

# A New Approach to Non-Coordinating Anions: Lewis Acid Enhancement of Porphyrin Metal Centers in a Zwitterionic Metal–Organic Framework

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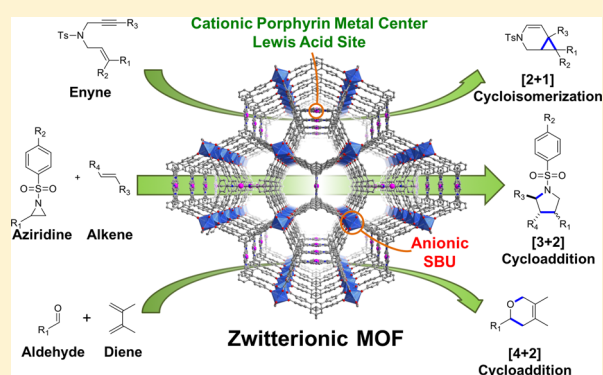
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## Supporting Information

**ABSTRACT:** We describe a new strategy to generate non-coordinating anions using zwitterionic metal–organic frameworks (MOFs). By assembly of anionic inorganic secondary building blocks (SBUs) ( $[\text{In}(\text{CO}_2)_4]^-$ ) with cationic metalloporphyrin-based organic linkers, we prepared zwitterionic MOFs in which the complete internal charge separation effectively prevents the potential binding of the counteranion to the cationic metal center. We demonstrate the enhanced Lewis acidity of  $\text{Mn}^{\text{III}}$ - and  $\text{Fe}^{\text{III}}$ -porphyrins in the zwitterionic MOFs in three representative electrocyclic reactions:  $[2 + 1]$  cycloisomerization of enynes,  $[3 + 2]$  cycloaddition of aziridines and alkenes, and  $[4 + 2]$  hetero-Diels–Alder cycloaddition of aldehydes with dienes. This work paves a new way to design functional MOFs for tunable chemical catalysis.



## INTRODUCTION

Cationic transition-metal complexes are frequently used to promote organic reactions, during which the ion pairing interaction between the metal center and the counteranion significantly affects the activation of substrates and catalytic activity in general.<sup>1</sup> Oftentimes, weakly coordinating anions (WCAs),<sup>2,3</sup> realized by either increasing the volume or introducing electron-withdrawing substituents,<sup>4</sup> are employed to increase the net positive charge of the cationic metal center and enhance the Lewis acidity (i.e., electrophilicity).<sup>5</sup> Another attractive approach involves the use of zwitterionic metal complexes, in which a cationic metal fragment and a negatively charged ancillary ligand are covalently bonded together to achieve a formal charge separation.<sup>6</sup> The internal charge neutralization and tunable electrophilicity of zwitterionic metal complexes have been particularly appealing for a variety of catalytic reactivity studies.<sup>7</sup>

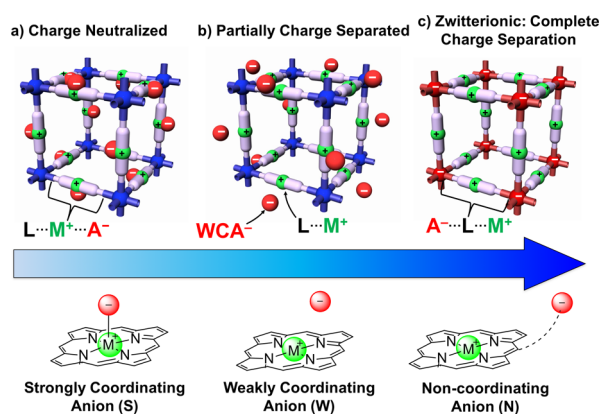
Metal–organic frameworks (MOFs) are a class of highly porous crystalline solid materials<sup>8</sup> that have found vast application potential in chemical catalysis.<sup>9</sup> Since both components of MOFs, the inorganic SBU (secondary building

unit) and organic linker, can be constructed to exhibit net ionic charge,<sup>10</sup> it is therefore possible to prepare zwitterionic MOFs,<sup>11</sup> for example, by the assembly of anionic inorganic SBUs with cationic metal complex-based linkers (Scheme 1). Importantly, in such zwitterionic MOFs the anionic SBU is essentially “non-coordinating”, which results in an enhanced Lewis acidity of the cationic metal center in the organic linker (Scheme 1c). Zwitterionic MOFs should also compare favorably to MOFs that are composed of cationic metal-ligands with extra framework WCAs in which only the partial charge separation is present (Scheme 1b). Herein, we describe a proof of concept study by synthesizing porphyrinic MOFs<sup>12</sup> that are comprised of anionic  $[\text{In}(\text{CO}_2)_4]^-$  SBUs and cationic metalloporphyrin linkers. We demonstrate that, with increased net positive charge in the cationic metal center, such zwitterionic MOFs exhibit enhanced catalytic activities for three representative organic transformations, that is, the  $[2 + 1]$  cycloisomerization of enynes, the  $[3 + 2]$  cycloaddition of

