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ARTICLE

Bonded- and Discreted- Linqvist Hexatungstate-Based Copper hybrids as Heterogeneous Catalysts for One-pot Synthesis of 2-Phenylquinoxalines *via* 2-Haloanilines with Vinyl Azides or 3-Phenyl-2*H*-azirines

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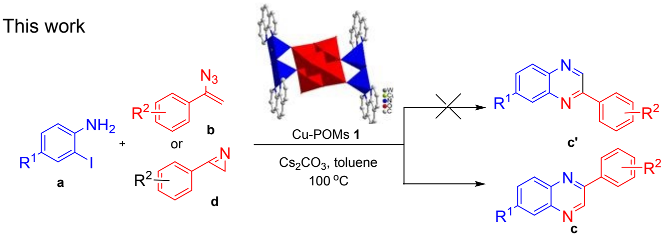
One bonded- and one discreted- Linqvist hexatungstate-based copper hybrids (Cu-POMs) ($[Cu_2(O)OH(phen)_2]_2[W_6O_{19}]\cdot6H_2O$ (**1**) and $[Cu_2(phen)_4Cl]$ $[HW_6O_{19}]\cdot2H_2O$ (**2**) (phen= 1,10-phenanthroline)) were controllably synthesized and routinely characterized. Cu-POMs **1-2** consisted of identical $[W_6O_{19}]$ unit and similar copper-phen complexes, the two units are bonded via four Cu-O chemical bonds in compound **1**, however, compound **2** is discreted and stabilized by intermolecular electrostatic interactions. Importantly, these Cu-POMs catalysts were first applied in the novel reaction for preparation of 2-phenylquinoxalines *via* the one-pot coupling and oxidation reactions of 2-haloanilines with vinyl azides or 3-phenyl-2*H*-azirines under mild conditions, and Cu-POMs **1** showed higher catalytic performance in good yields (79-84%). The reactions exhibit some functional group tolerance and allow for the preparation of a number of 2-phenylquinoxalines.

Introduction

Polyoxometalates (POMs) are a unique class of discrete, anionic metal oxides, which are generally constructed by early transition elements (W, V, Mo, Nb and Ta, etc) in high oxidation states.[1] POMs are also good prospects in the areas of catalysis, molecular electronics, biomedicine and dye-sensitized solar cells, etc.[2] Especially, POMs involved organic reactions have aroused widespread interest and become a powerful tool in chemical synthesis.[3] For instance, Dwight, et al. presented the aerobic oxidative coupling of arenes in the presence of $Pd(OAc)_2$ and $H_4PMo_{11}VO_{40}$;[4] Sanford's group reported the sp^3 C-H olefination catalyzed by $Pd(OAc)_2$ and $H_4PMo_{11}VO_{40}$.[5] In the previous work, the oxidation of alcohols and benzyl hydrocarbon can be achieved by transition metal-organic POMs catalysts.[6] Among the transition metal catalysts, cheap copper-catalyzed reactions have attracted much attention owing to inexpensive and wide varieties, especially the majority of the already developed combination of Cu salts and phen catalyzed strategies have been made in catalytic C-N bond forming reactions.[7] However, these protocols usually require a lot of copper salts (10-20 mol%) and corresponding ligands. In the past decade, lots of the structure of Cu-POMs have been synthesized and showed great advantages in the field of molecular electronics, adsorption and function materials, etc.[8] However, the combination of Cu-POMs has seldom been used in the organic synthesis for construction of new C-C and C-N bonds, especially the assembly of heterocyclic compounds *via* one-pot cascade coupling strategies.

Functionalized quinoxalines are an important class of bioactive molecules and core unit in pharmaceuticals, dyes, antibiotics and other applications.[9] A large number of synthetic methods have been developed to construct quinoxalines for these important applications.[10] Among these methods, there are few synthetic methods for the synthesis of 2-phenylquinoxalines including the oxidation-condensation or condensation reaction, cross-coupling reaction and oxidation reaction. Most catalytic methods for the synthesis of 2-phenylquinoxalines rely on the oxidation-condensation or condensation reaction of condensing partners and 1, 2-



Scheme 1 Synthesis of 2-phenylquinoxalines.

