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# Imidazole-Directed Fabrication of Three Polyoxovanadatesbased Copper Frameworks as Efficient Catalysts for Constructing of C-N bonds

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The synthetic pathway for the directed preparation of three novel polyoxovanadates-based copper frameworks (POVCFs), i.e.,  $[Cu_{0.5}(1-ipIM)_2]_2[V_4O_{11}]$  (POVCFs **1**) and  $[Cu(1-ipIM)_2](VO_3)_2$  (POVCFs **2**) and  $[Cu(1-pIM)_4](HpIM)_4[V_{10}O_{28}]$  (POVCFs **3**) (1-ipIM = 1-isopropylimidazole; 1-pIM = 1-propylimidazole) using bifuncational imidazole molecules as organic ligands and base has been developed. Systematic studies revealed the variable of base enviroment in the reaction is the key step in the preparation of 1D to 3D supermolcular networks of POVCFs **1-3**. Single crystal X-ray diffraction analyses demonstrated that the Cu<sup>2+</sup> atoms of POVCFs **1-2** were coordinated with four imidazole derivates molecules and two different polyoxovanadate { $[V_4O_{11}]^2$ ,  $[V_{10}O_{28}]^{6-}$  clusters, respectivley, exhibiting a [ $CuN_4O_2$ ] binding set and the distorted octahedral geometry. Especially, the POVCFs **1** exhibited the adjacent [ $V_4O_{11}$ ]<sup>2-</sup> updown linked into a parallel 2D network and further coordinated with [ $Cu(1-ipIM)_4$ ]<sup>2+</sup> into a 3D supramolecular structure. On the other hand, POVCFs **3** presented one tetrahedral coordinated vanadium atom and one four-coordinated copper atom and they futher gave rise to a 1D network by the Cu-O and V-O bonds. More importantly, these POVCFs were further studied in constructing of C-N bonds reactions of primary amines under mild conditions, and found POVCFs **1** displayed efficient heterogeneous catalytic activities in the Chan-Lam reaction (yields up to 89%).

## Introduction

Construction of C-N bonds is one of the most important organic reactions as well as formation of C-C bonds and have become a cornerstone of synthetic, pharmaceutical and medical chemistry. <sup>1,2</sup> Over the past few years, various synthetic strategies for constructing C-N bonds has been widely reported, such as the famous Buchwald Hartwig and Ullmann cross-coupling reaction, etc. <sup>3-5</sup> However, these cases mostly involved with the noble metal Pd salts or Pd complexes. Compared with the above cross-coupling procedure, low-cost copper-catalyzed Chan-Lam reaction also represented one of the most powerful and straightforward tools to construct C-N bonds and many excellent results have been presented. <sup>6</sup> In terms of Chan-Lam reaction, various homogeneous catalysts have been employed for the catalytic generation of C-N bonds. <sup>7-8</sup> Nevertheless, homogeneous catalytic systems generally suffer from the inherent

limitations of the separation of the products and catalyst recycling. <sup>9-</sup> <sup>10</sup> One major challenge for these cross-coupling approaches is the recycling of catalysts. To overcome these limitations, heterogeneous catalysts including covalent organic framework, metal–organic framework and functional coordination polymers have been well developed. <sup>11-12</sup> Very recently, the emerging polyoxometalates–based frameworks, as a class of promising heterogeneous candidate catalysts, have attracted increasing interest. <sup>13-14</sup>

In this context, polyoxovanadates (POVs) as the classical family of polyoxometalates (POMs) have attracted considerable attention in regard to their bioinorganic chemistry, single molecular magnets, and medicine as well as in homogeneous and heterogeneous catalysis. <sup>15</sup> To achieve the heterogeneity of these catalysts and improve the catalytic activity of POVs, transition-metal species have been introduced into the POVs systems and led to a varieties of novel heterogenous catalysts in various organic reactions.<sup>16</sup> Recently, our reported three Pd-decavanadates have exhibited group heterogeneous aerobic oxidation of benzylic C-H bonds; 17 lately, unprecedented Zn-POVs Wei's Group discovered an effective  $\{V_6O_{13}[ZnC_{61}H_{58}N_5O_4]_2\}^{2-1}$ with heterogeneous photocatalytic activity toward removal of rhodamine B.<sup>18</sup> To the best of our knowledge, although several methods of transmit metalpolyoxovanadates hybrids have been reported, the controllable synthesis strategy of the POVs-based copper-frameworks with 1D, 2D and 3D structure have been limited and study on the Chan-Lam