Received: June 1, 2016

Published: July 20, 2016

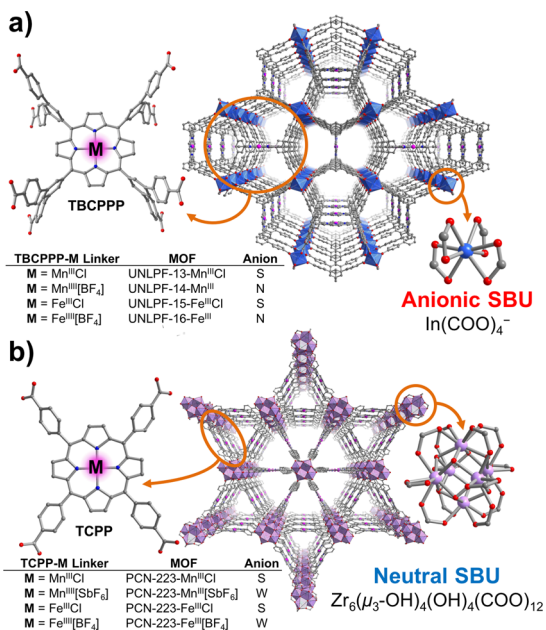
### Scheme 1. Design Strategy To Enhance Lewis Acidity of a Metal Center Using Zwitterionic MOFs



aziridines and alkenes, and the [4 + 2] hetero-Diels–Alder cycloaddition of aldehydes with dienes. Due to the increased Lewis acidity of the porphyrin metal center, the zwitterionic MOFs indeed afford higher reaction yields as well as an improved chemo- and/or regioselectivity in all three reactions.

## RESULTS AND DISCUSSION

**Ligand and MOFs Synthesis.** Using the extended octatopic ligand TBCPPP (tetrakis-3,5-bis((4-carboxy)phenyl)phenyl)porphyrin) developed in our group,<sup>13</sup> we first synthesized TBCPPP-Mn<sup>III</sup>Cl and -Fe<sup>III</sup>Cl linkers (Figure 1a)



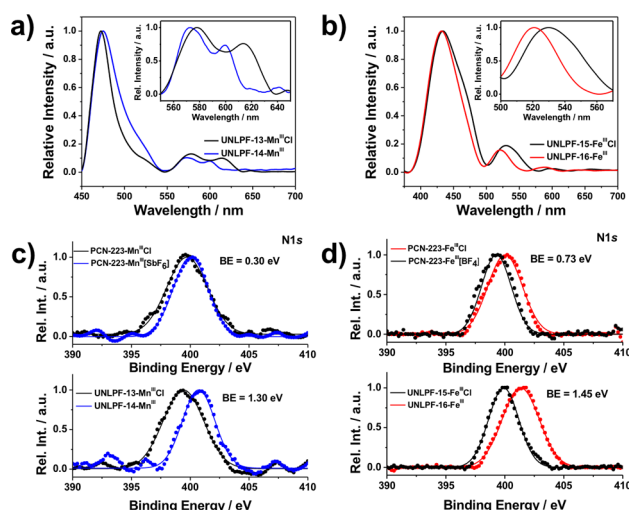
**Figure 1.** Structures of porphyrinic MOFs used in this work: (a) UNLPF-13-Mn<sup>III</sup>Cl, UNLPF-14-Mn<sup>III</sup>, UNLPF-15-Fe<sup>III</sup>Cl, and UNLPF-16-Fe<sup>III</sup>; (b) PCN-223-Mn<sup>III</sup>Cl, PCN-223-Mn<sup>III</sup>[SbF<sub>6</sub>], PCN-223-Fe<sup>III</sup>Cl, and PCN-223-Fe<sup>III</sup>[BF<sub>4</sub>].