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diamines.[11] There are only several reports about synthesis of 2-phenylquinoxalines by the cross-coupling reaction including the coupling of 2-haloquinoxalines with triphenylaluminum (triphenylbismuthane, phenylboronic acid and etc.).[12] Because the limitation of the reaction substrates, the dehydrogenation reactions of 2-phenyl-1,2,3,4-tetrahydroquinoxaline or 2-phenyl-1,2-dihydroquinoxaline are also rare.[13]

In the above perspective, the use of catalysts based on cheap copper and POMs in the organic reactions is especially beneficial for large-scale and industrial applications. Thus, design and synthesis of one-component Cu-POMs is highly desirable for investigating novel organic reactions, in particular the construction of heterocyclic compounds owing to their excellent biological activities. Importantly, as a simple and easily-handling precursor for constructing 2-phenylquinoxalines, vinyl azides is not frequently used as the raw materials thus far. In continuation of our ongoing efforts to synthesis functional POMs and assemble heterocycles,[6, 14] we reported two copper-polyoxometalates (Cu-POMs: $[Cu_2(O)OH(phen)_2]_2[W_6O_{19}]\cdot 6H_2O$ **1** and $[Cu_2(phen)_4Cl][HW_6O_{19}]\cdot 2H_2O$ **2**) (Fig. 1-2), and the catalytic performance of $[Cu_2(O)OH(phen)_2]_2[W_6O_{19}]\cdot 6H_2O$ **1** has showed higher efficiency for the preparation of 2-phenylquinoxalines *via* the one-pot coupling and oxidation reactions of 2-haloanilines with vinyl azides or 3-phenyl-2*H*-azirines in good yield under mild conditions (scheme 1).

Results and discussion

The reaction of $Na_2WO_4\cdot 2H_2O$, $CuCl_2\cdot 2H_2O$, $NaVO_3$ and phen at 160 °C for 120 h under pH = 8.9 afforded green-crystals of compound **1**, the reaction of $Na_2WO_4\cdot 2H_2O$, $CuCl_2\cdot 2H_2O$, NH_4VO_3 and phen at 160 °C for 120 h under pH = 8.0 afforded black-crystals of compound **2** (Fig. 1 and Table S1). Interestingly, compounds **1**-**2** consisted of identical $[W_6O_{19}]$ unit and similar copper-phen complexes, the two units are bonded via four Cu-O chemical bonds in compound **1**, however, compound **2** is discreted and stabilized by intermolecular electrostatic interactions. All of the W atoms in **1**-**2** are in the +6 oxidation state, however, the copper oxidation state in compounds **1**-**2** are +2 and +1, respectively, as revealed from bond valence sum (BVS) values (Table S3)[15].

Single crystal X-ray diffraction indicates that **1** crystallize in the triclinic space group P-1. **1** is assembled of two dinuclear copper counter cations $[Cu_2(O)OH(phen)_2]^+$, one Lindqvist shaped polyanion $[W_6O_{19}]^{2-}$ and six free lattice H_2O molecules. The two $[Cu_2(O)OH(phen)_2]^+$ cations are bridged with $[W_6O_{19}]^{2-}$ by $O(1)_t$ (terminal oxygen, connected to one W atom), $O(2)_b$ (bridging oxygen, connecting edge-shared WO_6 octahedra) and form the $[Cu_2(O)OH(phen)_2]_2[W_6O_{19}]$ molecule. In the unit of $[Cu_2(O)OH(phen)_2]^+$, the Cu(II) atoms is coordinated by two N atoms from two bidentate phen ligands, one μ_2-O hydroxyl oxygen atom, one μ_2-O oxygen atom and one O_t or O_b from the polyanion in a distorted square pyramidal geometry, and the bond lengths around Cu atoms lie in the range 1.697 (10)-1.733 (8) Å (average 1.713 Å) for Cu-N 1.895 (9)-1.949 (7) Å (average 1.923 Å) for Cu-O, which are similar with those of reported complexes.[16] Remarkably, in the case, each $[W_6O_{19}]^{2-}$ anion acts as an polyanion inorganic ligand covalently bonded with two$[Cu_2(O)OH(phen)_2]^+$ cations only through two O_t and two O_b atoms. This kind of four-connection coordination mode of the hexatungstate in compound **1** is rare and may play an important role in the stabilization of the whole skeleton. [17]

