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At the Copper, Coppercabana: Stable, porous polymer-attached phenanthrolines were successfully prepared from solvothermal copolymerization of divinylbenzene with N-(1,10-phenanthrolin-5-yl)acrylamide (PCP-Phen). After coordination with copper species, a heterogeneous copper catalyst



was obtained that displayed a higher activity in Glaser and Huisgen couplings than commonly used homogeneous and nonporous polystyrene-supported copper catalysts. The copper catalyst has excellent recyclability due to the strong coordination ability of phenanthrolines.

Supported Catalysts

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Abstract: A family of polymer-attached phenanthrolines was prepared from solvothermal copolymerization of divinylbenzene with N-(1,10-phenanthroline-5-yl)acrylamide in different ratios. The polymer-supported copper catalysts were obtained through typical impregnation with copper(II) salts. The polymers and supported copper catalysts have been characterized by N₂ adsortion, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetric analysis (TG); they exhibit a high surface area, hierarchical porosity, large pore volume, and high thermal and chemical stabilities. The copper catalyst has proved to be highly active for Glaser homocoupling of alkynes and Huisgen 1,3-diolar cycloaddition of alkynes with benzyl azide under mild conditions at low catalyst loading. The

Keywords: copper • Glaser coupling • heterogeneous catalysis • Huisgen 1,3-dipolar cycloaddition • phenanthroline ligand • polymers heterogeneous copper catalyst is more active than commonly used homogeneous and nonporous polystyrene-supported copper catalysts. In particular, the catalyst is easily recovered and can be recycled at least ten times without any obvious loss in catalytic activity. Metal leaching was prevented due to the strong binding ability of phenanthroline and products were not contaminated with copper, as determined by ICP analysis.

Introduction

Transition-metal-catalyzed carbon-carbon and carbon-heteroatom bond-forming reactions have been pivotal in current organic synthesis as well as in pharmaceutical and material sciences.^[1] Among the metal-catalyzed transformations, copper-mediated reactions have been attracting continuous attention over the last two decades due to the low cost and low toxicity of copper compared to noble metal catalysts.^[2] However, the copper-catalyzed transformation involving carbon-carbon and carbon-heteroatom bond formation usually requires harsh reaction conditions (e.g., high temperature, large amount of copper catalyst). Therefore, the development of more versatile and efficient copper/ ligand systems for the formation of carbon-carbon and

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201300690.

carbon-heteroatom bonds under relatively mild conditions is important.^[3] Although copper-based homogenous catalysts show good activity and selectivity, the difficulties of their separation from the products and the reusability of the catalysts restrict their wide applications. Copper-based heterogeneous catalysts can be easily separated from the reaction system, but usually they have a lower activity. Because conventional inorganic supports such as silica-based materials usually show low wettability to organic reactants and organic supports such as polystyrene have a low degree of active sites due to their low surface area,^[4] the development of catalytically active and recyclable copper-based heterogeneous catalysts is still a challenge.

Recently, we have reported a series of unique and stable porous cross-linked polymers (PCPs) featuring a high surface area, hierarchical porosity, large pore volume, high thermal and chemical stabilities, and easy introduction of organic ligands.^[5] Phenanthroline (Phen) has a strong coordination ability towards copper and an excellent activity in many copper-catalyzed reactions;^[6] thus, PCPs incorporating Phen may constitute good polymeric ligands that combine the advantages of low leaching of metals and recyclability. Herein, we describe the synthesis of porous PCP-Phen and the corresponding polymer-supported copper catalyst, which possesses an excellent catalytic activity and recyclability in Glaser coupling and Huisgen cycloaddition reactions.