(see Supporting Information for detailed synthetic procedure). Anion metathesis with AgBF<sub>4</sub> was then employed to replace the strongly (S) coordinated Cl<sup>-</sup> with weakly (W) coordinated BF<sub>4</sub><sup>-</sup>. The subsequent solvothermal reaction of octatopic TBCPPP-Mn<sup>III</sup>[BF<sub>4</sub>] and -Fe<sup>III</sup>[BF<sub>4</sub>] ligands with In(NO<sub>3</sub>)<sub>3</sub> resulted in non-coordinating (N) UNLPF-14-Mn<sup>III</sup> and UNLPF-16-Fe<sup>III</sup>, respectively. We also prepared the following

MOFs as controls for the catalytic studies (*vide infra*): (1) UNLPF-13-Mn<sup>III</sup>Cl and UNLPF-15-Fe<sup>III</sup>Cl using TBCPPP-M<sup>III</sup>Cl linkers (M = Mn and Fe) (Figure 1a); (2) neutral metalloporphyrinic MOFs PCN-223-Mn<sup>III</sup>Cl and PCN-223-Fe<sup>III</sup>Cl using tetratopic TCPP-M<sup>III</sup>Cl linkers (TCPP = tetrakis(4-carboxyphenyl)porphyrin, M = Mn and Fe); and (3) PCN-223-Mn<sup>III</sup>[SbF<sub>6</sub>] and PCN-223-Fe<sup>III</sup>[BF<sub>4</sub>] via post-synthetic anion metathesis with AgSbF<sub>6</sub> and AgBF<sub>4</sub>, respectively (reported by Zhou et al.)<sup>14</sup> (Figure 1b).

Single crystal X-ray diffraction structural analysis revealed that UNLPF-13-Mn<sup>III</sup>Cl, UNLPF-14-Mn<sup>III</sup>, UNLPF-15-Fe<sup>III</sup>Cl, and UNLPF-16-Fe<sup>III</sup> crystallize in the same orthorhombic *Pnmm* space group and are isostructures of UNLPF-10 (Tables S1–4). A chloride anion was crystallographically located on the porphyrin metal centers in the case of UNLPF-13-Mn<sup>III</sup>Cl and -15-Fe<sup>III</sup>Cl, with M<sup>III</sup>...Cl distances of 2.16 and 2.20 Å, respectively (Figure S2). As expected, anion coordination was not present in UNLPF-14-Mn<sup>III</sup> and -16-Fe<sup>III</sup>. Instead, the coordination of water was observed with M<sup>III</sup>...O distances of 2.25 and 2.29 Å, respectively, in good agreement with reported values.<sup>15</sup> Thorough solvent treatment of UNLPF-14-Mn<sup>III</sup> and -16-Fe<sup>III</sup> ensured the complete removal of the labile extra-framework BF<sub>4</sub><sup>-</sup>, evidenced by the absence of the signal of <sup>19</sup>F ( $\delta \sim -149$  ppm) in the <sup>19</sup>F NMR spectra of acid-digested MOF samples (Figure S4). The cationic dye uptake analysis<sup>13c</sup> for UNLPF-14-Mn<sup>III</sup> and -16-Fe<sup>III</sup> reveals an overall framework charge of “-1” per cage, consistent with the average charge occupation of the two [In(CO<sub>2</sub>)<sub>4</sub>]<sup>-</sup> SBUs and one [M<sup>III</sup>-porphyrin]<sup>+</sup> center per cage.

The change of coordination environment in the porphyrin metal center resulted from anion metathesis was further confirmed using UV–vis and X-ray photoemission spectroscopy (XPS). Specifically, in the absence of a strongly binding of the chloride ligand, a small blue shift of 5 and 8 nm of the Q1 band of the metalloporphyrin macrocycle in UNLPF-14-Mn<sup>III</sup> and in -16-Fe<sup>III</sup> (Figure 2a,b), respectively, consistent with the literature values<sup>16</sup> as well as the corresponding linkers (Figure S1). Moreover, the disappearance of the Cl (2p) signal at 201.2 and 200.6 eV, respectively (Figure S5), as well as the increase of