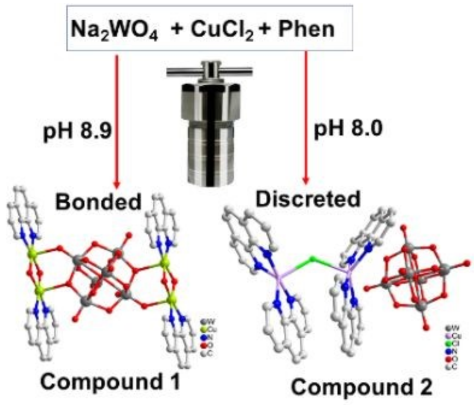


Fig. 1 The simplified representation of the controlling synthesis of **1**-**2**

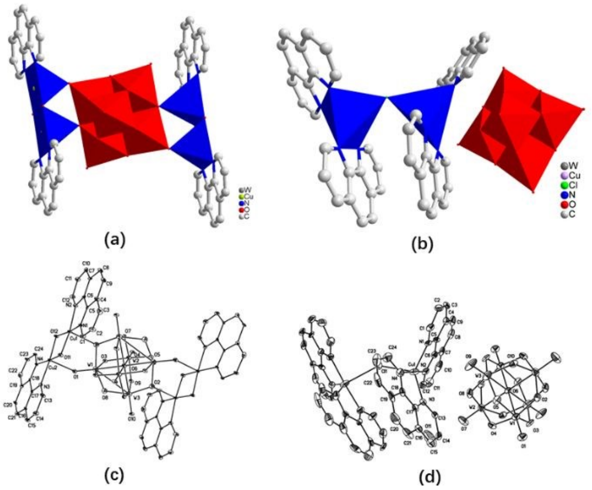
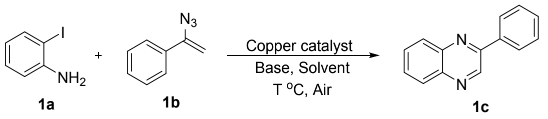


Fig. 2 (a) the polyhedron structure of compound **1**; (b): the polyhedron structure of compound **2**; (c) the thermal ellipsoidal plots of compound **1**; (d): the thermal ellipsoidal plots of compound **2**. For clarity, the hydrogen atoms and free water molecules are omitted, thermal ellipsoids are drawn at the 30% probability level.

Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst	Base	Solvent	T (°C)	Yield (%)[b]
1	Cu-POMs **1**	Cs_2CO_3	DMF	100	26

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2	Cu-POMs **2**	Cs_2CO_3	DMF	100	19
3	Cu-POMs **1**	Cs_2CO_3	toluene	100	67
4	Cu-POMs **2**	Cs_2CO_3	toluene	100	54
5	Cu-POMs **1**	Cs_2CO_3	dioxane	100	23
6	Cu-POMs **2**	Cs_2CO_3	dioxane	100	20
7	Cu-POMs **1**	K_2CO_3	toluene	100	60
8	Cu-POMs **1**	K_3PO_4	toluene	100	59
9	Cu-POMs **1**	DBU	toluene	100	9
10	**Cu-POMs 1**	**Cs_2CO_3**	**toluene**	**100**	**84[c]**
11	Cu-POMs **1**	Cs_2CO_3	toluene	90	61[c]
12	Cu-POMs **1**	Cs_2CO_3	toluene	110	66[c]
13	/	Cs_2CO_3	toluene	100	0[c,d]
14	$CuCl_2$	Cs_2CO_3	toluene	100	0[c,d]
15	CuI	Cs_2CO_3	toluene	100	45[c]
16	CuBr	Cs_2CO_3	toluene	100	38[c]
17	$CuCl_2$/phen	Cs_2CO_3	toluene	100	23[c]
18	$CuCl_2$/phen/Na_2WO_4	Cs_2CO_3	toluene	100	33[c,e]
19	$CuCl_2$/phen/O_2	Cs_2CO_3	toluene	100	28[c,f]

