Catalysis Science & Technology

This article can be cited before page numbers have been issued, to do this please use: Z. Jia, K. Wang, T. Li, B. Tan and Y. Gu, *Catal. Sci. Technol.*, 2016, DOI: 10.1039/C5CY02260F.

View Article Online
DOI: 10.1039/C5CY02260F

Journal Name

ARTICLE

Functionalized hypercrosslinked polymers with knitted *N*-heterocyclic carbene–copper complexes as efficient and recyclable catalysts for organic transformations

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Zhifang Jia,[†ab] Kewei Wang,[†ab] Tao Li,[a] Bien Tan,*[a] and Yanlong Gu*[ac]

An *N*-heterocyclic carbene (NHC)–copper complex supported on hypercrosslinked polymers (HCPs) was successfully synthesized through a simple external cross-linking reaction. The structure and composition of the catalyst were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), nitrogen sorption, fourier transform infrared spectrometer (FT-IR), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and atomic emission spectrometry (AES). The obtained HCP–NHC–Cu possesses a large BET surface area, large pore volume, and good chemical and thermal stability. Hence, it was used as a solid catalyst for some organic transformations. An oxidative condensation reaction of indoles, 1,3-dicarbonyl compounds, and phenylglyoxal monohydrate was developed with the aid of the HCP–NHC–Cu catalyst, which produced various polysubstituted olefins in high yield. The three-component click reaction of NaN_3, phenylacetylene, and benzyl halide; the Ullmann C–N coupling; and the Glaser coupling reaction proceeded satisfactorily under the action of the HCP–NHC–Cu catalyst. At the end of these reactions, the catalyst was easily recovered, and reused several times without significant loss of activity in all the reactions.

Introduction

Catalysis can be characterized by the competition between homogeneous and heterogeneous systems. Heterogeneous catalysts are preferred for industrial processes because of their easily separation and reuse in consecutive cycles. Homogeneous catalysts, however, possess identical catalytic sites and usually exhibit high selectivity. Consequently, heterogenizing homogeneous catalysts by immobilization is a trend toward the development of chemically homogeneous but physically heterogeneous catalysts.[1]

Microporous materials, which have pores smaller than 2 nm, have recently attracted much attention. Owing to their unique properties, these materials have been utilized in various technological areas, such as gas separation and storage, conduction, and heterogeneous catalysis.[2] In the past few years, substantial research has been conducted on microporous materials, such as carbon materials,[3] zeolites,[4] silica,[5] metal–organic frameworks,[6] zeolitic imidazolate frameworks,[7] polysilsesquioxanes,[8] and porous organic cages.[9] Microporous organic polymers (MOPs), as an important class of microporous materials, are currently at the forefront of materials research because of their unique properties, including superior chemical, thermal, and hydrothermal stabilities; synthetic diversity; low skeletal density; and high surface area. One particular advantage of MOPs is the fine control over the chemical nature of available surface areas, which is critical for heterogeneous catalysis.[10] However, the application of MOPs as heterogeneous catalysts is rather limited because of the high-cost of synthesizing MOPs. In some cases, preparing MOPs entail the use of expensive noble metal catalysts.[11] This drawback can be overcome by using hypercrosslinked polymers (HCPs), which have recently emerged as low-cost MOPs with tunable pore sizes and surface areas. The permanent porosity in HCPs is the result of extensive chemical cross linkage, which prevents the collapse of polymer chains to a dense nonporous state. HCPs are highly desirable for the heterogenization of homogeneous catalysts because some electron-donor ligands can be installed in the skeletal framework without any additional chemical modification.[12] We recently reported a cost-effective method for preparing HCPs, which involves "knitting" a triphenylphosphine ligand with an external cross-linker.[13] The process involves a one-step Friedel–Crafts reaction of a low-cost cross-linker and a less-functionalized aromatic compound. Through this method, a microporous polymer with high surface area can be produced. This "knitting" strategy is compatible with the use of a wide range of building blocks, thereby facilitating the heterogenization of catalytically active components onto the porous channel.

---

[a] Key laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, 430074, Wuhan, China. Phone: (0)86-(0)27-87 54 37 32, Fax: (0)86-(0)27-87 54 45 32, E-mail: taoli@hust.edu.cn; klgyl@hust.edu.cn.
[b] Department of Chemistry and Chemical Engineering, Shanxi Datong University, Datong, 037009, People's Republic of China.
[c] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Lanzhou, 730000 (P.R. China)e.

† Z. Jia and K. Wang contributed equally to this work.

Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C5CY02205F

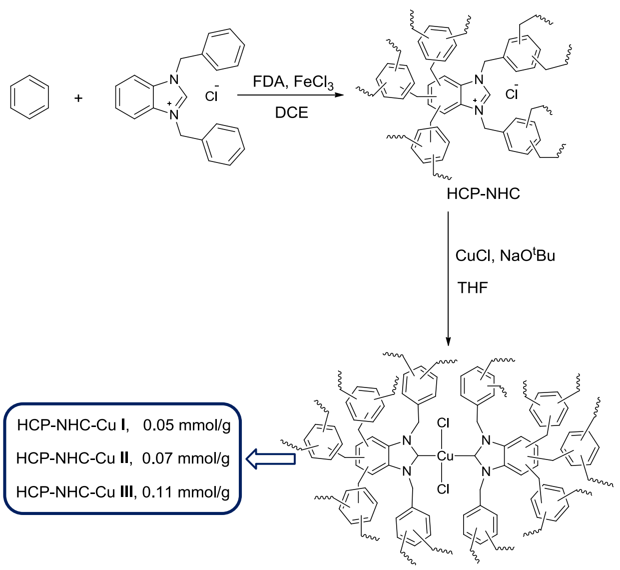
N-heterocyclic carbenes (NHCs), also called "phosphine mimics" in catalysis, possess many favorable properties, such as good coordinating ability of the electron-rich site and structural tunability. In particular, its strong σ-electron-donating ability highly strengthens the NHC–metal bonds. Therefore, their metal complexes exhibit good thermal stability and can be utilized as catalysts at high temperatures without decomposition. Previously, NHC–metal complexes were often used as homogeneous catalysts.[14] The high dissociation energies of metal–carbon bonds in NHC–metal complexes also enable the NHCs to serve as high-performing ligands in establishing heterogenized systems.[15] To date, several supporting materials, such as polymer, nanoparticle, and silica, have been used to immobilize NHC–metal complexes.[16] A polystyrene–supported bis-NHC–Pd catalyst has been used in a Suzuki reaction.[17] Iridium NHC complexes immobilized on magnetic nanoparticles were proven to be quite effective for catalyzing ketone reduction.[18] However, a small amount of iridium leaching was observed during its use, and the good catalytic activity was observed to only last for two runs. An SBA-15-supported NHC–Cu catalyst has been utilized in the hydrothiolation of alkynes and electron-deficient alkenes.[19] Although various methods have been reported, the diversity of immobilizing NHC metal complexes and their downstream catalytic utilization is rather limited at the moment.

We recently prepared a knitted NHC porous polymer that could be utilized in the synthesis of a highly active palladium catalyst for Suzuki–Miyaura coupling reactions.[20] Our study demonstrated that adopting the knitted NHC porous polymer as dual ligand and solid support to immobilize homogeneous metal complex catalysts is feasible. On the other hand, copper complexes have been widely used as catalysts in organic reactions.[21] For example, copper catalysts have boosted the development of click reactions, which were well adopted in material, biology and medicine.[22] In organic synthesis, the recent developments of some C–C and C–N coupling reactions should also be linked to the uses of copper-based catalysts.[23] Particularly, copper NHC catalysts played pivotal roles in these areas.[24] Consequently, we noted that HCP–NHC–Cu, if synthesized through a simple procedure, could sever as a catalyst of choice for some important organic reactions. We report herein, for the first time, the preparation and use of HCP–NHC–Cu (**Scheme 1**), as catalyst in the oxidative condensation reaction of indole, 1,3-dicarbonyl compound, and phenylglyoxal monohydrate. The process generated high yields of densely substituted olefins. The remarkable catalytic ability of HCP–NHC–Cu was also demonstrated by some well-known organic reactions, such as the three-component click reactions of NaN_3, phenylacetylenes, and alkyl halides, as well as the Ullmann C–N and Glaser coupling reactions.

Results and Discussion

The supporting material HCP–NHC was prepared from *N*,*N*-dibenzylbenzimidazolium chloride and benzene as described previously using $FeCl_3$ as catalyst.[20] The following treatment of HCP–NHC with CuCl in the presence of sodium *tert*-butoxide in THF produced three HCP–NHC–Cu catalysts (**Scheme 1**). The FT-IR spectra of NHC, HCP–NHC, and HCP–NHC–Cu **III** (**Fig. 1**) display a series of bands at around 1600–1450 and 900–650 cm^{-1}, which correspond respectively to the benzene skeleton stretching and the C–H out-of-plane bending vibrations of the benzene ring. Meanwhile, the bands at approximate 1600-1650 cm^{-1} could be assigned to the –C=N– stretching vibrations.