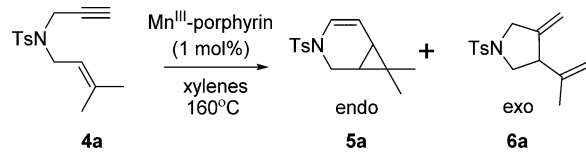


**Figure 2.** UV–vis spectra of (a) UNLPF-13,14 and (b) UNLPF-15,16 and XPS spectra showing the binding energy of N 1s for (c) UNLPF-13,14, PCN-223-Mn<sup>III</sup>Cl, and PCN-223-Mn<sup>III</sup>[SbF<sub>6</sub>] and (d) UNLPF-15,16, PCN-223-Fe<sup>III</sup>Cl, and PCN-223-Fe<sup>III</sup>[BF<sub>4</sub>].

the binding energy of N 1s in the XPS spectra (Figure 2c,d) of UNLPF-14-Mn<sup>III</sup> ( $\Delta BE = 1.30$  eV) and -16-Fe<sup>III</sup> ( $\Delta BE = 1.45$  eV) also provide experimental proof of successful preparation of zwitterionic MOF structures that exhibit the complete charge separation of the anionic SBUs and metalloporphyrin's cationic center. Notably, the observed increase in the binding energy for the anion-exchanged PCN-223-Mn<sup>III</sup>[SbF<sub>6</sub>] and PCN-223-Fe<sup>III</sup>[BF<sub>4</sub>] was smaller (0.30 and 0.73 eV, respectively), likely due to the presence of the labile extra-framework counteranions (i.e., SbF<sub>6</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup>). In addition, thermalgravimetric analysis (TGA) reveals a substantial initial weight loss (61.5–68.2 wt %) internally trapped solvent molecules, demonstrating the highly porous nature of UNLPF-13-Mn<sup>III</sup>Cl, -14-Mn<sup>III</sup>, -15-Fe<sup>III</sup>Cl, and -16-Fe<sup>III</sup> (Figure S7).

**[2 + 1] Cycloisomerization of Enynes.** In order to demonstrate the enhanced Lewis acid catalytic activity of the synthesized zwitterionic MOFs, we first examined their reactivity toward the cycloisomerization of enynes.<sup>17</sup> Cationic Mn<sup>III</sup>-porphyrin is known to catalyze the cycloisomerization of 1,6-enynes where the coordination capability of the counteranion is essential toward the chemoselectivity.<sup>18</sup> In general, weakly coordinated anions seem to promote the rare cyclopropane-annulated endocyclized six-membered product via an intramolecular stepwise [2 + 1] cycloaddition, with the highest yield of 75% (with TFPB, tetrakis[3,5-bis-(trifluoromethyl)-phenyl]-borate).<sup>18</sup> To our delight, employing only 1 mol % of UNLPF-14-Mn<sup>III</sup> as the catalyst, an excellent yield and selectivity toward the endproduct **5a** (95% isolated yield) was obtained within only 8h (Table 1, entry 1). In

**Table 1.** [2 + 1] Cycloisomerization of Enynes<sup>a</sup>



entry	catalyst	<i>t</i> (h)	yield <b>5a</b> (%)	yield <b>6a</b> (%)
1	UNLPF-14-Mn <sup>III</sup>	8	95	<1
2	UNLPF-13-Mn <sup>III</sup> Cl	24	<1	<1
3	PCN-223-Mn <sup>III</sup> Cl	24	<1	<1
4	PCN-223-Mn <sup>III</sup> [SbF <sub>6</sub> ]	24	63	31
5 <sup>b,c</sup>	MnTPPCl	24	<1	<1
6 <sup>b,c</sup>	MnTPP[OTf]	24	<1	95
7 <sup>b,c</sup>	MnTPP[SbF <sub>6</sub> ]	24	61	30
8 <sup>d</sup>	UNLPF-14-Mn <sup>III</sup>	8	92	<1

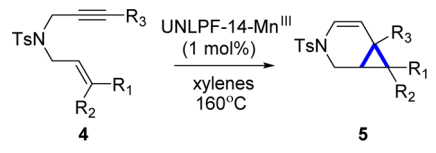
<sup>a</sup>Reaction conditions: Mn<sup>III</sup>-porphyrin catalysts (1 mol %) and enyne (0.2 mmol) in 1.6 mL of anhydrous xylenes at 160 °C. <sup>b</sup>From ref 18. <sup>c</sup>Catalyst loading: 10 mol %. <sup>d</sup>After third catalyst recycle.