[a] Reaction conditions: catalyst (0.015 mmol), **1a** (0.5 mmol), **1b** (1.0 mmol) and base (1.0 mmol) in solvent (2.0 mL) under air for 24 h. [b] The yield was determined by ^{1}H NMR analysis of crude products using 1, 3, 5-trimethoxybenzene as the internal standard. [c] Reaction conditions: catalyst (0.015 mmol) or copper salt (0.015 mmol), ligand (0.03 mmol), **1a** (0.5 mmol), **1b** (1.0 mmol) and base (1.0 mmol) in toluene (2.0 mL) under air atomsphere for 12 h, then 0.5 mmol **1b** was added in two portions at 6 h intervals *via* syringe. [d] No catalyst was used. [e] 0.03 mmol Na_2WO_4 was used. [f] Oxygen balloon was used.

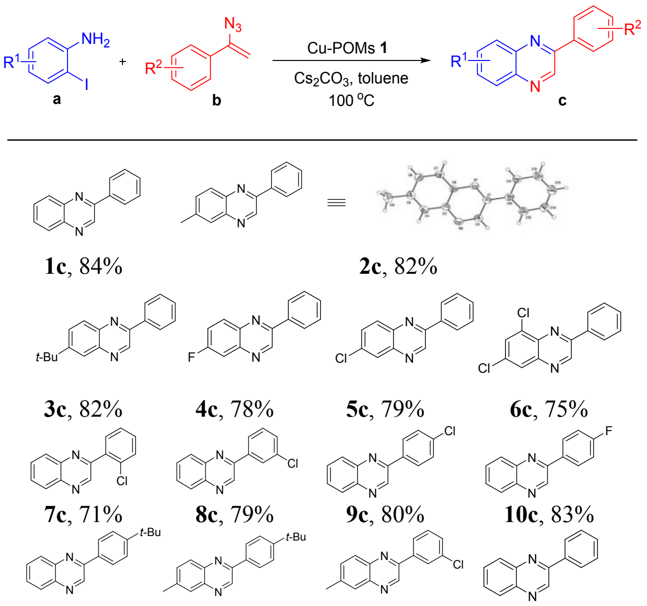
For $[W_6O_{19}]^{2-}$, the polyanion comprises six edge-shared WO_6 octahedra and exhibits approximate O_h point symmetry (Fig. 2a). The O atoms can be divided into three groups: O_t, O_b and O_c (the central O atom, common to all six WO_6 octahedra). The W-O distances are comparable with those found in the reported compounds.[18] In addition, the supramolecular structure of **1** was stabilized by intermolecular strong hydrogen-bonding interactions [O3···O8 (-x+1/2, -y+1/2, -z+2): 2.741(7) Å; O10···O4 (-x-1, -y, -z): 2.713(7) Å; O5···O11(-x+1/2, -y+1/2, -z+2): 2.720(6) Å] (Table S2) forming a 3D network (Fig. S1).