The HCP–NHC–Cu catalysts were also subjected to XPS analysis, and the results are shown in **Fig. 2**. The Cu 2p XPS spectra of the HCP–NHC–Cu catalysts show peaks at 933.8–934.0 eV with strong shake-up satellites, indicating that the immobilized Cu species is Cu^{2+} rather than metallic copper and Cu^{+}.[25] The oxidation of Cu^{+} clearly occurred during the preparation of the HCP–NHC–Cu catalysts. Compared with the homogeneous counterpart, $CuCl_2$ (934.2 eV), the Cu^{2+} binding energy in the Cu 2p XPS spectra of HCP–NHC–Cu **I**, **II**, and **III** shifted negatively by 0.4, 0.3 and 0.2 eV, respectively. This result may be attributed to the strong electron-donating effect



Scheme 1 HCP–NHC–Cu catalysts.

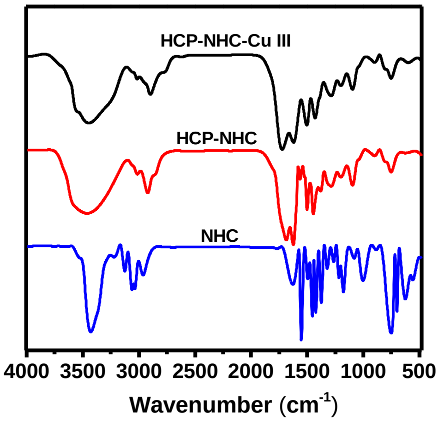


Fig. 1 FT-IR spectra of NHC (a), HCP–NHC (b), and HCP–NHC–Cu **III** (c).

View Article Online
DOI: 10.1039/C5CY02260F

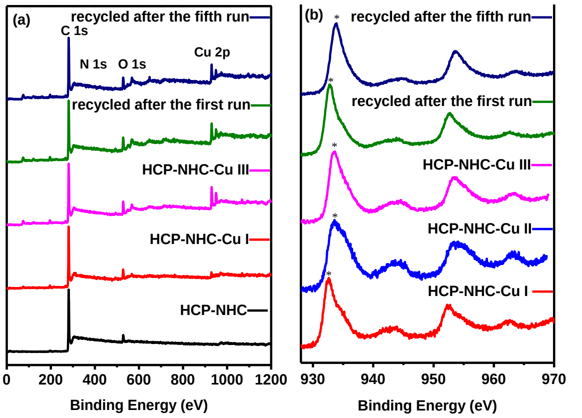


Fig. 2 (a) XPS spectra of the HCPs in the regions of Cu 2p, C 1s, O 1s, and N 1s (left); (b) XPS spectrum of HCP–NHC–Cu in the region of Cu 2p.

Table 1 Physical properties of the HCP–NHC and HCP–NHC–Cu catalysts.

Samples	S_{BET} [a] (m^2/g)	V_{Micro} [b] (m^2/g)	V_{total} [c] (m^2/g)	Cu^+_{AES} [d] (mmol/g)
HCP–NHC	831	155	0.17	0
HCP–NHC–Cu **I**	511	198	0.10	0.05
HCP–NHC–Cu **II**	503	200	0.10	0.07
HCP–NHC–Cu **III**	494	209	0.11	0.11

[a] Surface area calculated from the nitrogen adsorption isotherm using the BET method. [b] The micropore volume derived using a t-plot method based on the Halsey thickness equation. [c] Total pore volume at P/P^0 = 0.99. [d] Data were obtained by AES.

of the NHC ligand. As shown in **Fig. 2b**, the copper loadings in HCP–NHC–Cu **I**, **II**, and **III** are 3.32, 4.44, and 7.78 wt%, respectively. These findings are consistent with the results obtained by AES (0.05, 0.07 and 0.11 mmol/g, respectively).

The porous properties of the samples were analyzed by nitrogen sorption analysis at 77.3 K. The BET surface area of HCP–NHC was found to be 831 m^2/g. The adsorption of copper salt resulted in a dramatic decrease of surface area. This finding can be attributed to the partial pore filling. A slight increase in material density is also partially responsible. Despite this tendency, the obtained HCP–NHC–Cu **I**, **II**, and **III** exhibit large surface areas, with values of 511, 503, and 494 m^2/g, respectively (**Table 1**).

The adsorption and desorption isotherms of HCP–NHC–Cu **I**–**III** in **Fig. 3a** display a steep nitrogen gas uptake curve at low relative pressure (P/P^0 < 0.001), indicating the existence of abundant micropore structures. At relative high–pressure regions (P/P^0 = 0.5–1.0), a slight hysteresis loop and a sharp rise are clearly observed. This finding implies that a certain amount of mesopores and a spot of macropore are present in the material. These results coincide well with the pore-size distribution of HCP–NHC–Cu shown in **Fig. 3b**. The presence of a spot of mesopore and macropore structure in the heterogeneous support is essential to ensure the favorable catalytic performance of the catalyst because these structures enable the frameworks to be highly swollen in certain solvents, thereby maximizing the accessibility of the catalytically active sites toward the substrates. In addition, the abundant micropore with a suitable size distribution favors the dispersion and anchoring of the metal catalyst.

TGA shows that the HCP–NHC support (**Fig. 4**) exhibits good thermal stability in air (T_{dec} > 300 °C). HCP–NHC, fresh HCP–NHC–Cu **III**, and recycled HCP–NHC–Cu **III** were also subjected to SEM and TEM analyses. As shown in **Fig. 5**, no significant change in terms of the morphology of the materials occurs after loading the copper species.

We then investigated the activities of HCP–NHC–Cu catalysts to determine potential relationships between structure and catalyst activity. Copper salts are extensively used as oxidation catalysts in organic reactions; hence, we first examined the HCP–NHC–Cu catalysts in such reactions. We recently studied the three-component condensation reactions of aldehydes with two nucleophiles.[26] These reactions are normally established by a tandem process involving (i) the generation of an active intermediate through a reaction between an aldehyde and the first nucleophile and the (ii) trapping of this intermediate by the second nucleophile. Although numerous multi-component reactions have been reported in the past

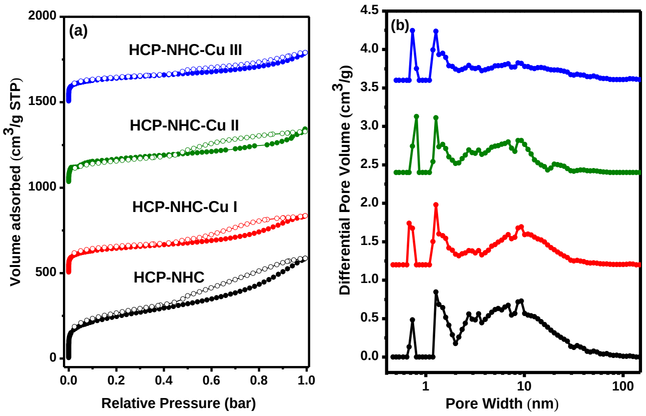


Fig. 3 (a) N_2 sorption isotherms of the samples at 77.3 K (left); (b) pore-size distributions calculated using the DFT methods *via* the adsorption branch (slit pore models, differential pore volumes, and pore width) of the samples.

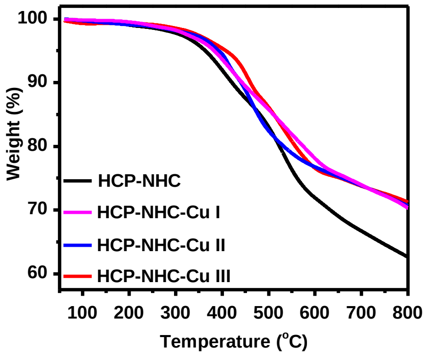


Fig. 4 TGA spectra of HCP–NHC, HCP–NHC–Cu **I**, HCP–NHC–Cu **II**, and HCP–NHC–Cu **III**.

