycled for five times with no evident decline in activity (Fig. S14). The recovered *m*-PhPZr catalyst after five cycles was further characterized by NH₃-TPD, XRD, pyridine-adsorbed FT-IR, and N₂ adsorption-desorption (Fig. S15). It was revealed that the acid-base properties and textural structures between the fresh and used *m*-PhPZr catalysts

GVL in <i>i</i> -PrOH- <i>d</i> ⁸	4b	3b	2b 1b	0 4b 1b 3b 2b
EtOH in <i>i</i> -PrOH- <i>d</i> 8				
Reaction mixture after 6 h		3b ³ 2	b' 1b'	° + , , , , , , , , , , , , , , , , , ,
Reaction mixture after 4 h	y <u> </u>	L	l	
Reaction mixture after 2 h		Lun	L	
Reaction mixture after 1 h	l	<u> </u>	the	
EL in <i>i</i> -PrOH- <i>d</i> ⁸	5a	2a 4a 3a	1a 	2a $4a$ $5a$ $5a$
<i>i</i> -PrOH- <i>d</i> ₈	1			

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 11 (page

Fig. 4. Reaction kinetics study on CTH of EL to GVL in isotopic *i*-PrOH- d_{θ} using ¹H NMR (Reaction conditions: EL 2 mmol, *m*-PhPZr 0.14 g, *i*-PrOH- d_{θ} 10 mL, and 160 °C)

Mechanistic insight into CTH of EL to GVL was performed with ex situ Nuclear Magnetic Resonance (NMR) studies in *i*-PrOH-d₈ (completely deuterated isopropanol) in the presence of *m*-PhPZr by varying reaction time (1-6 h), and the obtained ¹H NMR spectra of the reaction mixture are provided in Fig. 4. For clear comparison, the NMR spectra of sole *i*-PrOH-d₈, as well as normal EL, GVL and ethanol (EtOH) in i-PrOH-d₈ are also supplied. The protons belonging to 1a, 4a and 5a of EL gradually disappeared with increasing addition of deuterium (D) from isotopic i-PrOH-d₈ to its C=O group, which can be straightforwardly detected from the NMR spectra of the mixture after reacting for 1-6 h. A slight chemical shift migration of 2a and 3a protons in EL to 2b' and 3b' of in situ formed GVL, and even to 2b and 3b of the normal GVL in i-PrOH-d₈ can be observed, respectively, which may be resulted from the presence of deuterium element in the in situ produced GVL despite of their similar proton environments. Compared to the normal GVL, the absence of 4a' proton in the partially deuterium-exchanged GVL throughout the reaction, and the gradually increased proton intensity of EtOH at around 5.7 ppm (Fig. 4) formed by intramolecular transesterification in reaction system prove the proceeding of CTH reaction. Nevertheless, it is still ambiguous to know whether the reaction occurs through direct hydrogen transfer or metal hydride route due to the lack of selectivity towards D addition ^[25]. To clarify these two pathways, *i*-PrOH-d₁ [i.e., CH₃CD(OH)CH₃] instead of *i*-PrOH-d₈ was used as hydrogen-donor and solvent for CTH of EL. Accordingly, GVL should be produced in a molecular weight of either MS+1 with 100% yield via direct hydrogen transfer, or 50% MS+0 and 50%

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MS+1 by the way of metal hydride (Scheme S2). Expectedly, GC-MS analysis shows the molecular ion peak of the generated GVL only containing an additional 1 amu (m/z = 101), which explicitly substantiates the happening of direct hydrogen transfer over m-PhPZr (Fig. S16).

Delighted by the pronounced catalytic performance of *m*-PhPZr in CTH of EL to GVL, the substrate scope was further extended to other carbonyl compounds including aliphatic and aromatic ketones, and biomass-derived aldehydes (Table 2). All examined ketones and aldehydes can be efficiently catalyzed by *m*-PhPZr to produce corresponding alcohols in high yields. Notably, harsh reaction conditions are required for CTH of ketones (entries 1-2), due to the steric hindrance and electron donating nature of the alkyl groups in these molecules. In contrast, biomass derivatives like citral, cinnamaldehyde, furfural, 5-methylfurfural, HMF, and veratraldehyde give near quantitative yields of corresponding alcohols in the presence of m-PhPZr under mild conditions (entries 3-8). These results indicate the great potential applications of *m*-PhPZr for the CTH reactions in both organic synthesis and biomass transformation.