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reactions catalysed by these POVs-based copper-frameworks is rather rare. Hence, there is still a focus of ongoing research on POVs-based frameworks catalysts for highly effective catalytic construction of C-N bonds under ambient conditions.

Inspired by these previous works, we tried to introduce transition metal copper ions into the POVs clusters to obtain hybrid copperpolyoxovanadates, which might be a feasible way to improve their catalytic property in the Chan-Lam reaction. Herein, we report three POVs-based copper frameworks [Cu<sub>0.5</sub>(1-*i*pIM)<sub>2</sub>]<sub>2</sub>[V<sub>4</sub>O<sub>11</sub>] (POVCFs 1) and  $[Cu(1-ipIM)_2](VO_3)_2$  (POVCFs 2) and  $[Cu(1-pIM)_4](1-iPIM)_4](1-iPIM)_4]$  $HpIM)_{4}[V_{10}O_{28}]$  (POVCFs 3), which are assembled by chemical covalent interactions and formed 3D, 2D and 1D frameworks, respectively. The three POVCFs were characterized by single crystal X-ray diffraction (SCXRD), fourier transform infrared spectroscopy (FT-IR), powder X-ray diffraction (PXRD) and elemental analyses. Specially, the POVCFs 1 exhibited the two rare  $[V_4O_{11}]^{2-}$  clusters which dangle up and down linked into parallel 2D network, and further coordinated with  $[Cu(2)(ipIM)_4]^{2+}$  into 3D supramolecular structure, it is different from the reported  $[V_4O_{11}]^2$ -polyhedron. <sup>19</sup> In this study, much attention is devoted to obtain a deep insight into the catalytic studies of POVCFs towards coupling reaction of phenylboronic acids with amines derivatives.

#### **Results and discussion**

#### Syntheses

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In order to controllable synthesize the various supramolecular architectures of POVCFs with potential applications, we picked up the simple vanadium source V<sub>2</sub>O<sub>5</sub> as the starting material along with 1-*i*pIM to react with CuCl<sub>2</sub>·2H<sub>2</sub>O. At first, 1-*i*pIM as the organic ligand and organic base bifunctional material was used as solvent and ligand in the synthetic procedure, POVCFs **1** with 3D network was obtained. When the amount of 1-*i*pIM was only reduced, remaining V<sub>2</sub>O<sub>5</sub> as the vanadium source, the 2D supramolecular network POVCFs **2** was formed due to the different alkaline environment. Then, we further used 1-pIM and 25% (CH<sub>3</sub>)<sub>4</sub>NOH instead of the l-*i*pIM and NEt<sub>3</sub> to change the reaction environment, POVCFs **3** was obtained fortunately in a 1D chain. Based on the above results, the base environment played a key role in the formation of these 3D, 2D and 1D frameworks.