Single-crystal X-ray diffraction analysis reveals that compound (**2**) comprises a twofold-symmetric dicopper(I) cation, $[Cu_2(phen)_4Cl]^+$, a centrosymmetric Lindqvist polyanion $[HW_6O_{19}]^-$ and with two free water (Fig. 1), which is similar with the reported compound.[19] In the $[Cu_2(phen)_4Cl]^+$ cation, two Cu (I) atoms adopt the square pyramidal coordination geometry (Fig. 2b), coordinated by two phen ligands and one bridging chloride (Table S1). In the compound 2, the copper oxidation state is +1, we inferred that phenanthroline or the NH_4^+ group in NH_4VO_3 might be used as reducing agent in the synthesis of compound 2.[20] The supramolecular structure of **2** was stabilized by intermolecular electrostatic attraction and strong hydrogen-bonding interactions [O3···O8 (-x+1/2, -y+1/2, -z+2): 2.741(7) Å; O10··· O4 (-x-1, -y, -z): 2.713(7) Å; O5···O11(-x+1/2, -y+1/2, -z+2): 2.720(6) Å] (Table S2) and forming a 3D network (Fig. S2).

The electronic absorption spectra for the compounds **1** and **2** were conducted and the results were illustrated in Fig. S8. Because the copper atoms of compounds **1-2** are d^9 system, d^{10} system, respectively, the diffuse reflectance spectra of compounds **1** and **2** are slightly different.[21] The broad valley of compounds **1** and **2** were observed at 522 nm and 512nm, respectively.

Then 2-iodoaniline **1a** and (1-azidovinyl)benzene **1b** were selected as the model substrates to identify and optimize the reaction parameters. The reaction was firstly carried out in DMF with Cu-POMs **1** (3 mol%), Cs_2CO_3 (2.0 equiv.) at 100 °C under air. 24 h later, the reaction was stopped and the anticipated product **1c** was detected in 26% yield (Table 1, entry 1). Then Cu-POMs **2** was tested and 19% of **1c** was detected (Table 1, entry 2). The two catalysts were also examined in other solvents (dioxane and toluene), Cu-POMs **1** and toluene was found to be the best choice (Table 1, entries 3-6). During the study of bases, Cs_2CO_3 showed the best efficiency (Table 1, entries 7-9). From the TLC monitoring of the reactions, it was found that the starting material **1b** was consumed completely and **1a** was still left. Then the reaction was repeated with Cu-POMs **1** (3 mol%), **1a** (0.5 mmol), **1b** (1.0 mmol) and Cs_2CO_3 (1.0 mmol) in toluene (2.0 mL) under air atomsphere for 12 h, then another 0.5 mmol **1b** was added in two portions at 6 h intervals *via* syringe. To our delight, the starting substrate of **1a** was consumed and the reaction yield of **1c** was detected in 84% (Table 1, entry 10). The reaction at lower (90°C) temperatures evidently decreased the reaction yields (Table 1, entry 11). When the reaction was carried out at 110 °C, the yield of **1c** was not changed obviously (Table 1, entry 12). Without the catalyst or only using $CuCl_2$ as the catalyst, no product of **1c** was detected (Table 1, entries 13-14). Some other simple cuprous salts (CuI and CuBr) were used to repeat the reaction, and the product yields were not high (Table 1, entries 15-16). Other catalyst systems were also surveyed ($CuCl_2$/1,10-phen, $CuCl_2$/1,10-phen/Na_2WO_4 and $CuCl_2$/1,10-phen/O_2), but the yields did not improve (Table 1, entries 17-19). From the above experiments, entry 10 shows the best reaction conditions.