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Results and Discussion

N-(1,10-Phenanthroline-5-yl)acrylamide (Phen-MA) was easily obtained from 1,10-phenanthroline through nitration, reduction, and amidation, as depicted in Scheme 1. Co-poly-



Scheme 1. Synthesis of PCP-Phen-Cu catalyst.

merization of N-(1,10-phenanthroline-5-yl)acrylamide with divinylbenzene (DVB) under solvothermal conditions afforded the copolymer of DVB and Phen-MA. Variation of the mass ratio (x) of Phen-MA and DVB gave PCP-x-Phen with different surface areas, pore volumes, and pore size distributions (Table S1, Supporting Information). When the Phen-MA/DVB ratio was 1:4, the co-polymer had a high surface area (574 m²g⁻¹), a large pore volume (0.72 cm³g⁻¹), and a large pore size (average BJH pore size of ca. 10.8 nm). Therefore, PCP-1/4-Phen prepared from Phen-MA and DVB at ratio of 1:4 (henceforth abbreviated as PCP-Phen) was selected as the catalyst support for subsequent studies. The polymer-supported copper catalyst was obtained through the reaction of PCP-Phen with Cu- $(CH_3COO)_2$ ·H₂O in an acetone/water mixture (1:1 v/v), and PCP-Phen-Cu was obtained after washing and drying.

Next, PCP-Phen and PCP-Phen-Cu were characterized. Figure 1 shows that PCP-Phen-Cu exhibits a uniform distribution of C, N, and Cu. The results suggest that PCP-Phen is a copolymer rather than a mixture of polydivinylbenzene and polymerized Phen-MA and that the dispersion of Cu species is uniform. Thermographic analysis of PCP-Phen shows that there is no weight loss below 300 °C (Figure S1, Supporting Information) suggesting its good thermal stability. Figure 2A shows the N₂ adsorption-desorption isotherms of PCP-Phen and PCP-Phen-Cu samples. Both PCP-Phen and PCP-Phen-Cu exhibit a typical type-IV plus type I behavior. The steep increase that occurs in the relative pressure less than 0.01 is due to the filling of micropores, and the hysteresis loop that appears at a relative pressure of 0.45-0.90 is assigned to the presence of mesoporosity in the samples. These results indicate that PCP-Phen-Cu also has a high surface area $(542 \text{ m}^2 \text{g}^{-1})$, as well as a large pore volume (0.41 cm³g⁻¹) and pore size (average BJH pore size



Figure 1. (A) Representative SEM image of PCP-Phen-Cu. (B–D) C, N, and Cu elemental mapping in the area marked by the rectangle in panel a. Scale bars, $60 \ \mu m$.



Figure 2. (A) N_2 adsorption–desorption isotherms. (B) Pore size distributions of PCP-Phen (a) and PCP-Phen-Cu (b) samples. For the latter, isotherms in (A) have been offset by 200 cm³g⁻¹. (C, D) SEM images of PCP-Phen (C) and PCP-Phen-Cu (D). TEM images of PCP- Phen (E) and PCP-Phen-Cu (F).

of ca. 7.5 nm) (Figure 2B and the Supporting Information, Figure S2 and Table S1). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of PCP-Phen and PCP-Phen-Cu samples are shown in Figure 2C-2F, and they provide direct evidence of hierarchical porosity. The N 1s XPS (X-ray photoelectron spectroscopy) spectra of PCP-Phen and PCP-Phen-Cu are shown in Figure 3. PCP-Phen shows a binding energy at 399.4 eV, and PCP-Phen-Cu exhibits a relatively high binding energy at

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Figure 3. N 1s XPS spectra of PCP-Phen (a) and PCP-Phen-Cu (b).

400.2 eV. Obviously, the higher binding energy of PCP-Phen-Cu originates from the strong coordination of copper species to Phen.^[7] The molar ratio of Phen:Cu is 1.07 in the PCP-Phen-Cu sample according to elemental and inductively coupled plasma analyses.

Diyne derivatives are a very important class of compounds used as key structural elements in natural product synthesis and material science.^[8] We examined the catalytic activity of PCP-Phen-Cu for oxidative homocouplings of alkynes. For comparision, a variety of other copper-based catalysts were also studied under the same conditions, and the results are summarized in Table 1. Notably, PCP-Phen-Cu was highly active under oxygen atmosphere at 120 °C for the conversion of phenylacetylene giving 1,4-diphenyl-1,3-butadiyne in quantitative yield (Table 1, entry 1). Even under atmospheric air (entry 2) or at room temperature (entry 3), 1,4-diphenyl-1,3-butadiyne could also be obtained in nearly quantitative yields at an elongated reaction time. At a cata-