#### Structure Analysis of POVCFs $[Cu_{0.5}(1-ipIM)_2]_2[V_4O_{11}]$ (1)

SCXRD analysis displayed that the asymmetric unit of compound  $[Cu_{0.5}(1-ipIM)_2]_2[V_4O_{11}]$  (1) comprises two  $Cu^{2+}$  cations (the refined occupancy factors of both Cu atoms are 0.5), one  $[V_4O_{11}]^2$  cluster and four 1-*i*pIM N-ligands (Fig. 1). The structure of 1 may be described as built from *trans*-[Cu(1-*i*pIM)\_4O\_2] octahedron and  $[VO_4]$  tetrahedra linked by shared  $\mu_2$ -O oxygen atom vertices. All Cu atoms of POVCFs 1 were six-coordinated by bonding to four N atoms from 1-*i*pIM ligands and two O atoms from  $[VO_4]$  tetrahedron, and presented the distorted octahedral geometry, and each vanadium atom attains its distorted tetrahedral geometry by coordinating to one terminal O atom and three  $\mu_2$ -bridging O atoms. The details of bond distances and bond angles of 1 are listed in Table S1. The Cu(II)–N bonds vary from 2.035(4) to 2.037(5) Å, while the lengths of the Cu–O bonds are 2.407(4) Å. The V=O terminal bond distances in the range of 1.593(5)-1.636(6) Å, which are similar to those of reported POVs clusters. <sup>20</sup>



Figure 1. The asymmetric unit of POVCFs 1



Figure 2. Coordination environment of Cu atom in the POVCFs 1



Figure 3. 2D network parallel to the bc plane of POVCFs 1



Figure 4. 3D supramolecular structure of POVCFs 1

In addition, the crystal of **1** adopts a 3D covalent network structure. Such an intriguing structure can be described in the following three steps: first, the adjacent VO<sub>4</sub> tetrahedrons are linked by the corner-sharing oxygen atoms and formed an intact  $[V_4O_{11}]^2$ -anion cluster, and then the adjacent  $[V_4O_{11}]^2$ - cluster further connect with each other to form a 1D chain structure along crystallographic

*c*-axis by the sharing of oxygen vertices (O6) between [V(2)O<sub>4</sub>] and [V(3)O<sub>4</sub>] tetrahedrons. Then, the [V<sub>4</sub>O<sub>11</sub>]<sup>2</sup>-cluster formed by [V(1)O<sub>4</sub>] and [V(2)O<sub>4</sub>] tetrahedrons serves as a tetradentate ligand to coordinate to a [Cu(1)(1-*i*pIM)<sub>4</sub>]<sup>2+</sup> subunit by its vertex oxygen atom (O3) to connect the adjacent 1D chains into a 2D network parallel to the *bc* plane. At last, the [V<sub>4</sub>O<sub>11</sub>]<sup>2-</sup> cluster formed by [V(3)O<sub>4</sub>] and [V(4)O<sub>4</sub>] tetrahedrons in the 2D network coordinate to [Cu(2)(1-*i*pIM)<sub>4</sub>]<sup>2+</sup> subunit along crystallographic *a*-axis constructing a 3D supramolecular structure, which is different with those of [Ni(phen)<sub>2</sub>V<sub>4</sub>O<sub>11</sub>] (phen = 1,10-Phenanthroline) and [Ni<sub>2</sub>(mIM)<sub>7</sub>·H<sub>2</sub>O)]V<sub>4</sub>O<sub>12</sub>·H<sub>2</sub>O.<sup>21</sup>

#### Structure Analysis of Compound [Cu(1-ipIM)<sub>2</sub>](VO<sub>3</sub>)<sub>2</sub> (2)



Figure 5. The asymmetric unit of POVCFs 2

When we reduce the amount of 1-*i*pIM (ligand/base) and keep other synthetic conditions the same with POVCFs **1**, POVCFs **2** was achieved. As presented in Fig. 5, the result of SCXRD analysis reveals that POVCFs **2** contains only one crystallographically independent vanadium atom and it is in a tetrahedral coordination environment. The [VO<sub>4</sub>] tetrahedrons are connected to each other through two of their vertex [O(2) and O(2)#, # represents symmetric code:-x, y+1/2, -z+1/2], forming  $[VO_3]_n^n$  chains along crystallographic *b*-axis. The adjacent  $[VO_3]_n^n$  chains are further linked together by [Cu(1-*i* $pIM)_2]^{2+}$  subunits, giving rise to a 2D network, parallel to the *bc* plane (Fig. 6). The coordination environment of Cu atoms in **2** is different with that of POVCFs **1** and the Cu atoms are four-coordinated by two O atoms derived from two adjacent  $[VO_3]_n^n$  chains and two N atoms from 1-*i*pIM ligands and formed a square planar geometry.