Table 2 Scope of the one-pot Cu-POMs -catalyzed coupling reaction for the synthesis of 2-phenylquinoxalines.[a]



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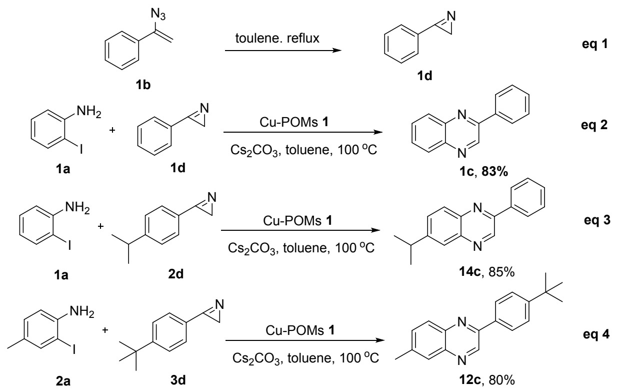
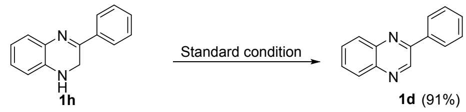
11c, 81%	**12c**, 82%	**13c**, 80%	**1c**, 35%[c]

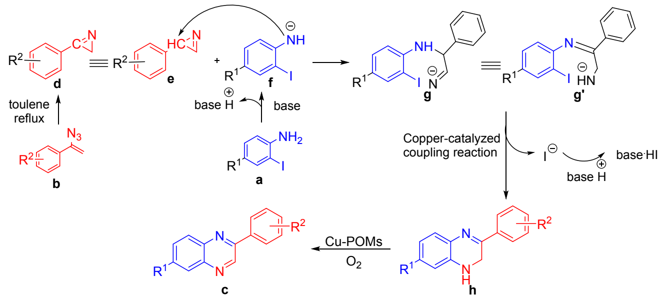
[a] Reaction conditions: Cu-POMs **1** (0.015 mmol), **a** (0.5 mmol), **b** (1.0 mmol) and Cs_2CO_3 (1.0 mmol) in toluene (2.0 mL) under air for 12 h, then 0.5 mmol **b** was added in two portions at 6h intervals *via* syringe. [b] Isolated yield after flash chromatography based on **a**. [c] 2-bromoaniline was used.



Scheme 2 Synthesis of 2-phenylquinoxalines by Cu-POMs **1** Catalyzed Coupling of 2-iodoanilines with 3-phenyl-2*H*-azirines.



Scheme 3 Synthesis of 2-phenylquinoxaline by 3-phenyl-1,2-dihydroquinoxaline *via* the standard condition.



Scheme 4 Proposed mechanism of the reaction.

With the optimized reaction conditions in hand, the scope of substrates was further investigated (Table 2). Firstly, we used the substituted 2-iodoanilines **a** to react with **1b**. The substrates of **a** with electron-donating groups (CH_3, *i*-Pr and *t*-Bu) and electron-withdrawing groups (F, Cl and CF_3) could generated the desired products in good yields (Table 2, **2c**-**6c**). The structure of **2c** was unambiguously elucidated by X-ray crystallography (CCDC No. 2008846). When 2-(2-chlorophenyl)-2H-azirine was used to repeat the reaction, the yield decreased obviously because of the steric effect (Table 2, **7c**). Other substituted (1-azidovinyl)benzenes (0.5 mmol) **b** were also investigated, the products were got in moderate yields (Table 2, **7c**-**11c**). Then we carried out the cross-reaction experiment, the results did not change obviously (Table 2, **12c** and **13c**). Finally, 2-bromoaniline was used to repeat the reaction, only 15% of **1c** was got. Further expansion of the substrate scope was focused on 3-phenyl-2*H*-azirines **d**, it can be synthesized by (1-azidovinyl)benzenes **b** in toluene under reflux condition (Scheme 2). The reactions of **a** with **d** were got in good yields under the optimized reaction conditions (Scheme 2, **1c**, **14c** and **12c**).