Table 2. Results of *m*-PhPZr-catalyzed CTH of different carbonyl compounds to alcohols

Entry	Reactant	Product	Temp (ºC)	Time (h)	Conv (%) ^[b]	Yield (%) ^[b]
1		UH OH	160	8	97	96
2		\mathbf{Q}^{T}	160	6	99	99
3	Ç.	С	120	6	96	94
4		О	120	6	98	98
5	$\sqrt{1}$	ОЦОН	120	2	>99	99
6	-01-0	- ОН	120	2	>99	98
7	HO	но он	120	2	>99	93
8		ОН	120	2	98	97

^[a] Reaction conditions: 2 mmol substrate, 0.14 g *m*-PhPZr, and 10 mL *i*-PrOH. ^[b] Conversion (Conv) and yield were quantified using GC.

In brief, a facile and effective approach has been developed to prepare a series of orderly layered and mesoporous zirconium phosphonate by simply reacting ZrCl₄ with different xylylenediphosphonic acids. The resulting *m*-PhPZr nanohybrid shows prominent performance for CTH of various carbonyl compounds to corresponding alcohols, particularly for cascade CTH-cyclization of EL to GVL under mild conditions. Deuterium labeling experiments affirm the CTH reaction proceeding through direct intermolecular hydrogen transfer, other than metal hydride route. Comprehensive studies indicate that both Lewis acidic (Zr⁴⁺) and basic (PO₃²⁻) moieties contribute significantly to the excellent catalytic activity of m-PhPZr. The robust and heterogeneous nanohybrid shows great potential for biomass valorization and organic transformations mediated by acid-base couple sites, and the simple method can be used to synthesize other organic-inorganic functional hybrids.

Acknowledgements

We wish to thank the financial supports from Nanjing Agricultural University (68Q-0603), Postdoctoral Science Foundation of China (2016M600422), and Jiangsu Postdoctoral Research Funding Plan (1601029A).

Keywords: nanoparticles · heterogeneous catalysis · cascade reaction • mesoporous material • biomass conversion