Table 1. Catalytic performance in oxidative homocoupling of phenylacetylene over various catalysts.^[a]

	2	} -≡-≡	₩ H ₂ O	
Entry	Catalyst	<i>t</i> [min]	Yield [%] ^[b]	TON
1	PCP-Phen-Cu	40	>99(97)	40
2 ^[c]	PCP-Phen-Cu	240	>99	40
3 ^[d]	PCP-Phen-Cu	1080	>99	40
4 ^[e]	PCP-Phen-Cu	1440	93	930
5 ^[f]	PCP-Phen-Cu	180	2.7	1.1
6	PS-Phen-Cu	1440	32	320
7 ^[g]	Cu-Y zeolite	900	97	3.3
8 ^[h]	Cu-HPA	1080	93	468
9 ^[i]	Cu(OH) _x /TiO ₂	30	90	9
10 ^[j]	Cu(OH) _x /OMS-2	10	94	666
$11^{[k]}$	CuNP/TiO ₂	240	>99	100
12	Cu-MCM-41	180	<1	< 0.4
13	Cu(OAc) ₂ ·H ₂ O	180	18	7.3
14	CuI	180	31	10
15 ^[1]	Phen + $Cu(OAc)_2 \cdot H_2O$	30	>99	40
16 ^[m]	Phen + $Cu(OAc)_2 \cdot H_2O$	1440	67	670

[a] Reaction conditions: alkyne (1 mmol), DMF (4 mL), Cu catalyst (2.5 mol%), 120 °C, and 1 atm of O₂. [b] GC yield (isolated yield). [c] In air. [d] At room temperature. [e] Phenylacetylene (5 mmol) and Cu (0.5 mol%). [f] In N₂. [g] Ref. [9a]. [h] Ref. [9b]. [i] Ref. [9c]. [j] Ref. [9d]. [k] Ref. [9e]. [l] Cu(OAc)₂·H₂O (2.5 mol%) and 1,10-phenanthroline (2.5 mol%) were used as the catalyst. [m] Phenylacetylene (5 mmol), Cu (0.5 mol%) and 1,10-phenanthroline (0.5 mol%).

lyst loading of 0.1 mol%, the turnover number (TON) reached up to 930 (entry 4). To the best of our knowledge, this TON is the highest among those known heterogeneous copper-based catalysts.^[9] For comparison, a polystyrenephen (PS-Phen)-supported copper catalyst showed much lower activity for the oxidative coupling of phenylacetylene (entry 6). The polystyrene used has a low surface area of less than $1 \text{ m}^2 \text{g}^{-1}$. These results suggest that the surface area of the catalysts may play an important role in determining the efficiency of the catalysts.

The PCP-Phen-Cu catalyst can be easily recovered by filtration after the reaction. The recovered catalyst can be reused at least ten times without any obvious loss in activity (Table 2). Meanwhile, no copper species could be detected in the filtrate by ICP analysis, thus suggesting that the heterogeneous catalyst is very stable with no detectable copper leaching.

Table 2. Recycling of PCP-Phen-Cu in the oxidative homocoupling of $\ensuremath{\mathsf{phenylacetylene}}.^{[a]}$

Cycle	1	2	3	4	5	6	7	8	9	10
Yield(%) ^[b]	99	99	99	99	98	99	97	98	97	97

[a] Reaction conditions: alkyne (1 mmol), DMF (4 mL), PCP-Phen-Cu (2.5 mol%), 1 atm of O_2 , 120 °C, 40 min. [b] GC yield.

Encouraged by the results described above, we extended the homocouplings catalyzed by PCP-Phen-Cu to other alkynes, and the results are presented in Table 3. The results show that the PCP-Phen-Cu catalyst is highly active for homocouplings of a variety of alkynes. The reactions of aromatic alkynes could be completed within 40 minutes, affording the corresponding diynes in nearly quantitative yields. Terminal aliphatic alkynes could also be oxidized to the cor-

Table 3. Oxidative homocouplings of alkynes under various reaction conditions. $^{\left[a\right] }$