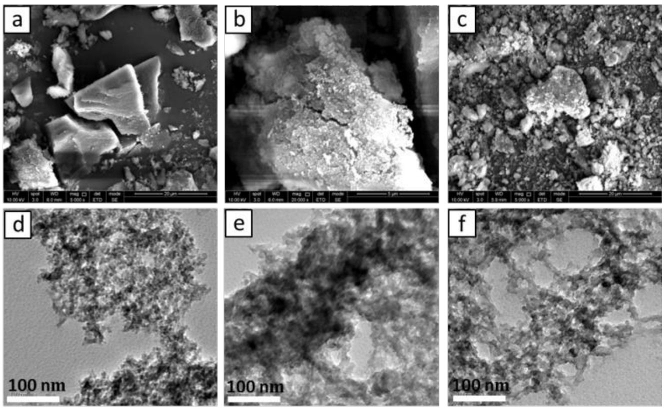
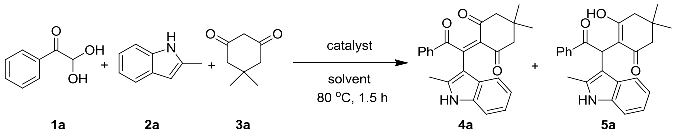


Fig. 5 SEM images of HCP materials: a) HCP–NHC in 20 μm, b) fresh HCP–NHC–Cu **III** in 5 μm, and c) recycled HCP–NHC–Cu **III** in 50 μm. TEM images of HCP materials: d) HCP–NHC, e) fresh HCP–NHC–Cu **III**, f) recycled HCP–NHC–Cu **III**.

decade,[27] the catalog of generated products is rather limited because most of these compounds possess similar molecular skeletons. To increase the diversity of the reaction products, we attempted to integrate a foreign reaction step, for instance, oxidation, in these condensation reactions. Therefore, developing a catalyst is necessary, particularly, one that can promote the modular three-component condensation and induce an oxidation step. To this end, the obtained HCP–NHC–Cu materials were used in the three-component condensation of phenylglyoxal monohydrate **1a**, 2-methylindole **2a**, and dimedone **3a**. The reaction was performed in ethanol (EtOH) at 80 °C. In the presence of a catalytic amount of HCP–NHC–Cu **I**, two products were formed. The following spectroscopic analysis reveals that the major product is **4a**, and another one is **5a** (**Table 2**, entry 1). Under catalyst-free conditions, only **5a** was obtained (entry 2). This result indicated the necessity of using a catalyst in the oxidation step. Some homogeneous copper salts, such as $Cu(OAc)_2·H_2O$, $CuSO_4·5H_2O$, copper (II) gluconate, and cupric acetylacetonate, were then used in this reaction. Cupric acetate and cupric acetylacetonate clearly became prominent among all the examined copper salts, and the yields of **4a** reached 80% and 78%, respectively (entries 5 and 6). By contrast, the performances of monovalent copper salts, such as Cu_2O, CuCl, CuBr, and CuI, as catalysts are not successful because the formation of **5a** is predominant in these cases (entries 7–10). The yield of **4a** reached only 67% with HCP–NHC–Cu **I**. Even so, this result is highly promising because the material is a solid, which can facilitate catalyst recycling in such a liquid phase reaction. Encouraged by this result, we then investigated other

Table 2 Oxidative condensation reactions of **1a**, **2a**, and **3a**.[a]



Entry	Catalyst	Solvent	Product Yield (%)	
			4a	**5a**
1	HCP–NHC–Cu **I**	EtOH	67	29
2	—	EtOH	—	95
3	$CuSO_4·5H_2O$	EtOH	24	75
4	Copper gluconate	EtOH	20	74
5	$Cu(OAc)_2·H_2O$	EtOH	80	17
6	$Cu(acac)_2$	EtOH	78	15
7	Cu_2O	EtOH	trace	87
8	CuCl	EtOH	23	60
9	CuBr	EtOH	17	71
10	CuI	EtOH	trace	79
11	HCP–NHC–Cu **III**	EtOH	99	trace
12	HCP–NHC–Cu **II**	EtOH	82	16
13	HCP–NHC	EtOH	—	90
14	NHC–Cu	EtOH	82	16
15	PS–NHC–Cu	EtOH	21	76
16	HCP–NHC–Cu **III**	1,4-dioxane	35	51
17	HCP–NHC–Cu **III**	CH_3CN	32	49
18	HCP–NHC–Cu **III**	CH_3NO_2	trace	62
19	HCP–NHC–Cu **III**	H_2O	trace	89
20	HCP–NHC–Cu **III**	DCE	trace	91
21	HCP–NHC–Cu **III**	DMSO	49	47
22[b]	HCP–NHC–Cu **III**	EtOH	57	34
23[c]	HCP–NHC–Cu **III**	EtOH	72	22
24	HCP–NHC–Cu **III**	EtOH	94[d] (94)[e]	trace

[a] **1a** (1.0 mmol), **2a** (1.0 mmol), **3a** (1.0 mmol), catalyst (0.53 mol%), solvent (2 mL), 80 °C, 1.5 h. [b] 50 °C. [c] 0.5 h. [d] The reaction was performed under 10 mmol scale. [e] The catalyst was used in the fifth run.

View Article Online
DOI: 10.1039/C5CY02260F

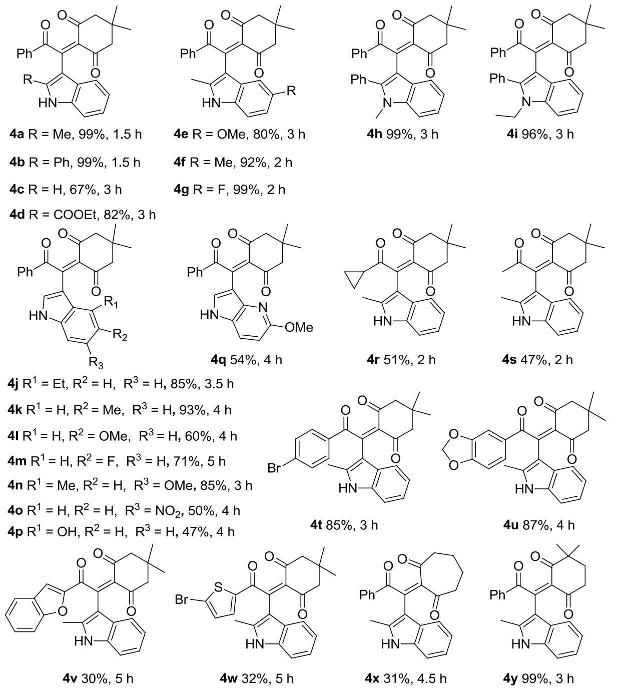


Fig. 6 Substrate scope of the oxidative condensation reaction.

HCP–NHC–Cu catalysts. A maximum yield of 99% was obtained with HCP–NHC–Cu **III** (entry 11). The increase of copper loading in HCP–NHC–Cu **III** catalyst seems beneficial for the formation of **4a** with excellent yield. Under identical conditions, the reaction was also conducted under the HCP–NHC system. In this case, **5a** was readily formed and no **4a** could be detected (entry 13). These results clearly indicated that the copper species is essential for ensuring the good catalytic activity of the HCP–NHC–Cu **III** catalyst in the oxidation step. Interestingly, with a homogeneous counterpart of this catalyst, NHC–Cu, only 82% yield was obtained under the same conditions (entry 14). When a referential copper catalyst (PS–NHC–Cu) prepared through a reported nucleophilic substitution reaction[28] was used, the yield of **4a** reached only 21% (entry 15). This result demonstrated that the hierarchical porous structure of HCP–NHC–Cu **III** is indeed beneficial for this reaction. The effect of solvents on the model reaction was also then investigated. 1,4-Dioxane and CH_3CN were found to be inappropriate as solvents for this reaction (entries 16 and 17). In dimethyl sulfoxide (DMSO), **4a** was obtained in 49% yield (entries 21). Finally, ethanol was proven to be the best choice of solvent. The polar protic solvents were known to be able to drive the three-component reactions of aldehydes and two nucleophiles toward the formation of the target product.[26(a)] This ability may ensure partially ethanol to be the best choice of the solvent. Further investigation revealed that the reaction was also affected by temperature and reaction time, and the optimal conditions were as follows: 0.53 mol% of HCP–NHC–Cu **III**, 80 °C, and 1.5 h (entries 22 and 23).