contrast, PCN-223-Mn<sup>III</sup>[SbF<sub>6</sub>] exhibits essentially the same catalytic activity and selectivity for the endproduct **5a** (63%/31% yield of endo/exo product) as the homogeneous catalyst MnTPP[SbF<sub>6</sub>] (entries 4 and 7), likely due to the presence of the extra-framework SbF<sub>6</sub><sup>-</sup>. As expected, the presence of the strongly coordinating chloride anion in UNLPF-13-Mn<sup>III</sup>Cl completely inhibits the catalytic activity (entry 2), consistent with PCN-223-Mn<sup>III</sup>Cl (entry 3) and the homogeneous catalyst MnTPPCl (TPP = tetraphenylporphyrin) (entry 5). This result highlights the essential role of the complete charge separation that is only attainable in our zwitterionic MOFs. Furthermore, UNLPF-14-Mn<sup>III</sup> exhibits an excellent recyclability: A 92% yield was obtained after three times of catalyst reuse (entry 8), while

still maintaining good crystallinity (Figure S8). Additionally, ICP-MS performed on the supernatant of the reaction mixture indicated a low catalyst leaching of 0.20 mol % (Scheme S3).

To demonstrate the scope of the cycloisomerization of 1,6-enynes using UNLPF-14-Mn<sup>III</sup> as the catalyst, we carried out the reaction using different enynes **4** (Table 2) under the

**Table 2.** Scope of [2 + 1] Cycloisomerization of Enynes<sup>a</sup>



<b>5a</b> , 8h, 95%	<b>5b</b> , 8h, 92%	<b>5c</b> , 8h, 96%
<b>5d</b> , 13h, 87%	<b>5e</b> , 24h, 88% 24h, 0% <sup>b</sup>	<b>5f</b> , 24h, 67% 24h, 0% <sup>b</sup>

<sup>a</sup>Reaction conditions: catalyst (1 mol %) and enyne (0.2 mmol) in 1.6 mL of anhydrous xylenes at 160 °C. <sup>b</sup>MnTPP[SbF<sub>6</sub>] as the catalyst.

optimized reaction condition (Table 1, entry 1). The reaction shows good tolerance toward terminal, alkyl-, and dialkyl-substituted as well as phenyl-substituted alkenes (**4a–4d**). Interestingly, we did not observe the decomposition of substrate **4d** in our catalytic system, as was the case in the presence of MnTPP[TFPB].<sup>18</sup> Our MOF-based catalyst also exhibits excellent to good reactivity toward 1,6-enynes that contain internal alkynes such as **4e** (88% yield of **5e**) and **4f** (67% yield of **5f**), for which the cationic MnTPP[SbF<sub>6</sub>] catalyst exhibited negligible catalytic activity (Table 2). According to the proposed mechanism<sup>18</sup> (Scheme S4), the coordination of the Lewis acid to the β-C of the alkyne with respect to the nitrogen tether is the first and likely the rate-limiting step leading to the endproduct.<sup>18</sup> However, in the presence of a weakly coordinating anion (e.g., OTf<sup>-</sup>), the catalysts' active site is likely sterically hindered, in which case the γ-C of the alkyne may coordinate instead further leading to the exoproduct (Table 1, entry 6). Thus, the high selectivity of UNLPF-14-Mn<sup>III</sup> toward the endproduct is likely due to the “non-coordinating” nature of the SBU-based counteranion. In effect this renders the Lewis acidic metal center more “naked”, allowing for substrates with sterically demanding internal alkynes (**4e** and **4f**) to coordinate and further undergo the [2 + 1] cycloaddition. To the best of our knowledge, transition-metal (Rh, Ir, Pt, and Au) complexes are usually required to prepare endo cyclic products **5e** or **5f** with however poor to moderate yields.<sup>19</sup>