$2 R \longrightarrow R \longrightarrow R$									
Entry	R	Solvent	$T[^{\circ}C]$	<i>t</i> [min]	Yield [%] ^[b]				
1	p-Methyl-phenyl	DMF	120	40	>99(97)				
2	p-Anisole	DMF	120	40	>99(96)				
3	m-Methyl-phenyl	DMF	120	40	>99(95)				
4	1-Hydroxycyclohexyl	DMF	120	180	>94(85)				
5	Butyl	DMF	120	180	98(95)				
6	Heptane	DMF	120	180	95(91)				
7	Ph	DMF	120	40	>99				
8	Ph	DMF	100	60	>99				
9	Ph	DMF	80	150	>99				
10	Ph	DMF	60	480	>99				
11	Ph	DMSO	120	40	89				
12	Ph	NMP	120	40	62				
13	Ph	benzonitrile	120	40	87				
14	Ph	acetonitrile	85	40	3				
15	Ph	toluene	110	40	<1				
16	Ph	1,4-dioxane	110	40	<1				
17	Ph	H_2O	120	180	37				
18	Ph	H_2O	RT	180	2.5				

[a] Reaction conditions: alkyne (1 mmol), solvent (4 mL), PCP-Phen-Cu (2.5 mol%), O₂ (1 atm). [b] GC yield (isolated yield).

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responding diynes, but they are relatively inert and thus required longer reaction times (entries 4–6). In addition, the results show that increased temperatures can accelerate the reaction (entries 7–10). Moreover, the effect of solvents shows that polar aprotic solvents such as N,N-dimethylformamide (DMF) are more suitable for the reactions (entries 11–18).

We observed that during the reaction the color of the PCP-Phen-Cu catalyst changed from dark green to brown within about 4 minutes and then turned back to dark green after about 40 minutes when phenylacetylene was nearly completely converted (Figure S3 in the Supporting Information). The color change might correspond to the change of the chemical state of the copper species,^[9b] and we characterized this change of PCP-Phen-Cu by XPS and ESR spectroscopies. The dark green PCP-Phen-Cu shows a binding energy of Cu $2p_{3/2}$ at 935.5 eV with a satellite peak at 943.3 eV (Figure 4A), thereby indicating that the oxidation



Figure 4. (A) XPS and (B) ESR spectra of fresh catalyst (a), the brown catalyst in the reaction (b), and the catalyst after the reaction (c).

state of the copper species is +2. The brown catalyst formed during the reaction exhibits a binding energy of Cu $2p_{3/2}$ at 933.9 eV without any satellite peaks, thus indicating that the chemical state of Cu has changed. When the reaction was finished, the catalyst became dark green again, indicating that the chemical state of copper species returned to +2.^[10] ESR spectroscopy (Figure 4B) revealed that both dark-green catalysts had characteristic ESR signals associated with Cu²⁺ species with *g*-values at about 2.2, while the brown one was ESR-inactive associated with Cu⁺ species.^[11]

Notably, when the reactions were carried out under N_2 atmosphere, the color change of the catalyst from dark green to brown was also very fast (ca. 4 min), and the brown color remained unchanged even after a long reaction time (3 h), after which the yield of diyne was close to the catalyst amount. However, after introducing oxygen to the reaction, the color of the catalyst turned to dark green (ca. 40 min) again, and the yield of diyne almost reached 99%. When the brown catalyst was used in phenylacetylene coupling, no diyne could be obtained. These results imply that the reduction of Cu^{2+} to Cu^{+} species by alkynes and re-oxidation of Cu^{+} to Cu^{2+} species by oxygen are involved in the catalytic cycles.

The copper-catalyzed azide–alkyne cycloaddition discovered by Melda and Sharpless has attracted much attention due to its wide applications for synthesizing fine chemicals, pharmaceuticals, and functional materials,^[12] where Cu⁺ species are catalytically active.^[13] As PCP-Phen-Cu is reduced to a Cu⁺ catalyst in the presence of alkynes, the PCP-Phen-Cu catalyst should be active for Huisgen couplings. Indeed, we found that PCP-Phen-Cu is quite efficient for azide– alkyne cycloaddition of various alkynes (Table 4), even

Table 4. Azide-alkyne cycloaddition reactions over PCP-Phen-Cu catalyst. $^{\left[a\right] }$