Under the optimized conditions, we probed the scope of the model reaction substrates. As shown in **Fig. 6**, many substituted indoles reacted readily with **1a** and **3a** under the optimal conditions. In particular, high yields were obtained with 2-methyl- or 2-phenyl-substituted indoles. The presence of an electron-withdrawing ethoxycarbonyl group in the indole ring exerted no detrimental effect on the reaction yield (**Fig. 6**, **4a**–**4i**). C2-unsubstituted indoles also participated readily in the condensation reaction, producing the corresponding products in high good yields (**4c** and **4j**–**n**). Only moderate yields were obtained when 6-nitro and 4-hydroxy indoles were used (**4o**, **4p**). Remarkably, 5-methoxyl-4-azaindole could also be used as a nucleophilic reagent, and the corresponding product **4q** was obtained in 54% yield. Substrate scope with respect to the alkylglyoxal component was then investigated. With the aid of the HCP–NHC–Cu **III** catalyst, the alkylglyoxals with cyclopropyl and methyl groups reacted readily with **2a** and **3a**, producing the expected products **4r** and **4s** in 51% and 47% yield, respectively. When 1-(4-bromophenyl)glyoxal and 1, 3-benzodioxol-5-ylglyoxal hydrate were used as substrates, the reactions proceeded favorably, with yields of **4t** and **4u** reaching over 85%. HCP–NHC–Cu **III** was also been used in the condensation reactions of **2a**, **3a**, and arylglyoxals with a heterocyclic substituent, such benzofuranyl and thienyl. The expected products **4v** and **4w** were obtained in 30% and 32% yields respectively. The low yields were resulted mainly from the easy formation of by-product through a reaction of 2-methylindole and arylglyoxals. The scope of the reaction with respect to cyclic-1,3-dicarbonyl component was next investigated. Because of the low activity of cycloheptane-1,3-dione in this reaction, the corresponding product **4x** was obtained only in 30% yield. Notably, the three-component reaction of **1a**, **2a**, and 4,4-dimethylcyclohexane-1,3-dione also proceeded readily under the same conditions, and the desired product **4y** was obtained in almost quantitative yield. However, our attempts to use linear 1,3-dicarbonyl compounds as substrates were unsuccessful. This result could be attributed to the relatively lower activities of linear 1,3-dicarbonyl compounds compared with those of the cyclic compound. The generated products are a unique class of tetrasubstituted alkenes, which are highly attractive synthetic targets for efficient and selective synthetic methods because of the compouds' usefulness in organic synthesis.[29] However, the reported methods involve the use of either expensive reagents or environmentally unfavorable conditions.[30] The present reaction offers a convenient and environmentally benign route to access these densely substituted olefins.

Notably, the reactions of **1a**, **2a**, and **3a** can be effectively scaled up with similar efficiency. For example, the reaction

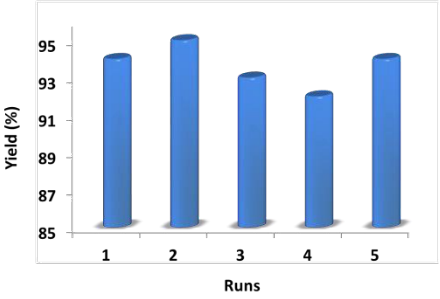


Fig. 7 Reuse of HCP–NHC–Cu **III** catalyst.

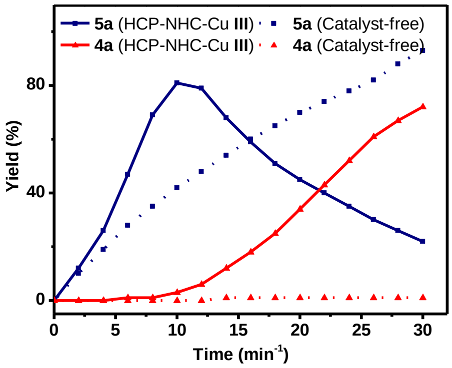


Fig. 8 Comparison of kinetic profiles between the model reactions with and without HCP–NHC–Cu **III** catalyst.

under the 10 mmol scale generated **4a** in 94% yield (3.62 g). The recyclability of the HCP–NHC–Cu **III** catalyst was also investigated in the 10 mmol scale. We found that the catalyst was recycled for five runs without significant loss of its activity (**Table 2**, entry 24), as shown in **Fig. 7**. These results indicated that HCP–NHC–Cu **III** catalyst is a robust catalyst. An SEM image of the recycled HCP–NHC–Cu **III** shows that its particle size did not change significantly, and the integrity of the catalyst remained intact (**Fig. 5**). XPS analysis of the recycled HCP–NHC–Cu **III** demonstrated that all the elements were retained (**Fig. 2**). ICP–MS showed that the Cu content of the catalyst did not change appreciably after the reaction.

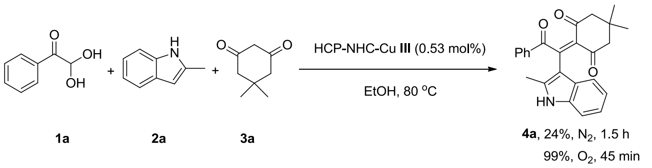
To shed light on the mechanism, some experiments were then carried out. First, a mixture of **1a**, **2a**, and **3a** was treated in ethanol in the presence of HCP–NHC–Cu **III**. After 10 min of stirring, compound **5a** was clearly detected (**Fig. 8**). However, the concentration of **5a** decreased rapidly in the next 20 min, while the concentration of **4a** increased. In the absence of HCP–NHC–Cu **III**, **4a** was hardly detected, though **5a** could be generated. These results imply that a Cu^{2+} species is responsible for the dehydrogenation of **5a**. The three-component reaction was also performed under a nitrogen atmosphere. In this case, **5a** was predominantly formed, and **4a** was obtained only in 24% yield after 1.5 h of stirring at 80 °C (**Scheme 2**). A high yield of **4a** in 99% was achieved by performing the same reaction under an oxygen atmosphere. Remarkably, the reaction time could be halved in this case (**Scheme 2**). These results indicate that the presence of molecular oxygen also plays a crucial role in the dehydrogenation of **5a** to form **4a**.

Literature survey revealed that an aerobic dehydrogenation reaction of some linear polycarbonyl compounds can be initiated by some metallic salts that exhibit certain oxidation capacity, such as $Pd(OAc)_2$[31] or $AgNO_3$.[32] Notably, the use of inorganic bases is necessary in these dehydrogenative reactions. Sullivan et al[33] have found that the linear polycarbonyl compound diethyl diacetylsuccinate shows no evidence of enolization by infrared and nuclear magnetic resonance (NMR) spectra. We therefore deduced that, in the reported homogeneous catalytic systems of aerobic dehydrogenation of polycarbonyl compounds, adding an inorganic base probably strengthens the enolization of the polycarbonyl compound. However, we found by NMR analysis that compound **5a** exists exclusively in its enol form. In addition, such a clear enolization was not observed with **5b** (see ESI), which is a congener of **5a** synthesized from linear a 1,3-diketone. This result coincides well with Sullivan's report.[33] Compound **5b** was also subjected to the conditions of model condensation. However, no dehydrogenative product was obtained with the HCP–NHC–Cu **III** catalyst (**Scheme 3**). These results led us to speculate that the inherent tendency of **5a** to present as its enol form probably conferred **5a** a high reactivity toward aerobic dehydrogenation.

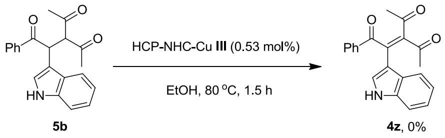
On the basis of these observations, we proposed a plausible mechanism. The formation of **5a** through a selective assembly of **1a**, **2a**, and **3a** possibly corresponds to the initial event (**Fig. 9**). The enol form of **5a** allows the proton in the center carbon to be highly active and hence easily absorbed by the metallic species. Thus, it is easy to be oxidized to **4a**. We believe that the high tendency of **5a** for oxidation is also related to the extension of the conjugated system.

Give the high tendency of **5a** toward oxidation, we explored the possibility of using other aldehydes containing a hydrogen bond acceptor to react with 2-methylindole and dimedone. Under the use of HCP–NHC–Cu **III** as catalyst, 2-chlorobenzaldehyde **6a** reacted with **2a** and **3a**, producing compound **7a** in 41% yield (**Scheme 4**). The existence of C2-chloro substituent in the phenyl ring of the aldehyde was proven to be critical because our attempts to establish similar three-component oxidative condensations with 4-chlorobenzaldehyde or benzaldehyde failed.

To extend the utility of HCP–NHC–Cu, we then examined other organic reactions. The second reaction we investigated was the three-component click reaction of NaN_3, phenylacetylenes, and alkyl halides. The 1,3-dipolar cycloaddition reaction of organic azides and alkynes is an important organic transformation that can produce, with its mild conditions and high efficiency, triazole derivatives.[34] Although this reaction has been extensively investigated under various types of catalysts (homogeneous[35] and



Scheme 2 Model three-component reactions under a N_2 or O_2 atmosphere.



Scheme 3 Aerobic dehydrogenation of **5b** over an HCP–NHC–Cu **III** catalyst.

View Article Online
DOI: 10.1039/C5CY02260F

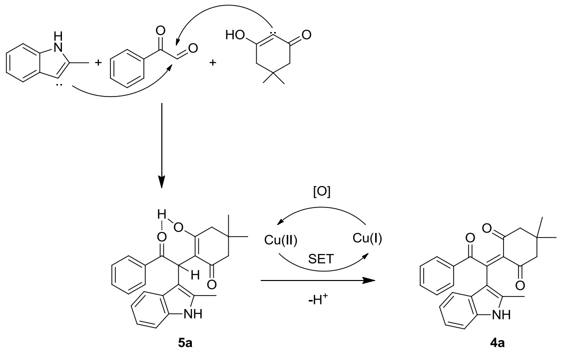
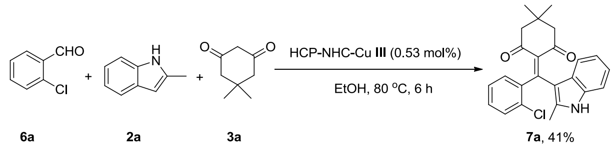


Fig. 9 Proposed mechanism.