Figure 6. 2D network parallel to the bc plane of POVCFs 2

#### Structure Analysis of POVCFs (3) [Cu(1-pIM)<sub>4</sub>](1-HpIM)<sub>4</sub>[V<sub>40</sub>Q<sub>28</sub>]<sub>nline</sub>

Crystal structure analysis reveals that POVCFs **3** contains a typical  $[V_{10}O_{28}]^{6-}$  polyanion, a planar four-coordinated  $[Cu(1-pIM)_4]^{2+}$  along with four protonated 1-HpIM<sup>+</sup> counteraction parts. The  $[V_{10}O_{28}]^{6-}$  of **3** has a crystallographic inversion center on the midpoint of the O8 and O8A and is made up of a ten distorted  $[VO_6]$  octahedra. The bond distances and angles of the  $[V_{10}O_{28}]^{6-}$  anion (Table S1) are comparable with structurally characterized  $[V_{10}O_{28}]^{6-}$  units. <sup>22</sup> As parts of the  $[V_{10}O_{28}]^{6-}$  cluster in **3**, the terminal oxygen atom O1 and O1A form the bridges to two outer-shell  $[Cu(1-pIM)_4]^{2+}$  cations. Remarkably, the observed bond distance of V(1)-O(1) is 1.623(5) Å, which is expected for the vanadyl oxygen double bonds, <sup>23</sup> whereas the bond length of Cu(1)-O(1) is 2.491(5) Å, as a result of being the relatively weak coordination bond. <sup>24</sup>



Figure 7 The asymmetric unit of compound of POVCFs 3

In addition, a 1D supramolecular structure of **3** is formed along crystallographic *c*-axis by Cu-O-V bridges as shown in Figure 8. The supramolecular structure was further stabilized by N-H<sup>...</sup>O strong hydrogen-bonding interactions between 1-HpIM<sup>+</sup> cations and  $[V_{10}O_{28}]^{6-}$  anions (N(6)<sup>...</sup>O(5) 2.750(6) Å).



Figure 8. 1D network to the bc plane of POVCFs 3

#### **IR** analysis

In generally, IR spectrum can provide some important information for investigation of polyoxovanadates-based copper frameworks. <sup>25</sup> The stretching bands of V = O<sub>t</sub> in **1** appear at 941cm<sup>-1</sup>, 925 cm<sup>-1</sup> for **2**, 941cm<sup>-1</sup> for **3**. Absorption bands at 817, 738 and 665 cm<sup>-1</sup> for compound **1** (Fig. S1), 827, 725 and 660 cm<sup>-1</sup> for compound **2** and 828, 756 and 625 cm<sup>-1</sup> for compound **3** (Fig. S2-3) can be attributable to the V–O–V stretching vibrations. <sup>26</sup> The apparent stretch

#### **PXRD** analysis

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To further investigate the repeatability and purity of the three polyoxovanadates-based copper frameworks, the obtained bulk POVCOFs **1-3** were grinded to suitable powder for analysis. The results of PXRD detection endorsed us to acknowledge that the three synthesized samples were pure phase materials, respectively. As shown in Fig. S4-6. These peaks positions of the simulated PXRD patterns of POVCOFs **1-3** were in well agreement with those of assynthesized PXRD patterns, which revealed that the phase purity of POVCOFs **1-3**.

#### **Chan-Lam catalytic reaction**

At the outset of the investigation, we focused our attention on the optimal conditions of Chan-Lam reaction and the reaction between aniline (1a) and phenylboronic acid (2) was taken as the template reaction to investigate the catalytic activities of these POVCFs (Scheme 1).