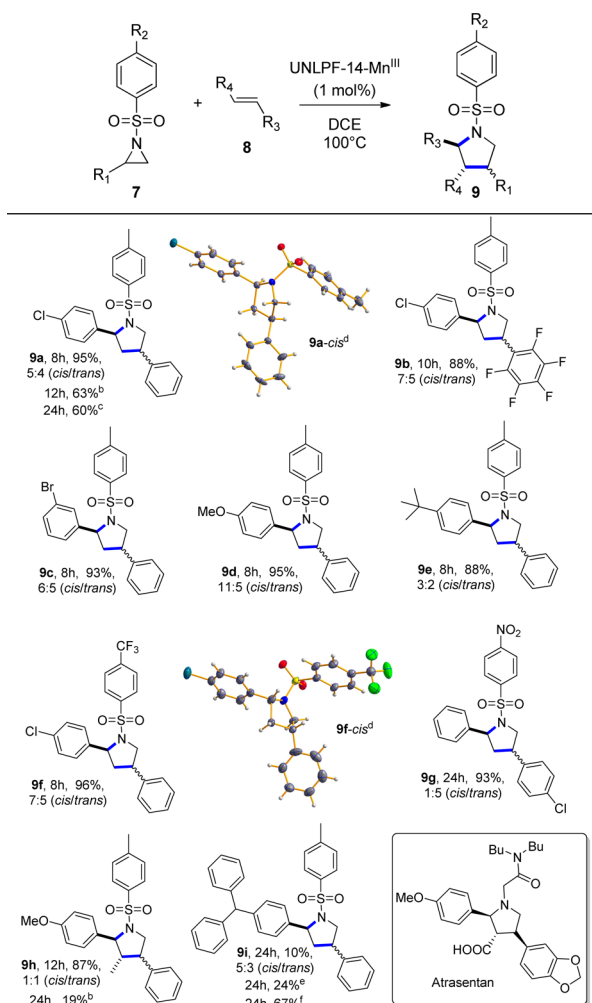
### [3 + 2] Cycloaddition of Aziridines and Alkenes.

Encouraged by this result, we next tested the catalytic activity of UNLPF-14-Mn<sup>III</sup> toward a Lewis acid-catalyzed bimolecular [3 + 2] cycloaddition of aziridines and alkenes. In general, Lewis acids are able to activate aziridines, generating a zwitterionic 1,3-dipolar intermediate via C–N bond cleavage, which may undergo stereo- and regioselective [3 + 2] cycloaddition to form pyrrolidines.<sup>20</sup> It was recently found that cationic Mn<sup>III</sup>-porphyrin allowed for styrene derivatives to react with aziridines in the presence of a WCA such as SbF<sub>6</sub><sup>-</sup>.<sup>21</sup> With



the essential non-coordinating SBU-based anions in UNLPPF-14-Mn<sup>III</sup>, an enhanced catalytic performance of the Mn<sup>III</sup>-porphyrin centers was anticipated. Indeed, the cycloaddition of 2-phenyl-1-tosylaziridine (**7a**) with 4-chlorostyrene (**8a**) in the presence of UNLPPF-14-Mn<sup>III</sup> (1 mol %) in 1,2-dichloroethane (DCE) at 100 °C for 8 h afforded the corresponding pyrrolidine **9a** in 95% yield as a diastereomeric mixture (Tables 3 and S5). UNLPPF-14-Mn<sup>III</sup> also exhibited excellent recycla-

**Table 3.** [3 + 2] Cycloaddition of Aziridines and Alkenes<sup>a</sup>



<sup>a</sup>Reaction conditions: catalyst (1 mol %), aziridine (0.2 mmol), and alkene (0.6 mmol) in 0.8 mL of anhydrous DCE at 80 °C. <sup>b</sup>From ref 21. <sup>c</sup>1 mol % of PCN-223-Mn<sup>III</sup>[SbF<sub>6</sub>] as the catalyst. <sup>d</sup>Thermal ellipsoids are set at the 50% probability level. <sup>e</sup>Catalyst loading increased to 5 mol %. <sup>f</sup>5 mol % of MnTPP[SbF<sub>6</sub>] as the catalyst.

bility. After reusing the catalyst three times, a 92% yield was obtained (Table S5). ICP-MS performed on the supernatant of the reaction mixture revealed a low catalyst leaching of 0.05 mol % (Scheme S6). The catalytic activity of zwitterionic UNLPPF-14-Mn<sup>III</sup> is significantly enhanced compared to that of MnTPP[SbF<sub>6</sub>] (5 mol %, 63% yield in 12 h),<sup>21</sup> TBCPPP-Mn<sup>III</sup>[BF<sub>4</sub>] (5 mol %, 54% yield in 12 h), and PCN-223-Mn<sup>III</sup>[SbF<sub>6</sub>] (1 mol %, 60% yield in 24 h) (see Table S5). Strong coordination of chloride completely quenched the reaction in UNLPPF-13-Mn<sup>III</sup>Cl and PCN-223-Mn<sup>III</sup>Cl (Table S5), similar to MnTPPCl.<sup>21</sup>