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From the X-ray crystallography we confirmed the structure of the products, the reactions of 2-haloanilines with vinyl azides or 3-phenyl-2*H*-azirines could react smoothly and get the corresponding products **c**, but not **c'** (Scheme 1). 2-Phenylquinoxalines **d** can be synthesized by the oxidation reaction of **1h** *via* the standard condition (Scheme 3). On the basis of the above results, a possible mechanism was proposed in Scheme 4. The intermediate species **e** and **f** could be formed under the optimized reaction conditions, and then the obtained intermediates **e** and **f** proceeded the nucleophilic attack reaction to get the intermediate **g** as the graphic shown,[22] which translated to the final product **h** after the classic copper-catalyzed coupling reaction and elimination reaction, the intermediate **h** could be detected by the GC-MS ($(M-1)^{+}$= 207.4) and HPLC-MS ($(M-1)^{+}$=207.0943, $(M+1)^{+}$ =209.1097) (Fig. S7). The products **c** could be got after the oxidation reaction.

Experimental

Materials and instruments

All reagents and solvents were pure analytical grade materials purchased from commercial sources and were used without further purification, if not stated otherwise. All melting points are uncorrected. All starting substrates were prepared according to the known literatures. The NMR spectra were recorded in $CDCl_3$ on a 400 MHz (Agilent) or 500 MHz (Bruker) instrument with TMS as internal standard. High-resolution mass spectra (HRMS) were obtained with a Q-TOF Premier (ESI). TLC was carried out with 0.2 mm thick silica gel plates (GF254). The FT-IR spectra were recorded as KBr pellets in the range of 4000-400 cm^{-1} on a Nicolet 170 SXFT/IR spectrometer. The powder X-ray diffraction pattern was collected by using a Rigaku D/max-2550 diffractometer with CuKα radiation. The diffuse reflectance measurements were collected using Cary 5000 UV-Vis-NIR Spectrophotometer. Visualization was accomplished by UV light. Column chromatography was hand packed with silica gel (200-300 mesh).

Typical procedure for the synthesis of $[Cu_2(O)OH(phen)_2]_2[W_6O_{19}]·6H_2O$ 1.

A mixture of $Na_2WO_4·2H_2O$ (0.18 mmol), $NaVO_3$ (0.014 mmol), $CuCl_2·2H_2O$ (0.02mmol), 1, 10'-phenanthroline (0.02 mmol) and H_2O (18 mL) was stirred for half an hour in air. Then the mixture transferred to a Teflon-lined autoclave (23 mL) and kept at 160 °C for 120 h. After the autoclave was slowly cooled to room temperature, green crystals were filtered out, washed with distilled water and dried in a desiccator at room temperature yield 32%. IR (KBr pellet, cm^{-1}): 3429(s), 2922(w), 1582(s), 1412(m), 1087(w), 908(m), 866(m), 812(m), 716(m), 646(m), 476(w). Elemental analysis for $C_{48}H_{44}Cu_2N_8O_{25}W_6$ (**1**) Calcd C, 24.40; H, 1.88; N, 4.74 (%); found: C, 24.57; H, 1.89; N, 4.81 (%).

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Typical procedure for the synthesis of $[Cu_2(phen)_4Cl][HW_6O_{19}]{\cdot}2H_2O$ 2.

A mixture of $Na_2WO_4{\cdot}2H_2O$ (0.18 mmol), NH_4VO_3 (0.014 mmol), $CuCl_2{\cdot}2H_2O$ (0.02mmol), 1, 10'-phenanthroline (0.02 mmol) and H_2O (18 mL) was stirred for half an hour in air. Then the mixture was adjusted to pH = 8.0 with dilute HCl and stirred for half an hour in air. Finally, the resulting mixture was transferred to a Teflon-lined autoclave (23 mL) and kept at 160 ℃ for 120 h. After the autoclave was slowly cooled to room temperature, black crystals were filtered out, washed with distilled water and dried in a desiccator at room temperature yield 46 %. IR (KBr pellet, cm^{-1}): 3436(s), 3016(w), 1580(s), 1476(m), 1083(w), 912(m), 872(m), 817(m), 723(m), 652(w), 485(m). Elemental analysis for $C_{48}H_{46}Cu_4N_8O_{29}W_6$ (**2**) Calcd C, 22.55; H, 1.81; N, 4.38; found: C, 22.35; H, 1.71; N, 4.23 (%).