- a) R. J. Kuppler, D. J. Timmons, Q. R. Fang, J. R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang, H. C. Zhou, *Coord. Chem. Rev.* **2009**, 253, 3042; b) Y.S. Bae, Snurr, R. Q. *Angew. Chem. Int. Ed.* **2011**, 50, 11586; c) P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris, C. Serre, *Chem. Rev.* **2012**, *112*, 1232; d) H. C. J. Zhou, S. Kitagawa, *Chem. Soc. Rev.* **2014**, *43*, 5415; b) K. He. W. Zhou; C. Qian, B. Chem. Soc. Baya **2014**, *43*, 5415; [1] e) Y. He, W. Zhou, G. Qian, B. Chen, *Chem. Soc. Rev.* **2014**, *43*, 5657; f) D.Farrusseng, *Angew. Chem. Int. Ed.* **2015**, *54*, 7480.
- a) Z. J. Lin, J. Lü, M. Hong, R. Cao, Chem. Soc. Rev. 2014, 43, 5867-[2] 5895; b) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C. Y. Su, *Chem.* Soc. Rev. **2014**, *43*, 6011; c) T. Zhang, W. Lin, *Chem. Soc. Rev.* **2014**, 43, 5982.
- J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450. [3]
- Z. Zhang, M. J. Zaworotko, Chem. Soc. Rev. 2014, 43, 5444 [4]
- W. Xuan, C. Zhu, Y. Liu, Y. Cui, *Chem. Soc. Rev.* **2012**, *41*, 1677. a) K. J. Gagnon, H. P. Perry, A. Clearfield, *Chem. Rev.* **2012**, *112*, 1034 [5] [6] b) J. Veliscek-Carolan, T. L. Hanley, V. Luca, Sep. Purif. Technol. 2014, 129 150
- [7]
- A. Cleatfield, *Curr. Opin. Solid State Mater. Sci.* 1998, 1, 268.
 Y. P. Zhu, T. Z. Ren, Z. Y. Yuan, *Catal. Sci. Technol.* 2015, 5, 4258.
 a) S. G. Wettstein, D. M. Alonso, E. I. Gürbüz, J. A. Dumesic, *Curr.* [8] [9] Opin. Chem. Eng. 2012, 1, 218; b) J. S. Luterbacher, D. Martin Alonso, A. Dumesic, Green Chem. 2014, 16, 4816; c) A. Corma, S. Iborra, A. Velty, Chem. Rev. 2007, 107, 2411; d) G. W. Huber, S. Iborra, A. Corma, Chem. Rev. 2006, 106, 4044.
 a) H. Li, Z. Fang, R. L. Smith Jr., S. Yang, Prog. Energ. Combust. 2016 55, 98; b) C. H. Zhou, X. Xia, C. X. Lin, D. S. Tong, J. Beltramini, Chem. Rev. 2014, 10, 55291; b) C. G. Carraon, Duiz, B. M. Wast, L.
- [10] Chem. Soc. Rev. 2011, 40, 5588; c) J. C. Serrano-Ruiz, R. M. West, J. A. Dumesic, Ann. Rev. Chem. Biomol. Eng. 2010, 1, 79; d) H. Li, Z.
- [11]
- A. Dumesic, Ann. Rev. Chem. Biomol. Eng. 2010, 1, 79; d) H. Li, Z.
 Fang, J. Luo, S. Yang, Appl. Catal. B: Environ. 2017, 200, 182.
 a) J. Lee, Y. Xu, G. W. Huber, Appl. Catal. B: Environ. 2013, 140-141, 98; b) M. Besson, P. Gallezot, C. Pinel, Chem. Rev. 2014, 114, 1827.
 a) M. J. Gilkey, B. Xu, ACS Catal. 2016, 6, 1420; b) A. H. Valekar, K. H
 Cho, S. K. Chitale, D. Y. Hong, G. Y. Cha, U-H. Lee, D. W. Hwang, C.
 Serre, J. S. Chang, Y. K. Hwang, Green Chem. 2016, 18, 4542.
 D. Wang, D. Astruc, Chem. Rev. 2015, 115, 6621.
 a) X. Tang, H. Chen, L. Hu, W. Hao, Y. Sun, X. Zeng, L. Lin, S. Liu, Annl. Catal. B: Environ 2014, 147, 827; b) H. Li, Z. Fang, S. Yang, Y. Sung, Y. Yang, Y. Sung, Y [12] [13]
- [14] Appl. Catal. B: Environ. **2014**, *147*, 827; b) H. Li, Z. Fang, S. Yang, ACS Sustainable Chem. Eng. **2016**, *4*, 236; c) K. Yan, Y. Yang, J. Chai, Y. Lu, Appl. Catal. B: Environ. **2015**, *179*, 292; d) W. Hao, W. Li, X. Tang, X. Zeng, Y. Sun, S. Liu, L. Lin, *Green Chem*. **2016**, *18*, 1080; e) H. Li, Z. Fang, S. Yang, *ChemPlusChem* **2016**, *81*, 135; f) J. Song, B. Zhou, H. Zhou, L. Wu, Q. Meng, Z. Liu, B. Han, Angew. Chem. Int. Ed. 2015, 54, 9399; Angew. Chem. 2015, 127, 9531; g) H. Li, J. He, A Riisager, S. Saravanamurugan, B. Song, S. Yang, ACS Catal. 2016, 6, 7722;
- C. M. Nam, J. S. Lee, Y. G. Kim, Korean J. Chem. Eng. 1993, 10, 93. [15]
- [16] F. Odobel, B. Bujoli, D. Massiot, *Chem. Mater.* **2001**, *13*, 163. F. Hibbert, *J. Chem. Soc., Perkin Trans.* **1978**, *11*, 1171.
- [17]
- F. Liguori, C. Moreno-Marrodan, P. Barbaro, *ACS Catal.* **2015**, *5*, 1882. J. Song, L. Wu, B. Zhou, H. Zhou, H. Fan, Y. Yang, Q. Meng, B. Han, [18] [19] Green Chem. 2015, 17, 1626.
- J. Wang, S. Jaenicke, G. K. Chuah, RSC Adv. 2014, 4, 13481. [20]
- [21] a) B. Tang, W. Dai, X. Sun, G. Wu, N. Guan, M. Hunger, L. Li, Green *Chem.* **2015**, *17*, 1744; b) H. J. M. Jaspers, *J.Catal.* **1996**, *161*, 551. Bosman, A. P. Pijpers, A. W. M. A.
- M. Chia, J. A. Dumesic, Chem. Commun. 2011, 47, 12233. [22] [23] M. Ohara, A. Takagaki, S. Nishimura, K. Ebitani, Appl. Catal. A: Gen. 2010, 383, 149
- [24] S. Yan, S. O. Salley, K.Y. Simon Ng, Appl. Catal. A: Gen. 2009, 353, 203.
- M. J. Gilkey, P. Panagiotopoulou, A. V. Mironenko, G. R. Jenness, D. G. Vlachos, B. Xu, ACS Catal. 2015, 5, 3988. [25]

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Two is better than one: Acid-base bifunctional Zr-benzylphosphonate nanohybrids, a class of unconventional metal-organic frameworks (UMOFs), are simply prepared to have unique properties (see image) and show predominant performance and stability in synthesis of valuable chemicals and biofules via bifunctional/cascade catalysis.



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Orderly layered Zrbenzylphosphonate nanohybrids for efficient acid/base-mediated bifunctional/cascade catalysis

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