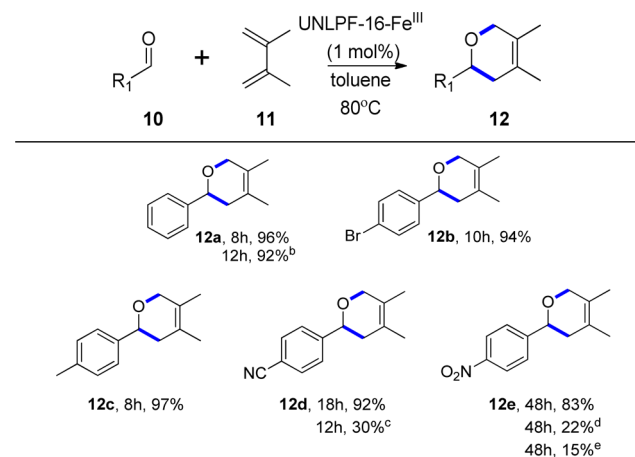
We next examined the UNLPPF-14-Mn<sup>III</sup> catalyzed [3 + 2] cycloaddition of aziridine **7** with different alkenes **8**. Styrenes with electron-withdrawing substituents such as chloride (**8a**) and bromide (**8c**) as well as electron-donating substituents such as methoxy (**8d**) and *tert*-butyl (**8e**) all gave rise to the pyrrolidine product **9** in excellent yields (>88%, Table 3). Remarkably, the internal alkene, anethole (**8h**), is also a suitable substrate for aziridine **7a** to give pyrrolidine **9h** (87% yield, 12h). In contrast, MnTPP[SbF<sub>6</sub>] only afforded a low yield (19%, 24h), in which the major byproduct was determined to be the Friedel–Craft arylation product.<sup>22</sup> We attribute this result to capability of UNLPPF-14-Mn<sup>III</sup> to better stabilize the 1,3-dipole intermediate following the C–N cleavage of the aziridine, further allowing for more challenging styrene substrates to attack (Scheme S5). To the best of our knowledge, this is the first reported example of a pyrrolidine formed from an aromatic internal alkene and an aziridine. Our catalyst protocol may be used to prepare the derivatives of pharmaceutically relevant compounds such as Atrasentan (Table 3, inset). Moreover, aziridines with electron-withdrawing substituting groups such as fluoride (**7b**), chloride (**7g**), and trifluoromethyl (**7f**) were also suitable substrates, and the functionalized pyrrolidines were obtained in excellent yields (>88%).

To further test the scope of this reaction, we employed an aziridine functionalized with an even stronger electron-withdrawing group, NO<sub>2</sub> (**7g**). Remarkably, when styrene is used as the alkene, the corresponding pyrrolidine (**9g**) can be obtained in 93% yield albeit a longer reaction time (24h) is required. This may be attributed to the decreased nucleophilicity of the nitrogen which, according to the proposed mechanism (Scheme S5), coordinates to the cationic Mn<sup>III</sup>-porphyrin center. When the sterically demanding substrate 4-benzhydrylstyrene (**8i**) was combined with **7a** in the presence of UNLPPF-14-Mn<sup>III</sup>, a poor yield (10% in 24h) was achieved for the corresponding pyrrolidine **9i**. Further, increasing the catalyst loading to 5 mol % had minimal effect on the catalysts' performance (24% in 24 h). However, the homogeneous catalyst MnTPP[SbF<sub>6</sub>], was capable of achieving a good yield of 67% in 24 h. We tentatively attribute the inferior performance of UNLPPF-14-Mn<sup>III</sup> toward this reaction to the inefficient product diffusion within the MOF pores due to the geometric dimensions of **9i** being too large to fit through cage windows of the framework (Figures S9–11). This result also strongly suggests that the catalytic reaction indeed mostly occurs inside the MOF's channels. Interestingly, pyrrolidines **9a** and **9f** crystallize in the chiral monoclinic space group *P*2<sub>1</sub>/*c* as a disordered mixture of diastereomers (Figure S13 and Tables S6–7).