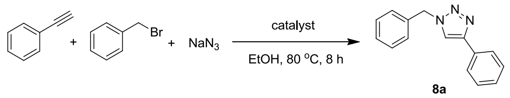
Scheme 4 Oxidative condensation reaction of **6a**, **2a**, and **3a**.

heterogeneous[36]), these catalyst systems are associated with one or more disadvantages, such as the use of sodium ascorbate as additive,[37] tedious procedure for preparation,and use of hazardous and carcinogenic organic solvents, including nitrobenzene, acetonitrile, and dioxane for reactions. Hence, a simple, green, and efficient procedure avoiding these drawbacks would be valuable.

HCP–NHC–Cu **III** catalyst was proven to be highly active in catalyzing this three-component click reaction in ethanol at 80 °C. A small amount of catalyst at 0.45 mol% was sufficient to promote these three-component click reactions (**Table 3**, entries 1–3). No reaction occurred in the absence of catalyst or with HCP–NHC (entries 4 and 5). With a homogeneous counterpart of HCP–NHC–Cu catalysts, NHC–Cu, only 22% yield was obtained (entry 6). When the referential catalyst, PS–NHC–Cu, was used, the yield of **8a** reached only 24% under identical conditions (entry 7). Reactions scaled up to multigram quantities provided uniform results (entry 8). In such reactions, the HCP–NHC–Cu **III** catalyst was reused at least five times without any significant loss of catalytic activity (entry 8).

The methodology established using the HCP–NHC–Cu **III** catalyst also displayed good substrate scope. The cycloaddition products **8a** to **8l** were obtained in yields ranging from 90% to 99% (**Table 4**, entry 1–12). The established spot-to-spot reaction allowed us to isolate the product by using an extremely simple procedure. After completion of the reaction, the reaction solution was centrifuged, and the solid was washed with ethanol three times. The product was in the acquired organic phase. Interestingly, the product was obtained directly by removing the volatile components. Isolation by the chromatographic method was needed when the products were formed in moderate yields (**8m** to **8o**). In this reaction, HCP–NHC–Cu **III** catalyst displayed some advantages, such as simple operation for catalyst preparation, avoidance of the use of reducing agent, minimal use of toxic and volatile organic solvents, and clean and easy work-up procedure. All these properties render this HCP–NHC–Cu catalyst highly desirable for practical use.

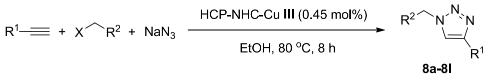
Table 3 Three-component click reaction of NaN_3, phenylacetylenes and benzyl bromide.[a]



Entry	Catalyst	Yield (%)[b]
1	HCP–NHC–Cu **III**	99
2	HCP–NHC–Cu **II**	89
3	HCP–NHC–Cu **I**	77
4	—	0
5	HCP–NHC	0
6	NHC–Cu	22
7	PS–NHC–Cu	24
8	HCP–NHC–Cu **III**	98[c] (96)[d]

[a] Phenylacetylene (1.0 mmol), benzyl bromide (1.0 mmol), NaN_3 (1.1 mmol), catalyst (0.45 mol%), ethanol (2 mL), 80 °C. [b] Isolated yield. [c] The reaction was performed under the 10 mmol scale. [d] The yield in parentheses was generated after the reuse of the catalyst in the sixth run.

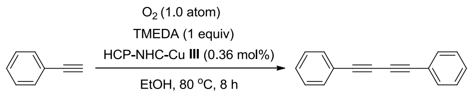
Table 4 Three-component click reactions of NaN_3, phenylacetylenes and alkyl halides catalyzed by HCP-NHC-Cu **III**.[a]



Entry	X	R^1	R^2	Product	Yield (%)
1	Cl	Ph	Ph	**8a**	91
2	Br	*p*-F-Ph	Ph	**8b**	99
3	Br	*p*-MeO-Ph	Ph	**8c**	92
4	Br	*p*-^{t}Bu-Ph	Ph	**8d**	99
5	Br	*p*-Et-Ph	Ph	**8e**	99
6	Br	*p*-^{n}amyl-Ph	Ph	**8f**	93
7	Br	*p*-^{n}Pr-Ph	Ph	**8g**	99
8	Br	Ph	Bn	**8h**	98
9	I	Ph	Et	**8i**	93
10	I	*p*-F-Ph	Et	**8j**	99
11	I	Ph	^{n}decyl	**8k**	90
12	Br	Ph	*p*-CO_2H-Ph	**8l**	92
13	Br	Ph	*p*-NO_2-Ph	**8m**	61
14	Br	1-MeO-Bn	Ph	**8n**	72
15	I	Ph	^{n}hexyl	**8o**	76

[a] Alkyne (1.0 mmol), halide (1.0 mmol), NaN_3 (1.1 mmol), Cu catalyst (0.45 mol%), EtOH (2 mL), 80 °C, 8 h.

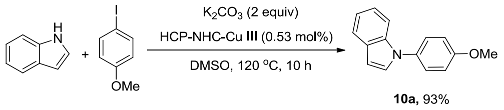
Two other reactions were also examined using HCP–NHC–Cu **III** as the catalyst. Glaser oxidative coupling reaction plays an important role in the synthesis of 1,3-diynes and is thus widely utilized in materials chemistry.[38] Some heterogeneous copper species, for example, polymer-supported copper,[39] Cu(II)-TD@nSiO_2,[40] and MCM-41-immobilized copper(I) complex,[41] have been used in this reaction, sometimes with remarkable results. In this case, HCP–NHC–Cu **III**, with lower catalyst loading and a cleaner catalyst system, was utilized to catalyze this reaction. The desired product **9a** was obtained in 99% yield in the Glaser oxidative coupling reactions of



9a, 99%

The catalyst was used in the third time: 94%

Scheme 5 Glaser reaction of phenylacetylene catalyzed by HCP–NHC–Cu **III**.



10a, 93%

The catalyst was used in the second time: 91%

Scheme 6 C–N coupling reaction of *p*-iodoanisole and indole catalyzed by HCP–NHC–Cu **III**.

phenylacetylene (**Scheme 5**). In this reaction, the HCP–NHC–Cu **III** catalyst was also recyclable. Meanwhile, the Ullmann C–N coupling of *p*-iodoanisole and indole also proceeded readily in the presence of the HCP–NHC–Cu **III** catalyst (**Scheme 6**). All these results demonstrate that HCP–NHC–Cu is indeed a versatile heterogeneous catalyst for organic transformations.

Conclusions

An NHC–copper complex supported on microporous and highly stable HCPs was synthesized through a simple external cross-linking reaction. The obtained HCP–NHC–Cu catalysts were characterized by various spectroscopic methods, such as SEM, TEM, N_2 sorption, FT-IR, TGA, XPS, and AES. These catalysts displayed outstanding catalytic performance in the oxidative condensation reaction of indole, 1,3-cyclohexandione and phenylglyoxal monohydrate. Various polysubstituted olefins were prepared with high yield. This catalyst also displayed good catalytic activity in many other organic reactions, such as three-component click, Ullmann C–N coupling, and Glaser coupling reactions. In all these reactions, the HCP–NHC–Cu catalyst was easily recovered and reused without significant loss of catalytic activity. The results obtained in this study revealed that HCPs of NHC are indeed an excellent supporting material for the immobilization of homogeneous copper complex catalysts. This method may be applied during the heterogenization of other metal complexes, a direction that we are actively investigating.

Experimental section

The polymer surface areas, N_2 adsorption isotherm (77.3 K), and pore-size distributions were measured using Micromeritics ASAP 2020 M surface area and porosity analyzer. Before analysis, the samples were degassed at 110 °C for 8 h under vacuum (10^{-5} bar). The FT-IR spectra were recorded under ambient conditions in the wavenumber range of 4000–400 cm^{-1} using an FT-IR Bruker (EQUINOX 55) spectrometer. Elemental analysis was determined using a Vario Micro cube Elemental Analyzer (Elementar, Germany). TGA was performed on a Perkin-Elmer Instruments Pyris1 TGA thermobalance at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The polymer morphologies were investigated using an FEI Sirion 200 field emission scanning electron microscope. TEM images were obtained on a Tecnai G20 microscope (FEI Corp. USA) instrument operated at an accelerating voltage of 200 kV. XPS was performed on an ESCALAB.MK II Spectrometer (VG, UK). Cu catalyst loading was obtained by atomic emission spectroscopy on a Agilent 4100 MP-AES. ^1H, ^{13}C NMR spectra were recorded on a Bruker AV-400. All the chemicals used were of reagent grade and used as received without further purification. 1,3-Dibenzyl-1*H*-benzo[*d*]imidazol-3-ium chloride was synthesized in accordance with a reported procedure.[42] All reactions were conducted in a 10 mL V-type flask equipped with a triangular magnetic stirring bar.