In the case of the reaction without any catalyst, the reaction failed to produce any product 3a (Table 1, entry 1). When the soluble copper salt CuCl<sub>2</sub> was used as a catalyst, 28% diphenylamine was obtained, which suggested that copper species play an important role in the cross-coupling reaction (Table 1, entry 2), which was agreement with the previous report. <sup>28</sup> When the reaction was performed with 3 mol% POVCFs catalysts, and we found that POVCFs 1-3 facilitated Chan-Lam reaction and the desired product 3a was initially produced in 56%, 50% and 45% yields, respectively (Table 1, entries 3-5), which all outperformed the result of using the CuCl<sub>2</sub> as the catalyst (Table 1, entry 2). Utilizing 3 mol % POVCFs 1 gave a considerably higher yield (56 %) in 16 h, and found POVCFs 1 was proved to be better catalyst than other two POVCFs 2-3, which indicated that the different imidazole ligands, the six-coordinated environment of copper ions and polyoxovantates cluster might affect their catalytic activity on Chan-Lam coupling reaction, the same result was observed with that of the previous work.<sup>29</sup>

Hence, POVCFs **1** (3 mol %) was chosen as the optimal catalyst for further screen the conditions for the Chan-Lam reaction. In the next step, to finalize screening, changing the solvent to either EtOH,  $H_2O$ CH<sub>3</sub>CN or DMF all led to depletion in isolated yields of 3a (Table 1, entries 6-9), whereas CH<sub>3</sub>OH proved to be more suitable solvent for the reaction (Table 1, entry 5). Additionally, when Na<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub> used as the base, respectively, the desired diphenylamine 3a was obtained in lower yields (Table 1, entries 10-11). When the loading of the catalyst was increased from 3 mol % to 6 mol %, pleasingly, the yield of 3a increased significantly from 56% to 88% (Table 1, entries 3, 12-14). Notably, increasing the catalyst **1** loading (7 mol%) had an no significant effect on product yield (Table 1, entry 15).



Scheme 1 The Chan-Lam reaction using aniline and phenylboronic acid as the substrates

1	-	$K_2CO_3$	CH₃OH	-
2	CuCl <sub>2</sub> (3)	K <sub>2</sub> CO <sub>3</sub>	CH₃OH	28
3	<b>1</b> (3)	K <sub>2</sub> CO <sub>3</sub>	CH₃OH	56
4	<b>2</b> (3)	K <sub>2</sub> CO <sub>3</sub>	CH₃OH	50
5	<b>3</b> (3)	K <sub>2</sub> CO <sub>3</sub>	CH₃OH	45
6	<b>1</b> (3)	K <sub>2</sub> CO <sub>3</sub>	EtOH	12
7	<b>1</b> (3)	K <sub>2</sub> CO <sub>3</sub>	CH₃CN	14
8	<b>1</b> (3)	K <sub>2</sub> CO <sub>3</sub>	DMF	0
9	<b>1</b> (3)	K <sub>2</sub> CO <sub>3</sub>	H₂O	10
10	<b>1</b> (3)	$Na_2CO_3$	CH₃OH	17
11	<b>1</b> (3)	Cs <sub>2</sub> CO <sub>3</sub>	CH₃OH	20
12	<b>1</b> (4)	K <sub>2</sub> CO <sub>3</sub>	CH₃OH	69
13	<b>1</b> (5)	K <sub>2</sub> CO <sub>3</sub>	CH₃OH	82
14	<b>1</b> (6)	K <sub>2</sub> CO <sub>3</sub>	CH₃OH	88
15	1(7)	K <sub>2</sub> CO <sub>3</sub>	CH₃OH	87
16	<b>1</b> (6)	-	CH₃OH	-

[a] All the reactions were carried out using **1a** (0.2 mmol), **2** (0.3 mmol), and base (0.4 mmol) in the presence of catalyst in solvent (2.0 mL) at room temperature for 16h. [b] Isolated yields.

With the optimal conditions in hand, the substrate scope of amines including primary aryl amines and aliphatic amines were successfully explored and found the variety of substituted amines was well compatible in the present reaction and gave the desired products in moderate to good yields (68-89%).

