Supporting Information

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Recyclable Porous Polymer-Supported Copper Catalysts for Glaser and Huisgen 1,3-Diolar Cycloaddition Reactions


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Chemicals and Regents.

Solvents were purified according to standard laboratory methods. THF was distilled over sodium/benzophenone. DMF was distilled over calcium hydride. CHCl$_3$ was distilled over anhydrous CaCl$_2$. Alkynes were purchased from Sigma-Aldrich Company, Ltd. DVB, and azobisisobutyronitrile (AIBN), dodecane, TEOS, were obtained from Tianjin Guangfu Chemical Reagent. Ultrastable Y zeolite was supplied by Sinopec Catalyst Co. 1,10-Phenanthroline monohydrate, HNO$_3$, H$_2$SO$_4$, acetic anhydride, NaN$_3$, n-Butyllithium, aliquot of polystyrene (Cl content 1-1.24 mmol/g), various copper salts, α,α'-Dichloro-p-xylene, and 1-Bromihexadecane were purchased from Aladdin Company, Co. Ltd.

Sample Synthesis

Synthesis of 5-nitrophenanthroline

As a typical run, 10 mL concentrated nitric acid was added into 60 mL of cool acetic anhydride under stirring, followed by the addition of 1 mL concentrated sulfuric acid (98%). Then, 1 g of 1,10-phenanthroline was added into the resulting solution and stirred at 0°C for 24 h. The solution was poured into ice water containing sodium hydroxide to yield yellow precipitate, which was recrystallized from water to obtain bright yellow crystals (0.76 g, 62%).$^{[1]}$ $^1$H NMR (400MHz, DMSO-d$_6$, 298K, TMS): $\delta$ 9.23 (t, 1H, J=6.8Hz), 9.19 (d, 1H, J=3.6Hz), 8.96 (s, 1H), 8.82 (d, 1H, J=4.4Hz), 8.72 (d, 1H, J=3.8Hz), and 7.87-7.93 (m, 2H) ppm.
Synthesis of 5-amino-1,10-phenanthroline

As a typical run, 1 g of 5-nitro-1,10-phenanthroline was dissolved in 10 mL concentrated hydrochloric acid (37%), followed by slow addition of 4 g tin dichloride. Then, the mixture was refluxed at 120°C for 2 h. After the mixture was cooled down to room temperature, sodium hydroxide was added to adjust pH at 8-9. The product was extracted by chloroform and recrystallized from ethanol to yield yellow-brown crystals (0.59 g, 68%).\[2\] \(^1\)H NMR (400MHz, DMSO-d6, 298K, TMS): \(\delta\) 9.04-9.06 (m, 1H), 8.66-8.68 (m, 2H), 8.03-8.05 (m, 1H), 7.72-7.75 (m, 1H), 7.49-7.52 (m, 1H), 6.86 (s, 1H), and 6.14 (s, 2H) ppm.

Synthesis of N-[1,10]phenanthrolin-5-yl-acrylamide

As a typical run, 5 mmol of 5-amino-1,10-phenanthroline was dissolved in 100 mL of dried CHCl₃ containing 10 mmol of K₂CO₃. After cooling down to 0-5 °C, acryl chloride (6 mmol) in 30 mL of CHCl₃ was dropped added in 1 h. After stirring at room temperature for 12 h, the resulted solution was filtered and washed with 5% NaHCO₃ solution and water in turn. All of the volatile components were removed under vacuum to give a yellow-brown powder (1.19g, 91%). \(^1\)H NMR (400MHz, CDCl₃, 298K, TMS): \(\delta\) 9.53 (s, 1H), 8.76 (d, 2H, J=28Hz), 8.30-8.32 (m, 1H), 7.90-7.94 (m, 2H), 7.41-7.45 (m, 1H), 6.46-6.84 (m, 2H), and 5.72 (d, 1H, J=11.6Hz) ppm.

Synthesis of PS-Phen-Cu catalyst
*Synthesis of PS-Phen.* Polystyrene (PS) with 1,10-phenanthroline ligands (Phen) was synthesized according to literature.\(^3\) As a typical run, under N\(_2\) atmosphere, 1 g of aliquot of polystyrene (Cl content 1-1.24mmol) was swelled for 24 h in DMF, followed by the addition of 0.5 g of 5-amino-1,10-phenanthroline. Then, the mixture was stirred and heated to 100°C. After refluxing for 24 h, a proper amount of 10% KOH solution was added to neutralize the HCl produced in the reaction. The resulting mixture was filtered and washed by ethanol and water until the filtrate become colorless and neutral. After drying, the brown solid was obtained, which was denoted as PS-Phen.