General procedure for the synthesis of 2-phenylquinoxalines 1c-14c.

An oven-dried round flask was charged with a magnetic stir bar, Cu-POMs **1** (0.015 mmol), 2-iodoanilines **a** (0.5 mmol), (1-azidovinyl)benzenes **b** or 3-phenyl-2*H*-azirines **d** (1.0 mmol), Cs_2CO_3 (1.0 mmol) and toluene (2.0 mL). The reaction mixture was stirred at 100 °C for 12 h, then another amount of 0.5 mmol **b** or **d** was added in two portions at 6h intervals *via* syringe. The reaction was monitored by TLC. When 2-iodoanilines **a** consumed completely, the reaction was stopped and cooled to room temperature, then the resulting suspension was filtered through a pad of filter paper with 20 mL of ethyl acetate for 3 times. After evaporating the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using petrol/EtOAc (10:1, v:v) as eluent to give **c**.

Conclusions

In conclusion, one bonded- and one discreted- Linqvist hexatungstate-based Cu-POMs **1-2** were controllably synthesized and routinely characterized. Importantly, these Cu-POMs catalysts were first applied in the novel reaction for preparation of 2-phenylquinoxalines *via* the one-pot coupling and oxidation reactions of 2-haloanilines with vinyl azides or 3-phenyl-2*H*-azirines under mild conditions, and Cu-POMs **1** showed higher catalytic performance in good yields. The reactions exhibit some functional group tolerance and allow for the preparation of a number of 2-phenylquinoxalines.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

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Bonded- and Discreted- Linqvist Hexatungstate-Based Copper hybrids as Heterogeneous Catalysts for One-pot Synthesis of 2-Phenylquinoxalines *via* 2-Haloanilines with Vinyl Azides or 3-Phenyl-2*H*-azirines

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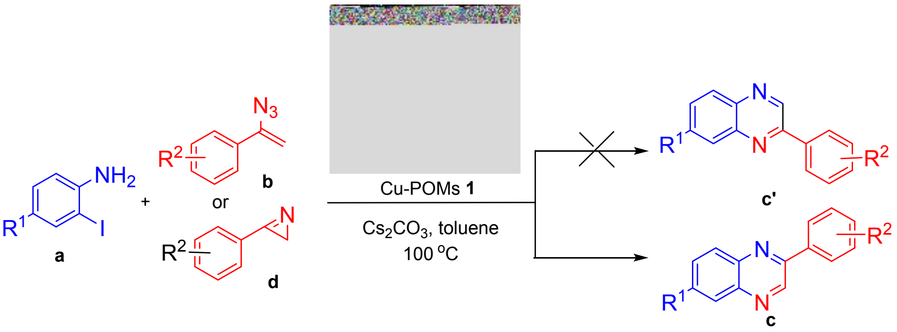

One bonded- and one discreted- Linqvist hexatungstate-based copper hybrids (Cu-POMs) ($[Cu_2(O)OH(phen)_2]_2[W_6O_{19}]\cdot 6H_2O$ (**1**) and $[Cu_2(phen)_4Cl][HW_6O_{19}]\cdot 2H_2O$ (**2**) (phen= 1,10-phenanthroline)) were controllably synthesized and routinely characterized. Cu-POMs **1-2** consisted of identical $[W_6O_{19}]$ unit and similar copper-phen complexes, the two units are bonded via four Cu-O chemical bonds in compound **1**, however, compound **2** is discreted and stabilized by intermolecular electrostatic interactions. Importantly, these Cu-POMs catalysts were first applied in the novel reaction for preparation of 2-phenylquinoxalines *via* the one-pot coupling and oxidation reactions of 2-haloanilines with vinyl azides or 3-phenyl-2*H*-azirines under mild conditions, and Cu-POMs **1** showed higher catalytic performance in good yields (79-84%). The reactions exhibit some functional group tolerance and allow for the preparation of a number of 2-phenylquinoxalines.

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