First, the Chan-Lam reaction of a series of *p*-substituted primary arylamines with phenylboronic acid were studied. The results showed that the substrates bearing electron-donating groups (4-CH<sub>3</sub>, 4-OMe) or electron-withdrawing groups (4-Cl, 4-Br) was generally supported and smoothly gave the desired products in moderate to good yields (82-89%), and the primary arylamines bearing electron-donating groups gave slightly better results (Table 2, entries 1-5).

Despite steric hindrance, 2-methylaniline and 3-chloroaniline successfully afforded the corresponding products 3f-3g in a 72-80% yields and it is obvious that the substrates with -Cl, -CH<sub>3</sub> groups at ortho- or meta-positions had no significantly effect on the C-N crosscoupling reaction (Table 2, entries 6-7). Interestingly, in the case of the reaction of aliphatic amine, cyclohexamine, with phenylboronic acid, it afforded the desired product 3h in 68% yield under the standard conditions (Table 2, entry 8). The results showed that aliphatic amine also successfully afforded the corresponding product in the presence of the POVCFs 1. The above experiments indicated that these cross-coupling reactions of corresponding amine derivatives catalyzed by POVCFs 1 exhibited good functional tolerance, which could be conveniently applied in organic synthesis for formation of C-N bonds. In view of the relatively milder reaction conditions, the observed catalytic efficiency of the POVCFs 1 is comparable with those of majority of the copper catalysts, even the PdCu bimetallic nanoparticles catalysts. 30-32

Recycling is very important advantages of heterogeneous catalysts for their further large-scale applications. Hence, the recycling of POVCFs **1** is selected to investigate the long-term stability for constructing C-N bonds performance in a heterogeneous system. After the completion of the reaction, the catalyst can easily be separated from the reaction mixture by filtration and reused without further treatment except drying under vacuum. The catalyst was recycled for at least 3 runs without significantly losing its catalytic activity (88% (first run); 86% (second run); 85% (third run)). In addition, atomic absorption analysis demonstrated that there were no copper and vanadium elements in the filtrate of the reaction, which further exhibited that the catalyst **1** is heterogeneous in the Chan-Lam coupling.

**Table 2** Substrate scope for Chan-Lam coupling of amines with phenylboronic acid.



[a] Reactions conditions: amines 1 (0.2 mmol), phenylboronic acid 2 (0.4 mmol), and  $K_2CO_3$  (0.4 mmol) POVCFs 1 (6 mol%) in CH<sub>3</sub>OH (2.0 mL) at room temperature for 16h. [b] Isolated yields.

#### Experimental

#### Materials and instruments

 $V_2O_5$ , 1-isopropylimidazole, 1-propylimidazole, triethylamine, copper (II) chloride dihydrate and other solvents and reagents purchased from Aladdin Co., Ltd.

The FT-IR spectra of POVCFs 1-3 were recorded on Nicolet 170 SXFT/IR spectrometer in the range 4000–400 cm $^{-1}$ . PXRD data was

obtained by using a Rigaku D/max-2550 diffractometer with Curka radiation. The elemental analyses measuremethts were done of the analyzer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on Bruker 500 MHz spectrometer by using tetramethylsilane (TMS) as the internal standard.

#### Synthesis

**Synthesis of**  $[Cu_{0.5}(1-ipIM)_2]_2[V_4O_{11}]$  (1): V<sub>2</sub>O<sub>5</sub> (2.75 mmol) and triethylamine (2.75 mmol) were successively added to 15 mL water in a clean beaker. The resulting solution was stirred at room temperature for 60 min, and then CuCl<sub>2</sub>·2H<sub>2</sub>O (0.6 mmol), 1-isopropylimidazole (3.6 mmol) were successively added to the mixed solution. The resulting mixture was stirred for 12 h and then heated at 50 °C for 30 min. Finally, the resulting mixture was filtrated and the resulted filtrate stood for five days, and several blue crystals suitable for X-ray diffraction were obtained. Yield: 47.8%. Anal. calcd. (%) (found) for C<sub>24</sub>H<sub>39</sub>N<sub>8</sub>O<sub>11</sub>V<sub>4</sub>Cu: C, 32.65 (32.47); H, 4.45 (4.49); N, 12.69 (12.53). IR (KBr, cm<sup>-1</sup>): 3445, 3121, 2984,1631, 1514, 1231, 1113, 983, 941, 862, 817, 738, 665, 492.