General procedure for the synthesis of HCP–NHC

HCP–NHC was synthesized as described previously.[20] Elemental analysis (%) showed the following components: C (77.64%), H (5.32%), N (1.55%).

General procedure for the synthesis of HCP–NHC–Cu

HCP–NHC (0.50 g), CuCl (0.40 g, 4.0 mmol), ^{t}BuONa (0.39 g, 4.0 mmol) and 100 mL anhydrous tetrahydrofuran were placed in a three-necked flask. Then, the reaction was stirred for 24 h under N_2 atmosphere at room temperature. Finally, the solid was filtered and washed with methanol several times. With this procedure, 0.62 g HCP–NHC–Cu **III** was obtained. HCP–NHC–Cu **I** and **II** were synthesized with the same procedure by altering the amounts of CuCl and ^{t}BuONa.

General procedure for the synthesis of 4a–4y and 7a

In a typical reaction, phenylglyoxal monohydrate (0.15 g, 1.0 mmol), 2-methylindole (0.13 g, 1.0 mmol), dimedone (0.14 g, 1.0 mmol), and HCP–NHC–Cu **III** (48 mg, 0.0053 mmol) were added to anhydrous ethanol (2 mL). The mixture was stirred for 1.5 h at 80 °C. After reaction completion, the mixture was cooled to room temperature and then centrifuged. The supernatant organic phase was isolated, and the bottom solid was washed with ethanol (2.0 mL × 3). All organic phases were combined and then concentrated under reduced pressure. Afterward, the desired product **4a** was obtained in 99% yield (0.38 g) by isolation with preparative thin-layer chromatography (TLC) [eluting solvent: ethyl acetate/ petroleum ether = 1/2 (v/v)]. The procedures for synthesizing **4b**–**4y** and **7a** resemble this method, and the yields of **4b**–**4y** and **7a** are listed in **Fig. 6** and **Scheme 4**.

General procedure for the synthesis of 8a–8o

In a typical reaction, phenylacetylene (0.10 g, 1.0 mmol), benzyl bromide (0.17 g, 1.0 mmol), NaN_3 (0.072 g, 1.1 mmol), and HCP–NHC–Cu **III** (40 mg, 0.0045 mmol) were added in anhydrous ethanol (2 mL). The resulting solution was stirred at 80 °C for about 8 h. After reaction completion, the mixture was cooled to room temperature and then centrifuged. The supernatant organic phase was isolated, and the bottom solid

View Article Online
DOI: 10.1039/C5CY02260F

was washed with ethanol (2.0 mL × 3). All organic phases were combined and then concentrated under reduced pressure. Afterward, the desired product **8a** was obtained in 99% yield (0.23 g). The procedures for synthesizing **8b**–**8n** are similar to this method. Compounds **8m**–**8o** were isolated using preparative TLC [eluting solvent: ethyl acetate/ petroleum ether = 1/5 (v/v)] and the yields are listed in **Table 4**.

General procedure for the synthesis of 9a

Phenylacetylene (0.06 g, 0.6 mmol) was added to EtOH (1 mL), HCP–NHC–Cu **III** (10 mg, 0.0011 mmol), and tetramethylethylenediamine (0.035 g, 0.3 mmol). Then, the mixture was stirred at 80 °C for 8 h under the precaution of oxygen. After reaction completion, the mixture was centrifuged, and all organic phases were combined and concentrated under reduced pressure. The white product **9a** was obtained in 99% yield (0.60 g).

General procedure for the synthesis of 10a

A mixture of indole (0.06 g, 0.5 mmol), 1-iodo-4-methoxybenzene (0.12 g, 0.5 mmol), K_2CO_3 (0.14 g, 1.0 mmol), HCP–NHC–Cu **III** (24 mg, 0.0026 mmol), and DMSO (1.5 mL) was stirred at 120 °C for 10 h. After reaction completion, the mixture was cooled to room temperature, and the product was obtained by isolation under preparative TLC [eluting solution: petroleum ether/ethyl acetate = 5/1 (v/v)] with 93% of yield (0.10 g).

General procedure for the recycle the catalyst

To test the recyclability of HCP–NHC–Cu **III** catalyst, the mixture of reaction system was filtrated at the end of the reaction. The obtained solid catalyst was washed with ethanol (2.0 mL × 4). After 12 h of drying under vacuum at 60 °C, the catalyst was subjected to the next run. The procedure for the reuse of the catalyst in the other reactions is similar to this method.

Acknowledgements

The authors thank for National Natural Science Foundation of China for the financial support (21373093, 21474033, 21473064, and 51273074) and also for the Analytical and Testing Center of HUST. Chutian Scholar Program of the Hubei Provincial Government and the Cooperative Innovation Center of Hubei Province are also acknowledged. This work is also supported by the Fundamental Research Funds for the Central Universities of China (2014ZZGH019).

References

1 C. M. A. Parlett, K. Wilson and A. F. Lee, *Chem. Soc. Rev.*, 2013, **42**, 3876–3893.

2 (a) R. Dawson, E. Stöckel, J. R. Holst, D. J. Adams and A. I. Cooper, *Energy Environ. Sci.*, 2011, **4**, 4239–4245; (b) Z. Chang, D. Zhang, Q. Chen and X. Bu, *Phys. Chem. Chem. Phys.*, 2013, **15**, 5430–5442; (c) R. Dawson, A. I. Cooper and D. J. Adams, *Polym Int.*, 2013, **62**, 345–352; (d) A. Thomas, *Angew. Chem. Int. Ed.*, 2010, **49**, 8328–8344; (e) S. Ding and W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 548–568; (f) L. Zhu, Q. Gao, Y. Tan, W. Tian, J. Xu, K. Yang and C. Yang, *Micropor. Mesopor. Mater.*, 2015, **210**, 1–9.

3 C. Zlotea, Y. Oumellal, S. Hwang, C. M. Ghimbeu, P. E. de Jongh and M. Latroche, *J. Phys. Chem. C*, 2015, **119**, 18091–18098.

4 J. E. Schmidt, D. Xie and M. E. Davis, *Chem. Sci.*, 2015, **6**, 5955–5963.

5 C. Knöel, J. Descarpentries, A. Benzaouia, V. Zeleňák, S. Mornet, P. L. Llewellyn and V. Hornebecq, *Micropor. Mesopor. Mater.*, 2007, **99**, 79–85.

6 J. Liu, L. Chen, H. cui, J. Zhang, L. Zhang and C. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011–6061.

7 W. Lee, H. Chien, Y. Lo, H. Chiu, T. Wang and D. Kang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 18353–18361.

8 J. Rathore, Q. Dai, B. Davis, M. Sherwood, R. D. Miller, Q. Lin and A. Nelson, *J. Mater. Chem.*, 2011, **21**, 14254–14258.

9 A. I. Cooper, *Angew. Chem. Int. Ed.*, 2011, **50**, 996–998.

10 A. I. Cooper, *Adv. Mater.*, 2009, **21**, 1291–1295.

11 (a) M. Jiang, Q. Wang, Q. Chen, X. Hub, X. Ren, Z. Li and B. Han, *Polymer*, 2013, **54**, 2952–2957; (b) V. Hanková, E. Slováková, J. Zedník, J. Vohlídal, R. Sivkova, H. Balcar, A. Zukal, J. Brus and J. Sedlček, *Macromol. Rapid Commun.*, 2012, **33**, 158–163; (c) L. Sun, Y. Zou, Z. Liang, J. Yu and R. Xu, *Polym. Chem.*, 2014, **5**, 471–478; (d) H. Li, Z. Li, Y. Zhang, X. Luo, H. Xia, X. Liu and Y. Mua, *RSC Adv.*, 2014, **4**, 37767–37772; (e) Z. Yang, Y. Zhao, H. Zhang, B. Yu, Z. Ma, G. Ji and Z. Liu, *Chem. Common.*, 2014, **50**, 13910–13913; (f) L. Sun, Z. Liang, J. Yu and R. Xu, *Polym. Chem.*, 2013, **4**, 1932–1938.

12 (a) S. Xu, Y. Luo and B. Tan, *Macromol. Rapid Commun.*, 2013, **34**, 471–484; (b) R. Dawson, A. I. Cooper and D. J. Adams, *Prog. Polym. Sci.*, 2012, **37**, 530–563.