	$R \longrightarrow + PhCH_2N_3$		R N=N N-CI	H ₂ Ph
Entry	R	<i>t</i> [min]	Yielid [%] ^[b]	$TOF[h^{-1}]$
1	Ph	40	99	2970
2	m-Methyl-phenyl	40	98	2940
3	p-Methyl-phenyl	40	99	2970
4	<i>p</i> -Anisole	40	97	2910
5	1-Hydroxycyclohexl	80	94	1410
6	Heptane	100	97	1164
7	Butyl	100	93	1116

[a] Reaction conditions: alkynes (5.25 mmol), benzyl azide (5 mmol), PCP-Phen-Cu (0.05 mol%), water (5 mL), RT. [b] Isolated yield.

when 0.05 mol% of PCP-Phen-Cu was used. The reactions of benzyl azide and alkynes could be accomplished within 100 min, thereby affording the corresponding products in 93–99% yields (entry 1–10). For example, the cycloaddition of benzylazide and phenylacetylene yielded the tetrazole in almost quantitative yield within 40 min, and the TOF reached 2970 h⁻¹ (entry 1), which is higher than those of most of the reported heterogeneous catalysts.^[12s]

The PCP-Phen-Cu catalyst can also be easily recovered by filtration in azide–alkyne cycloadditions. The catalyst can be recycled at least ten times without an obvious loss in activity (Table 5). More importantly, copper species are undetectable in the isolated triazole. By contrast, when CuSO₄ and Cu/C were used as catalysts, the concentration of copper is as high as 399 and 76 μ gg⁻¹ in the product. This is probably because phenanthroline (log *K*=9.2) has a much stronger coordination ability than triazole (log *K*<2.5),^[14]

Table 5. Recycling of PCP-Phen-Cu in the cycloaddition of benzylazide and phenylacetylene. $^{\left[a\right] }$

Cycle	1	2	3	4	5	6	7	8	9	10
Yield (%) ^[b]	99	99	99	99	98	99	97	98	97	97

[a] Reaction conditions: alkyne 1 mmol, DMF 4 mL, PCP-Phen-Cu 2.5 mol %, 1 atm of O₂ and reaction at 120 °C for 40 min. [b] GC yield.

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thus preventing copper leaching. Obviously, this feature is very important for the industrial production of fine chemicals and pharmaceuticals by Huisgen 1,3-diolar cycloaddition of azide–alkyne.

Similar to the homocoupling of alkynes, the color of the catalyst changed from dark green to brown within 5 min due to the reduction of Cu²⁺ to Cu⁺ (Figure S4 in the Supporting Information), and trace amounts of 1,3-diyne derivatives were detected. After the color of the catalyst changed to brown, no more 1,3-divne derivatives were formed in the system, and the azide-alkyne cycloaddition dominated immediately. As a result, the 1,4-substituted-1,2,3-triazole product was obtained with a very high selectivity and a high yield. Table 6 presents the dependence of the catalyst loading and solvent on the cycloaddition of benzylazide and phenylacetylene. When 1.0 mol% of PCP-Phen-Cu was used in water, the reaction of phenylacetylene and benzyl azide was completed within 5 min (Table 6, entry 1). At the catalyst loading of 0.01 mol%, the reaction was completed when the reaction time was extended to 6 h (entry 4). For comparison, Cu(OAc)₂·H₂O and 1,10-phenanthroline in water resulted in a much lower conversion (8% yield at 20 min and 50% yield at 1.5 h, entries 6 and 7). These results indicate that PCP-Phen-Cu is highly active for azide-alkyne cycloaddition. The solvent screening experiments showed that alcohols are also better solvents than aprotic solvents (entries 8-12).