**Synthesis of [Cu(1-ipIM)<sub>2</sub>](VO<sub>3</sub>)<sub>2</sub> (2):** The synthetic procedure of compound 2 is similar with that of compound 1, except that the amount of 1-isopropylimidazole reduced from 3.6 mmol to 3.0 mmol. After leaving the resulted solution to stand at ambient conditions for several days, blue crystals suitable for X-ray diffraction were obtained. Yield: 35.7%. Anal. calcd. (%) (found) for C<sub>12</sub>H<sub>20</sub>N<sub>4</sub>O<sub>6</sub>V<sub>2</sub>Cu: C, 29.92 (29.81); H, 4.18 (4.25); N, 11.63 (11.56). IR (KBr, cm<sup>-1</sup>): 3432, 3142, 2997, 2914, 1631, 1514, 1389, 1238, 1106, 971, 950, 897, 831, 756, 625, 474.

Synthesis of [Cu(1-pIM)<sub>4</sub>](HpIM)<sub>4</sub>[V<sub>10</sub>O<sub>28</sub>] (3): The synthetic procedure of compound 3 is similar with that of compound 1, except that the 25% (CH<sub>3</sub>)<sub>4</sub>NOH and 1-propylimidazole were used instead of triethylamine and 1-isopropylimidazole. Yield: 33.5%. Anal. calcd. (%) (found) for C<sub>48</sub>H<sub>80</sub>N<sub>16</sub>O<sub>28</sub>V<sub>10</sub>Cu: C, 30.31 (30.42); H, 4.24 (4.29); N, 11.78 (11.67). IR (KBr, cm<sup>-1</sup>): 3444, 3102, 2965, 1634,1528, 1398, 1277, 1109,960, 925, 827, 725, 660,452.

#### Characterization of the POVCFs crystals

SCXRD data for three POVCOFs **1-3** were performed on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated Mo-Ka radiation ( $\lambda = 0.71073$  Å) at 298 K. All absorption corrections were applied using multi-scan technique. The crystal structures of POVCOFs **1-3** were solved by the direct method and refined through full-matrix least-squares techniques method on F<sup>2</sup> using the SHELXTL 2018 crystallographic software package. The crystallographic data for POVCOFs **1-3** are summarized in Table 1.

#### General Procedure for Chan-Lam Coupling Reactions of Amines with phenylboronic Acids.

Amines (0.2 mmol), phenylboronic acid (0.4 mmo),  $K_2CO_3$  (0.4 mmol), POVCOFs (6 mol%) and CH<sub>3</sub>OH (2.0 mL) were added to a 25 mL Schlenk Tube. Then the tube was sealed and the reaction mixture was subsequently stirred at room temperature in a Wattecs Parallel Reactor for 16 h. After finished, the mixture was extracted with ethyl acetate (3×5mL). The organic phase was combined and concentrated. The resulting residue was purified by preparative thin

layer chromatography using petroleum ether/ethyl acetate as developing solvent to afford the desired products 3.

# Conclusions

In summary, we have demonstrated the facile synthesis of three new copper-polyoxovanadate with 3D, 2D and 1D frameworks by employing various imidazole ligands and base environment. Importantly, POVCFs **1** showed efficient catalytic activities (yields up to 89%) in the Chan-Lam at room temperature. Work is underway to explore the synthesis of new POVCFs and expand this approach to other potential catalytic reactions for these catalysts.

# **Conflicts of interest**

There are no conflicts to declare.

# Acknowledgements

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## Notes and references

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Three polyoxovanadates-based copper frameworks with 3D, 2D and 1D network using bifuncational imidazole molecules as organic ligands and base has been developed. More importantly, these polyoxovanadates-based copper frameworks displayed efficient heterogeneous catalytic activities in the Chan-Lam reaction under mild conditions.