*Synthesis of PS-Phen-Cu*

As a typical procedure, 1 g of PS-Phen was added to 50 mL of DMF containing 0.2 g of Cu(CH\(_3\)COOH)\(_2\)\(\cdot\)H\(_2\)O, then stirring at 70°C for 6 h under N\(_2\) atmosphere. After cooling down to room temperature, filtrating, washing by excessive water, and drying at 80°C, the dark green spheres were obtained, which was denoted as PS-Phen-Cu (Cu content: 4.3 wt %).

*Synthesis of Cu-MCM-41*

*Cu-MCM-41.* As a typical run,\(^4\) 0.2 g of copper acetate was dissolved in 26 mL of water, followed by addition of 12 mL ammonia solution (25%) and 1.1 g cetyltrimethylammonium bromide (CTAB). After stirring at room temperature for 3 h, 5 mL of tetraethyl orthosilicate (TEOS) was added. After stirring at room temperature
for 24 h, the mixture was transferred into an autoclave and kept at 100°C for 12 h.

The product was filtrated, washed with water, dried at room temperature, and calcined at 550 °C for 5 h to obtain Cu-MCM-41 (Cu content: 4.1 wt %).

Synthesis of azides

Azides were synthesized according to literature.\textsuperscript{[5]} As a typical run, benzyl chloride (5.0 g, 39.5mmol) and 3 equiv. excess of NaN\textsubscript{3} (7.7g, 118.5 mmol) were dissolved in 40 mL DMF and stirred overnight at room temperature. After that the mixture was poured into ice water, the product was extracted with diethyl ether. The combined organic phase was washed with brine and dried over MgSO\textsubscript{4}. After removal of the diethyl ether, the azide was obtained.

Preparation of Cu/C catalyst

Cu/C catalyst was synthesized as described at elsewhere.\textsuperscript{[6]} As a typical run, carbon (5g) was added to a flask. A solution of Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O (1.11g) in deionized water (10mL) was added to the flask, and further deionized H\textsubscript{2}O (10mL) was added to wash down the sides of the flask. The mixture was stirred for 30 min and then submerged in an ultrasonic bath for 7h. The Cu/C was obtained after water was evaporated under vacuum.

The brown catalyst in the reaction
As a typical run, 1 mmol of phenyl acetylene, 4 mL of DMF, and 2.5 mol% of catalyst were mixed and stirred at 120°C under N₂ for 40 min. After filtrating, washing with diethyl ether, and drying at room temperature, the brown catalyst was obtained.

*Analysis of Copper species in the products formed by Huisgen 1,3-diolar cycloaddition*

As a typical example, 5.25 mmol of phenylacetylene, 5 mmol of benzylazide, 5 mol% Cu catalysts (CuSO₄·5H₂O, Cu/C, and PCP-Phen-Cu), and 20 mol% of sodium ascorbate, were added to 5 mL of water. After reaction for 2 h at 50°C, the product was extracted with ethyl acetate. The heterogeneous catalysts were separated by centrifugation. After removing of ethyl acetate, the amount of Cu species in the product was detected by ICP-AES.

**Supporting Figure Captions**

**Figure S1.** (A) N₂ sorption isotherms and (B) pore size distributions of the PCP-x-Phen with Phen-MA/DVB mass ratios at (a) 1/6, (b) 1/4, (c) 1/3, and (d) 1/2 respectively. Isotherms of (a) and (b) have been offset by 250, and 100 cm³/g, respectively, along the vertical axis for clarity. Pore size distributions of (a) has been
offset by 0.3 cm$^3$/g, and each of them was estimated by BJH model from adsorption branch of the isotherms.

**Figure S2.** TG curve of PCP-Phen.

**Figure S3.** Color of the solution (a) before, (b) in, and (c) after the reaction over PCP-Phen-Cu catalyst before (A) and after (B) centrifugation.