**[4 + 2] Hetero-Diels–Alder Cycloaddition of Aldehydes with Dienes.** To extend our zwitterionic MOF catalysis protocol to other cationic metalporphyrin systems, we tested the catalytic activity of UNLPPF-16-Fe<sup>III</sup> toward the [4 + 2] hetero-Diels–Alder cycloaddition of aldehydes with dienes.<sup>23</sup> This reaction can be used to prepare pyrans, a class of synthetic targets for biologically relevant compounds.<sup>24</sup> It was recently reported that cationic Fe<sup>III</sup>-porphyrin can promote the chemoselective cycloaddition of unactivated, electron-deficient aldehydes with simple, poorly reactive dienes.<sup>25</sup> Similarly, the coordination strength of the counteranion dictates the catalytic activity in that the WCA, SbF<sub>6</sub><sup>−</sup>, or BF<sub>4</sub><sup>−</sup> was necessary for a high catalytic activity.<sup>25</sup> Indeed, the reaction of benzaldehyde (**10a**) with 2,3-dimethyl-1,3-butadiene (**11**) in the presence of

zwitterionic UNLPF-16-Fe<sup>III</sup> in toluene at 80 °C for 8 h afforded pyran **12a** in 96% yield (Tables 4 and S8), faster than

**Table 4.** [4 + 2] Hetero-Diels–Alder Cycloaddition of Aldehydes with Dienes<sup>a</sup>



<sup>a</sup>Reaction conditions: catalyst (1 mol %), aldehyde (0.5 mmol), and diene (2.0 mmol) in 2.0 mL toluene at 80 °C. <sup>b</sup>From ref 25. <sup>c</sup>From ref 14. <sup>d</sup>PCN-223-Fe<sup>III</sup>[BF<sub>4</sub>]<sup>-</sup> as the catalyst. <sup>e</sup>FeTPP[BF<sub>4</sub>]<sup>-</sup> as the catalyst.

FeTPP[BF<sub>4</sub>]<sup>-</sup> (5 mol % loading, 92% in 12 h).<sup>25</sup> Again a low catalyst leaching of 0.06 mol % was demonstrated by ICP-MS for the supernatant of the reaction mixture (Scheme S8). As expected, in the presence of UNLPF-15-Fe<sup>III</sup>Cl or PCN-223-Fe<sup>III</sup>Cl, the reaction became retarded (Table S8) due to the presence of the strongly coordinating Cl<sup>-</sup>, similar to the result from FeTPP[BF<sub>4</sub>]<sup>-</sup>.<sup>25</sup>

UNLPF-16-Fe<sup>III</sup> also has a good substrate scope: Benzaldehydes with both electron-withdrawing (bromide **10b**) and electron-donating (methyl **10c**) substituents are suitable to furnish the pyran products in excellent yields (Table 4). Nitrite and nitro substituents are also tolerated albeit a longer reaction time is required, likely due to the decreased nucleophilicity of the aldehyde oxygen, which must coordinate to the cationic Fe<sup>III</sup>-porphyrin center to activate the substrate according to the proposed mechanism (Scheme S7). Nevertheless, comparing to FeTPP[BF<sub>4</sub>]<sup>-</sup> and PCN-223-Fe<sup>III</sup>[BF<sub>4</sub>]<sup>-</sup>, UNLPF-16-Fe<sup>III</sup> clearly exhibited a faster reaction rate and higher reaction yield (92% and 83% yield for **12d** and **12e**, respectively). The enhanced reactivity is likely due to the better polarization and further activation of the C=O bond upon coordination of the benzaldehyde substrate to zwitterionic UNLPF-16-Fe<sup>III</sup>.

## CONCLUSIONS

In summary, we have provided a proof of concept study in which the zwitterionic MOFs indeed mimic the zwitterionic metal complexes and cationic metal complexes consisting of WCAs. The enhanced Lewis acid catalytic activities of the porphyrin metal centers in the anionic indium MOFs are due to the complete charge separation and the resulting change of the electronic properties including the orbital energies and the distribution of electronic density. This change in terms of electronic structure considerably affects the activation of substrates and lowers the activation barrier of subsequent transformation steps in three representative electrocycloaddition reactions. This study paves a new way for designing functional MOFs for tunable chemical catalysis, which is currently underway in our laboratory.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05626.

Materials, general experimental procedures, synthesis of UNLPF-13–16 and catalytic studies, characterizations of compounds (PDF)

Crystallographic data (CIF)

Crystallographic data (CIF)

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors acknowledge the support from the University of Nebraska–Lincoln and NSF through Nebraska MRSEC (DMR-0820521). ChemMatCARS Sector 15 is principally supported by the Divisions of Chemistry (CHE) and Materials Research (DMR), National Science Foundation, under grant number NSF/CHE-1346572. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under contract no. DE-AC02-06CH11357. A.K. thanks the Rosztoczy Foundation for a fellowship.

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