13 B. Li, Z. Guan, W. Wang, X. Yang, J. Hu, B. Tan and Tao Li, *Adv. Mater.*, 2012, **24**, 3390–3395.

14 (a) S. N. Sluijter, L. J. Jongkind and C. J. Elsevier, *Eur. J. Inorg. Chem.*, 2015, 2948–2955; (b) G. Lázaro, F. J. Fernández-Alvarez, J. Munárriz, V. Polo, M. Iglesias, J. J. Pérez-Torrentea and L. A. Oro, *Catal. Sci. Technol.*, 2015, **5**, 1878–1887; (c) A. P. Prakasham and P. Ghosh, *Inorganica Chimica. Acta.*, 2015, **431**, 61–100; (d) E. Kim, J. Jang and J. S. Chung, *Macromol. Res.*, 2014, **22**, 864–869; (e) A. Cavarzan, J. N. H. Reek, F. Trentin, A. Scarso and G. Strukul, *Catal. Sci. Technol.*, 2013, **3**, 2898–2901; (f) E. F. Dunn, D. Liu and E. Y. Chen, *Appl. Catal. A: General*, 2013, **1–7**, 460–461; (g) V. Gauchot, J. Gravel, M. Vidal, M. Charbonneau, V. Kairouz and A. R. Schmitzer, *Synlett*, 2015, **26**, 2763–2779.

15 (a) K. V. S. Ranganath, S. Onitsuka, A. K. Kumarc and J. Inanaga, *Catal. Sci. Technol.*, 2013, **3**, 2161–2181; (b) M. Rose, A. Notzon, M. Heitbaum, G. Nickerl, S. Paasch, E. Brunner, F. Glorius and S. Kaskael, *Chem. Commun.*, 2011, **47**, 4814–4816; (c) S. Würtz and F. Glorius, *Acc. Chem. Res.*, 2008, **41**, 1523–1533; (d) S. Díez-Gonz lez, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612–3676; (e) T. Dröge and F. Glorius, *Angew. Chem., Int. Ed.*, 2010, **49**, 6940–6952.

16 (a) K. Garcés, F. J. Fernández-Alvarez, P. García-Orduña, F. J. Lahoz, J. J. Pérez-Torrente and L. A. Oro, *ChemCatChem*, 2015, **7**, 2501–2507; (b) J. A. M. Torre and A. C. Albéniz, *ChemCatChem*, 2014, **6**, 3547-3552; (c) B. Karimi and P. Fadavi Akhavan, *Inorg. Chem.*, 2011, **50**, 6063–6072; (d) M. Ghiaci, M. Zarghani, A. Khojastehnezhad and F. Moeinpour, *RSC Adv.*, 2014, **4**, 15496–15501; (e) B. Tamami, F. Farjadian, S. Ghasemi and H. Allahyari, *New J. Chem.*, 2013, **37**, 2011–2018; (f) H. Yoon, J. Choi, H. Kang, T. Kang, S. Lee, B. Jun and Y. Lee, Synlett, 2010, 2518–2522; (g) J. –M. Collinson, J. D. E. T. Wilton-Ely and S. Díez-Gonzaíez, *Chem. Commun.*, 2013, **49**, 11358–11360; (h) P. Liu, J. Yang, P. Li, L. Wang, *Appl.*

View Article Online
DOI: 10.1039/C5CY02260F

Organometal. Chem., 2011, **25**, 830–835; (i) P. Li, L. Wang, Y. Zhang, *Tetrahedron*, 2008, **64**, 10825–10830.

17 N. B. Jokića, C. S. Straubinger, S. L. M. Goh, E. Herdtweck, W. A. Herrmann and F. E. Kuhn, *Inorg. Chim. Acta*, 2010, **363**, 4181–4188.

18 D. Iglesias, S. Sabater, A. Azuaab and J. A. Mata, *New J. Chem.*, 2015, **39**, 6347–6444.

19 Y. Yang, and R. M. Rioux, *Green Chem.*, 2014, **16**, 3916–3925.

20 S. Xu, K. Song, Tao Li and B. Tan, *J. Mater. Chem. A,* 2015, **3**, 1272–1278.

21 (a) C. Zhang, C. Tang and N. Jiao, *Chem. Soc. Rev.*, 2012, **41**, 3464–3484; (b) C. Sambiagio, S. P. Marsden, A. J. Blacker and P. C. McGowan, *Chem. Soc. Rev.*, 2014, **43**, 3525–3550; (c) P. Subramanian, G. C. Rudolf and K. P. Kaliappan, *Chem. Asian J.*, 2015, DOI: 10.1002/asia.201500361; (d) H. Zhang, X. Zhang, D. Dong and Z. Wang, *RSC Adv.*, 2015, **5**, 52824–52831.

22 (a) M. Meldal and C. W. Tornøe, *Chem. Rev.*, 2008, **108**, 2952–3015; (b) E. Haldón, M. C. Nicasio and P. J. Pérez, *Org. Biomol. Chem.*, 2015, **13**, 9528–9550; (c) S. Acherar, L. Colombeau, C. Frochot and R. Vanderesse, *Current Medic. Chem.*, 2015, **22**, 3217–3254; (d) B. S. Rana, S. L. Jain, B. Singh, A. Bhaumik, B. Sainb and A. K. Sinha, *Dalton Trans.*, 2010, **39**, 7760–7767; (e) J. Gierlich, G. A. Burley, P. M. E. Gramlich, D. M. Hammond and T. Carell, *Org. Lett.*, 2006, **17**, 3639–3642.

23 (a) D. K. T. Yadav, S. S. Rajak and B. M. Bhanage, *Tetrahedron Lett.*, 2014, **55**, 931–935; (b) D. Talukdar, G. Das, S. Thakur, N. Karaka and A. J. Thakur, *Catal. Commum.*, 2015, **59**, 238–243; (c) A. C. Bissember, R. J. Lundgren, S. E. Creutz, J. C. Peters, and G. C. Fu, *Angew. Chem. Int. Ed.*, 2013, **52**, 5129–5133; (d) D. T. Ziegler, J. Choi, J. Muñoz-Molina, A. C. Bissember, J. C. Peters and G. C. Fu, *J. Am. Chem. Soc.*, 2013, **135**, 13107–13112; (e) K. Pericherla, A. Jha, B. Khungar and A. Kumar, *Org. Lett.*, 2013, **17**, 4304–4307; (f) J. Kim, S. Park, J. Park and S. H. Cho, *Angew. Chem. Int. Ed.*, 2015, **54**, 1–5; (g) F. Calogero, P. Allegrini, E. Attolino and D. Passarella, *Eur. J. Org. Chem.*, 2015, 6011–6016; (g) R. R. Donthiri, S. Samanta and S. Adimurthy, *Org. Biomol. Chem.*, 2015, **13**, 10113–10116.

24 F. Lazreg, F. Nahra and C. S. J. Cazin, *Coord. Chem. Rev.*, 2015, **293–294**, 48–79.

25 Y. Yuan, W. Cao and W. Weng, *J. Catal*., 2004, *228*, 311–320.

26 (a) M. Li, A. Taheri, M. Liu, S. Sun and Y. Gu, *Adv. Synth. Catal*., 2014, **356**, 537–556; (b) M. Li, B. Zhang and Y. Gu; *Green Chem*., 2012, **14**, 2421–2428; (c) X. Pan, M. Li and Y. Gu, *Chem. Asian J.*, 2014, **9**, 268–274; (d) D. Jiang, X. Pan, M. Li and Y. Gu, *ACS Comb. Sci*., 2014, **16**, 652–660; (e) S. Sun, C. Cheng, J. Yang, A. Taheri, B. Zhang and Y. Gu, *Org. Lett*., 2014, **16**, 4520–4523; (f) L. Min, P. Pan, and Y. Gu, *Org. Lett*. 2016, DOI: 10.1021/acs.orglett.5b03287; (g) C. Liu, L. Zhou, D. Jiang, and Y. Gu, *Asian J. Org. Chem.* 2016, DOI: 10.1002/ajoc.201500497; (h) A. Taheri, B. Lai, C. Cheng, and Y. Gu, *Green Chem*. 2015, **17**, 812–816; (i) K. Zeng, Z. Huang, J. Yang, Y. Gu, *Chin. J. Catal.* 2015, **36**, 1606-1613; (j) B. Lai, Z. Huang, Z. Jia, R. Bai, and Y. Gu, *Catal. Sci. Technol*. 2016, DOI: 10.1039/C5CY01012h.