**Figure S4.** Color of the solution (a) before and (c) after addition of phenylacetylene in the presence of PCP-Phen-Cu catalyst.
### Table S1. Textural Parameters for PCP-x-Phen

<table>
<thead>
<tr>
<th>$x^a$</th>
<th>$S_{BET} (m^2/g)$</th>
<th>Pore size</th>
<th>Pore volume (cm$^3/g$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/6</td>
<td>618</td>
<td>9.4</td>
<td>0.66</td>
</tr>
<tr>
<td>1/4</td>
<td>574</td>
<td>10.8</td>
<td>0.72</td>
</tr>
<tr>
<td>1/3</td>
<td>462</td>
<td>7.5</td>
<td>0.43</td>
</tr>
<tr>
<td>1/2</td>
<td>195</td>
<td>3.2</td>
<td>0.14</td>
</tr>
</tbody>
</table>

$^a$ stands for mass ratios of Phen-MA to DVB.
Figure S1.
Figure S2.
Figure S3.
before “in-situ” generation of

Figure S4.
$^1$H NMR spectra of various phenanthroline ligands.
$^1$H NMR spectra of the products in Glaser couplings.
$^1$H NMR spectra of the products in Huisgen couplings
Brief summary of chemical structure and chemical shifts

\[ \text{5,7-dodecadiyne: 5,7-dodecadiyne was purified by column chromatography on silica} \]
\[ \text{gel to give as yellow oil (yield 95%).} \]
\[ ^1\text{H NMR (400MHz, CDCl}_3, 298\text{K, TMS):} \]
\[ \delta \text{ 2.18 (t, 4H, } J=6.8\text{Hz), 1.32-1.46 (m, 8H), 0.84 (t, 6H, } J=7.4\text{Hz) ppm.} \]

\[ \text{8,10-octadecadiyne: 8,10-octadecadiyne was purified by column chromatography on} \]
\[ \text{silica gel to give as yellow oil (yield 91%).} \]
\[ ^1\text{H NMR (400MHz, CDCl}_3, 298\text{K, TMS):} \]
\[ \delta \text{ 2.17 (t, 4H, } J=7\text{Hz), 1.41-1.47 (m, 4H), 1.21-1.32 (m, 16H), 0.81 (t, 6H, } J=6.8\text{Hz) ppm.} \]

\[ \text{1,4-diphenyl-1,3-butadiyne: 1,4-Diphenyl-1,3-butadiyne was purified by column} \]
\[ \text{chromatography on silica gel to give as white solid (yield 97%).} \]
\[ ^1\text{H NMR (400MHz, CDCl}_3, 298\text{K, TMS):} \]
\[ \delta \text{ 7.47 (d, 4H, } J=4\text{Hz), 7.25-7.31 (m, 6H) ppm.} \]

\[ \text{1,4-Diphenyl-1,3-butadiyne: 1,4-Diphenyl-1, 3-butadiyne was purified by column} \]
\[ \text{chromatography on silica gel to give as white solid (yield 96%).} \]
\[ ^1\text{H NMR (400MHz, CDCl}_3, 298\text{K, TMS):} \]
\[ \delta \text{ 7.35 (d, 4H, } J= 7.6 \text{ Hz), 7.08 (d, 4H, } J=7.6 \text{ Hz), 2.3 (s, 6H) ppm.} \]
1,4-bis(m-methylphenyl)buta-1,3-diyne: 1,4-bis(m-methylphenyl)buta-1,3-diyne was purified by column chromatography on silica gel to give as white solid (yield 95%). $^1$H NMR (400MHz, CDCl$_3$, 298K, TMS): $\delta$ 7.27 (d, 4H, $J$=8.8 Hz), 7.11-7.18 (m, 4H), 2.3 (s, 6H) ppm.

MeO
\[\begin{array}{c}
  \text{C} \\
  \text{C} \\
  \text{C} \\
  \text{C} \\
\end{array}\]
OMe

1,4-bis(p-methoxyphenyl)buta-1,3-diyne: 1,4-bis(p-methoxyphenyl)buta-1,3-diyne was purified by column chromatography on silica gel to give as white solid (yield 95%). $^1$H NMR (400MHz, CDCl$_3$, 298K, TMS): $\delta$ 7.40 (d, 4H, $J$=8.4 Hz), 6.79 (d, 4H, $J$=8.4 Hz), 3.76 (s, 6H) ppm.

\[\begin{array}{c}
  \text{C} \\
  \text{C} \\
  \text{C} \\
  \text{C} \\
\end{array}\]