Table 6. The effects of the catalyst amount and solvents on the activities in cycloaddition of benzylazide and phenylacetylene over PCP-Phen-Cu catalyst.^[a]

	Ph — = + PhC	H ₂ N ₃ ——	→ Ph	N-CH ₂ Ph		
Entry	Catalyst [mol %]	Solvent	<i>t</i> [min]	Yield [%] ^[b]	TOF [h ⁻¹]	
1	1	H ₂ O	5	>99	1188	
2	0.1	H_2O	20	>99	2970	
3	0.05	H_2O	40	>99	2970	
4	0.01	H_2O	300	>99	1980	
5	0.005	H_2O	720	82	1367	
6 ^[c]	1	H_2O	20	8	24	
7 ^[c]	1	H_2O	90	50	33	
8	0.05	butanol	40	97	2910	
9	0.05	MeOH	40	96	2880	
10	0.05	acetonitrile	40	97	2910	
11	0.05	DMF	40	53	1590	
12	0.05	toluene	40	82	2460	

[a] Reaction conditions: phenylacetylene (5.25 mmol), benzylazide (5 mmol), solvent (5 mL), RT. [b] GC yield. [c] $Cu(OAc)_2$ ·H₂O (2.5 mol%) and 1,10-phenanthroline (2.5 mol%) were used.

Conclusions

In summary, a phenanthroline-functionalized polymer (PCP-Phen) with a high surface area, large pore volume, hierarchical porosity, and high thermal stability has been successfully synthesized from the copolymerization of Phen-MA and DVB. The PCP-Phen-supported copper catalyst shows an excellent catalytic activity in Glaser coupling and Huisgen cycloaddition reactions. The PCP-Phen-Cu catalyst is easily recovered and can be reused for at least ten times without any obvious loss in catalytic activity. The copper is tightly anchored to the polymeric support due to the strong binding ability of phenanthroline and thus product contamination arising from metal leaching is avoided.

Experimental Section

Synthesis of PCP with Phen Ligands

In a typical procedure, DVB (15 mmol, 2 g) and Phen-MA (2 mmol, 0.5 g) were dissolved in DMF (20 mL), followed by addition of azobisisobutyronitrile (AIBN, 0.05 g). After stirring for 3 h at room temperature, the mixture was transferred into an autoclave for 24 h at 100 °C. After extraction of the solvent with EtOH, a brown solid product was obtained, which was denoted as PCP-Phen.

Synthesis of the PCP-Phen-Cu Catalyst

The PCP-Phen-Cu catalyst was synthesized by reacting the PCP-Phen sample with copper acetate in an acetone/water mixture (1:1 v/v). The mixtures were stirred at room temperature for 24 h, filtered off, and washed with excessive amounts of the acetone/water mixture and water in order to remove physisorbed copper species. Subsequently, the catalyst was dried overnight in air at 90 °C to afford a dark green copper-supported catalyst, denoted as PCP-Phen-Cu. Inductively coupled plasma (ICP) analysis showed a Cu content of 3.2 wt % in the resultant sample.

Catalytic Tests

Glaser couplings. A terminal alkyne (1mmol), DMF (4mL), and PCP-Phen-Cu (2.5 mol%) were added to a Schlenk tube, sealed, and purged with O_2 for four times. After the reaction, the catalyst was removed from the system by centrifugation (5 min, 8000 rpm) and the solution was analyzed by gas chromatography (GC-1690 Kexiao Co., equipped with a flame ionization detector) on a flexible quartz capillary column coated with DB-1. In some cases, the diynes were isolated and purified by column chromatography on silica gel (200–300 mesh) using EtOAc/petroleum ether (1:10 v/v) as eluent. All products were confirmed by ¹H NMR spectroscopy.

Huisgen 1,3-diolar cycloaddition. A terminal alkyne (5.25 mmol), an azide (5.0 mmol), H₂O (5 mL), and PCP-Phen-Cu (0.05 mol%) were added to a Schlenk tube, followed by sealing. After the reaction, EtOAc (20 mL) was added and the catalyst was removed by centrifugation. The solution was then analyzed by gas chromatography. In some cases, the products were isolated and purified by column chromatography on silica gel (200-300 mesh) using EtOAc/petroleum ether (1:10 v/v) as eluent. All products were confirmed by ¹H NMR spectroscopy.

Acknowledgements

This work was supported by theNSFC (U1162201 and 21003107), the National High-Tech Research and Development program of China (2013AA065301), the Science and Technology Innovative Team of Zhejiang Province (No. 2012R10014-01), and the Fundamental Research Funds for the Central Universities (2013XZZX001).

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Received: May 21, 2013 Published online: ■■ ■, 0000