27 (a) Y. Gu, *Green Chem*., 2012, **14**, 2091-2028; (b) M. Shiri, *Chem. Rev*., 2012, **112**, 3508–3549; (c) N. R. Candeias, F. Montalbano, P. M. S. D. Cal and P. M. P. Gois, *Chem. Rev.*, 2010, **110**, 6169–6193; (d) S. Brauch, S. S. Berkela and B. Westermann, *Chem. Soc. Rev.*, 2013, **42**, 4948–4962; (e) S. Klaus, S. Hübner, H. Neumann, D. Strübing, A. J. Wangelin, D. Gördes and M. Beller, *Adv. Synth. Catal.*, 2004, **346**, 970–978.

28 Y. Wang, J. Liu and C. Xia, *Adv. Synth. Catal*., 2011, **353**, 1534–1542.

29 (a) Z. Zhuang, J. –M. Chen, F. Pan and W. –W. Liao, *Org. Lett.*, 2012, **14**, 2354–2357; (b) S. Ahmar, E. Fillion, *Org. Lett*., 2014, **16**, 5748–5751; (c) A. M. Dumas and E. Fillion, *Org. Lett.*, 2009, **11**, 1919–1922; (d) A. Wilsily and E. Fillion, *Org. Lett.*, 2008, **10**, 2801–2804.

30 (a) Z. He, B. Wibbeling and A. Studer, *Adv. Synth. Catal*., 2013, **355**, 3639–3647; (b) N. Gigant, F. Quintin and J. -E. Baeckvall, *J. Org. Chem.*, 2015, **80**, 2796–2803; (c) H. Nakatsuji, Y. Ashida, H. Hori, Y. Sato, A. Honda, M. Taira and Y. Tanabe, *Org. Biomol. Chem.,* 2015, **13**, 8205–8210; (d) H. S. Lee, K. H. Kim, S. H. Kim and J. N. Kim, *Adv. Synth. Catal*., 2012, **354**, 2419–2426; (e) K. Endo, M. Hirokami and T. Shibata, *J. Org. Chem.*, 2010, **75**, 3469–3472; (f) J. Ruan, X. Li, O. Saidi and J. Xiao, *J. Am. Chem. Soc.*, 2008, **130**, 2424–2425.

31 W. Gao, Z. He, Y. Qian, J. Zhao and Y. Huang, *Chem. Sci*., 2012, **3**, 883–886.

32 R. M. Bodina, T. N. Lyamina, E. S. Lipina, V. V. Perekalin, *Metody Sinteza, Stroenie i Khim. Prevrashcheniya Nitgrosoed. i Aminokislot., L.,* 1989, 45-50.

33 S. C. Airy. C. Martin and J. M. Sullivan, *J. Org. Chem*., 1979, **44**, 1891-1892.

34 F. Amblard, J. H. Cho and R. F. Schinazi, *Chem. Rev*., 2009, **109**, 4207–4220.

35 (a) J. E. Moses and A. D. Moorhouse, *Chem. Soc. Rev.,* 2007, **36**, 1249–1262; (b) L. Ackermann, H. K. Potukuchi, D. Landsberg and R. Vicente, *Org. Lett.*, 2008, **10**, 3081–3084; (c) W. Zhang, X. He, B. Ren, Y. Jiang and Z. Hu, *Tetrahedron Lett.*, 2015, **56**, 2472–2475; (d) W. Wang, J. Wu, C. Xia and F. Li, *Green Chem*., 2011, **13**, 9528–3445.

36 (a) R. B. N. Baig and R. S. Varma, *Green Chem.*, 2013, **15**, 398–417; (b) A. Pourjavadi, S. H. Hosseini, F. M. Moghaddam and S. E. Ayati, *RSC Adv.*, 2015, **5**, 29609–29617; (c) A. Pourjavadi, M. Tajbakhsh, M. Farhangb and S. H. Hosseinia, *New J. Chem.*, 2015, **39**, 4591–4600; (d) F. Moghaddam and S. Ebrahim Ayati, *RSC Adv.*, 2015, **5**, 3894–3902; (e) R. Mirsafaei, M. M. Heravi, S. Ahmadi, M. H. Moslemin and T. Hosseinnejad, *J. Mol. Catal. A: Chem.*, 2015, **402**, 100–108; (f) Y. Monguchi, K. Nozaki, T. Maejima, Y. Shimoda, Y. Sawama, Y. Kitamura, Y. Kitadeb and H. Sajiki, *Green Chem.*, 2013, **15**, 490–495; (g) O. S. Taskin, S. Dadashi-Silab, B. Kiskan, J. Weber and Y. Yagci, *Macromol. Chem. Phys.,* 2015, **216**, 1746−1753; (h) Z. Xu, L. Han, G. Zhuang, J. Bai and D. Sun, *Inorg. Chem.*, 2015, **54**, 4737–4743; (i) B. Movassagh and N. Rezaei, *Tetrahedron*, 2014, **70**, 8885–8892; (j) H. Sharghi, M. S. Beyzavi, A. Safavi, M. M. Doroodmand and R. Khalifeh, *Adv. Synth. Catal.*, 2009, **351**, 2391–2410; (k) B. Dervaux and F. E. Du Prez, *Chem. Sci.*, 2012, **3**, 959–966; (l) F. Alonso, Y. Moglie, G. Radivoy and M. Yus, *Adv. Synth. Catal.*, 2010, **352**, 3208–3214; (m) A. Megia-Fernandez, M. Ortega-Munoz, J. Lopez-Jaramillo, F. Hernandez-Mateo and F. Santoyo-Gonzalez, *Adv. Synth. Catal.*, 2010, **352**, 3306–3320; (n) Z. Zhang, C. Dong, C. Yang, D. Hu, J. Long, L. Wang, H. Li, Y. Chen and D. Kong, *Adv. Synth. Catal.*, 2010, **352**, 1600–1604; (o) H. Sharghi, R. Khalifeh and M. M. Doroodmand, *Adv. Synth. Catal.*, 2009, **351**, 207–218; (p) R. B. N. Baig and R. S. Varma, *Green Chem.*, 2013, **15**, 398–417; (q) L. Jiang, Z. Wang, S. Bai and T. S. A. Hor, *Dalton Trans.*, 2013, **42**, 9437–9443; (r) H. M. Lima and C. J. Lovely, *Org. Lett.*, 2011, **13**, 5736–5739.

37 S. Sun, R. Bai and Y. Gu, *Chem. Eur. J.*, 2014, **20**, 549–558.

38 (a) K. Yin, C. Li, J. Li and X. Jia, *Green Chem.*, 2011, **13**, 591–593; (b) J. S. Lampkowaski, C. E. Durhanm, M. S. Padilla, D. D. Young, *Org. Biomol. Chem.*, 2015, **13**, 424–427; (c) M. Kitchin, K. Konstas, C. J. Sumby, M. L. Czyz, P. Valente, M. K. Hill, A. Polyzos and C. J. Doonan, *Chem. Commun.*, 2015, **51**, 14231–14234.

39 (a) Q. Sun, Z. Lv, Y. Du, Q. Wu, L. Wang, L. Zhu, X. Meng, W. Chen and F. Xiao, *Chem. Asian J.*, 2013, **8**, 2822–2827; (b) Y. He and C. Cai, *Catal. Sci. Technol.*, 2012, **2**, 1126–1129.

40 M. Nasr-Esfahani, I. Mohammadpoor-Baltork, A. R. Khosropour, M. Moghadam, V. Mirkhani, S. Tangestaninejad,

View Article Online
DOI: 10.1039/C5CY02260F

V. Agabekovb and H. A. Rudbaria, *RSC Adv.*, 2014, **4**, 14291–14296

41 R. Xiao, R. Yao and M. Cai, *Eur. J. Org. Chem.*, 2012, 4178–4184.

42 H. M. Lima and C. J. Lovely, *Org. Lett.*, 2011, **13**, 5736–5739.

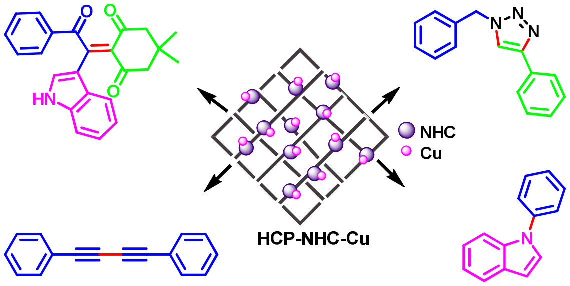
View Article Online
DOI: 10.1039/C5CY02260F

For Table of Contents Use Only

Functionalized hypercrosslinked polymers with knitted N-heterocyclic carbene–copper complexes as efficient and recyclable catalysts for organic transformations

Zhifang Jia, Kewei Wang, Tao Li, Bien Tan, and Yanlong Gu

Graphic Abstract



An *N*-heterocyclic carbene –copper complex supported on hypercrosslinked polymers was synthesized through a simple external cross-linking reaction and characterized by spectroscopic methods, which displayed very good catalytic activity in many organic reactions.