1,1’-(Buta-1,3-diyyne-1,4-diyl)dicyclohexanol: 1,1’-(Buta-1,3-diyyne-1,4-diyl)dicyclohexanol was purified by column chromatography on silica gel to give as white solid (yield 85%). $^1$H NMR (400MHz, DMSO-d$_6$, 298K, TMS): $\delta$ 5.49 (s, 2H), 1.71 (d, 4H, $J$=7.2 Hz), 1.57 (d, 4H, $J$=5.6 Hz), 1.31-1.49 (m, 10H), 1.18 (t, 2H, $J$=5.4 Hz) ppm.

\[\text{C} = \text{N} - \text{C} - \text{N} - \text{C} \]

1-Benzyl-4-phenyl-1H-[1,2,3]triazole: 1-Benzyl-4-phenyl-1H-[1,2,3]triazole was purified by column chromatography on silica gel to give as white solid (yield 99%).
1H NMR (400MHz, DMSO-d6, 298K, TMS):  δ 8.65 (s, 1H), 7.85 (d, 2H, J=7.6Hz), 7.32-7.45 (m, 8H), 5.65 (s, 2H) ppm.

1-Benzyl-3-m-tolyl-1H-[1,2,3]triazole: 1-Benzyl-3-m-tolyl-1H-[1,2,3]triazole was purified by column chromatography on silica gel to give as white solid (yield 98%).

1H NMR (400MHz, DMSO-d6, 298K, TMS):  δ 8.62 (s, 1H), 7.12-7.68 (m, 9H), 5.64 (s, 2H), 2.34 (s, 3H) ppm.

1-Benzyl-4-p-tolyl-1H-[1,2,3]triazole: 1-Benzyl-4-p-tolyl-1H-[1,2,3]triazole was purified by column chromatography on silica gel to give as white solid (yield 99%).

1H NMR (400MHz, DMSO-d6, 298K, TMS):  δ 8.57 (s, 1H), 7.72 (d, 2H, J=8Hz), 7.22-7.38 (m, 7H), 5.62 (s, 2H), 2.30(s, 3H) ppm.

1-Benzyl-4-(4-methoxy-phenyl)-1H-[1,2,3]triazole:

1-Benzyl-4-(4-methoxy-phenyl)-1H-[1,2,3]triazole was purified by column chromatography on silica gel to give as white solid (yield 97%). 1H NMR (400MHz, DMSO-d6, 298K, TMS):  δ 8.52 (s, 1H), 7.77 (d, 2H, J=8.8Hz), 6.99-7.39 (m, 7H), 5.62 (s, 2H), 3.77 (s, 3H) ppm.
1-Benzyl-4-butyl-1H-[1,2,3]triazole: 1-Benzyl-4-butyl-1H-[1,2,3]triazole was purified by column chromatography on silica gel to give as colorless oil (yield 93%). 

\[ ^1H \text{NMR (400MHz, DMSO-d}_6, 298K, TMS): \delta 7.88 (s, 1H), 7.27-7.37 (m, 5H), 5.53 (s, 2H), 5.62 (s, 2H), 2.59 (t, 2H, J=7.4Hz), 1.54 (t, 2H, J=7.6Hz), 1.26-1.32 (m, 2H), 0.857 (t, 3H, J=7.2Hz) \text{ ppm.} \]

1-Benzyl-4-heptyl-1H-[1,2,3]triazole: 1-Benzyl-4-heptyl-1H-[1,2,3]triazole was purified by column chromatography on silica gel to give white solid (yield 97%). \[ ^1H \text{NMR (400MHz, DMSO-d}_6, 298K, TMS): \delta 7.87 (s, 1H), 7.25-7.36 (m, 5H), 5.52 (s, 2H), 2.56 (t, 2H, J=7.6Hz), 1.55 (t, 2H, J=7.0Hz), 1.22-1.26 (m, 8H), 0.828 (t, 3H, J=6.6Hz) \text{ ppm.} \]

1-(1-Benzyl-1H-[1,2,3]triazol-4-yl)-cyclohexanol:

1-(1-Benzyl-1H-[1,2,3]triazol-4-yl)-cyclohexanol was purified by column chromatography on silica gel to give white solid (yield 94%). \[ ^1H \text{NMR (400MHz, DMSO-d}_6, 298K, TMS): \delta 7.91 (s, 1H), 7.30-7.38 (m, 5H), 5.53 (s, 2H), 4.83 (s, 1H), 1.37-1.84 (m, 10H) \text{ ppm.} \]
Supporting References


