

# Self-catalyzed Click Chemistry: Preparation and Characterization of Novel Hyperbranched NHC-Cu(I) Complex-based “Click Polymers”

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**Abstract:** Novel azide-tagged copper(I) complex of N-Heterocyclic carbenes (NHCs) analogues to the well known bis[2,6-diisopropylphenyl]imidazolin-2-ylidene (SIPr) was synthesized and characterized. The complex was able to act as catalyst and substrate in a model copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction with tris(4-ethynylphenyl) amine, yielding novel hyperbranched NHC-Cu(I) complex-based “click polymers” via the methodology of self-catalyzed click chemistry.

**Key words:** self-catalysis; click chemistry; N-heterocyclic carbene; polymer

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The “click” philosophy of chemistry, first introduced by Sharpless, Kolb and Finn in 2001<sup>[1]</sup>, which essence is efficiency and simplicity, has undoubtedly become one of the most remarkable synthetic methodology in this new century. In early 2002, Meldal and co-workers reported that catalytic amounts of copper(I) can lead to fast, highly efficient and regioselective azide-alkyne cycloadditions at room temperature which was known as the best “click reactions” (CuAAC)<sup>[2]</sup>. After that, much attention has been paid to the development of copper(I) catalytic system for CuAAC click reactions. Most often, catalytic systems enabling this transformation consist of a copper(II) salt and a reducing agent<sup>[3]</sup>, oxidation of Cu(0) metal<sup>[4]</sup>, cuprous salts or a combination of Cu(0)/Cu(II)<sup>[5]</sup>. The latter, employing amines as additives to the Cu(I) system has been developed<sup>[6]</sup>. Recently, the CuAAC has been proved to be accelerated by Cu(I) species supported by nitrogen<sup>[7]</sup>, sulfur<sup>[8]</sup>, phosphine<sup>[9]</sup> and N-heterocyclic carbene (NHC) ligands<sup>[10-13]</sup> since these

ligands could stabilize the Cu(I) centre and thus enhance its catalytic activity.

With above catalyst systems, various “click polymers” and novel functional polymer materials have been prepared through click chemistry, the CuAAC click reaction has vastly increased in broadness and application in the field of polymer science<sup>[14-15]</sup>. However, all the reported synthetic procedures of “click polymers” need the adding of extra catalysts which would cause the purification problem, what’s more important, the catalysts residue is detrimental to the electronic and optical properties of polymeric materials. In addition, although the CuAAC click reaction is efficient for small molecules, it is rather sluggish for the polymer preparation, taking as long as 10 days to complete a polymerization reaction.

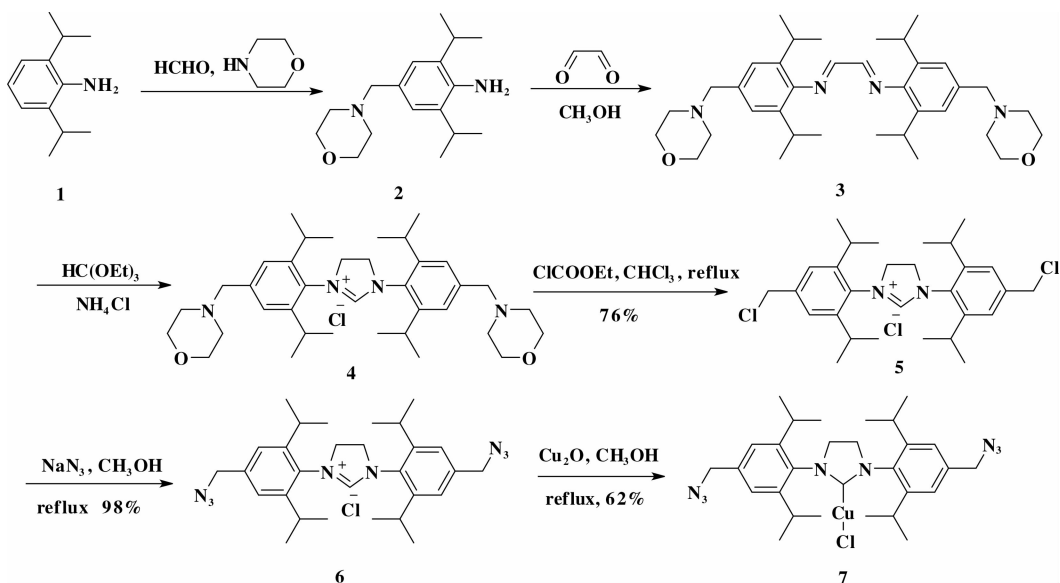
Herein, we propose a totally novel concept about click chemistry: self-catalyzed click chemistry. Using elaborate designed azide-tagged SIPr-Cu(I) complex **7** as monomer (Scheme 1), novel hyperbranched NHC-

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Scheme 1 Synthesis of monomer **7** azide-tagged SIPr-Cu(I) complex

Cu(I) complex-based “click polymers” was synthesized fast and efficiently with a yield of 62% in 3 days at room temperature without adding extra catalysts. In the polymerization process, monomer **7**, azide-tagged SIPr-Cu(I) complexes, plays the role of self-catalysts as well as monomers.

## 1 Experimental

### 1.1 Synthesis and characterization of azide-tagged SIPr-Cu(I)

The synthetic route of azide-tagged SIPr-Cu(I)

complex **7** was shown in scheme 1. Commercially available 2,6-diisopropylaniline (**1**) was easily converted to **5** via morphine functionalized [SIPr]. HCl (**4**) according to the reported procedure<sup>[16]</sup>, and subsequent treated with NaN<sub>3</sub> to form the functionalized azide-tagged [SIPr]. HCl (**6**) as white solid in high yields (98%). Following the reported methodology<sup>[17]</sup>, treated azide-tagged [SIPr]. HCl (**6**) with Cu<sub>2</sub>O, azide-tagged SIPr-Cu(I) complex (**7**) was obtained as white solid. The crystal structure of monomer **7** was shown in Fig. 1.

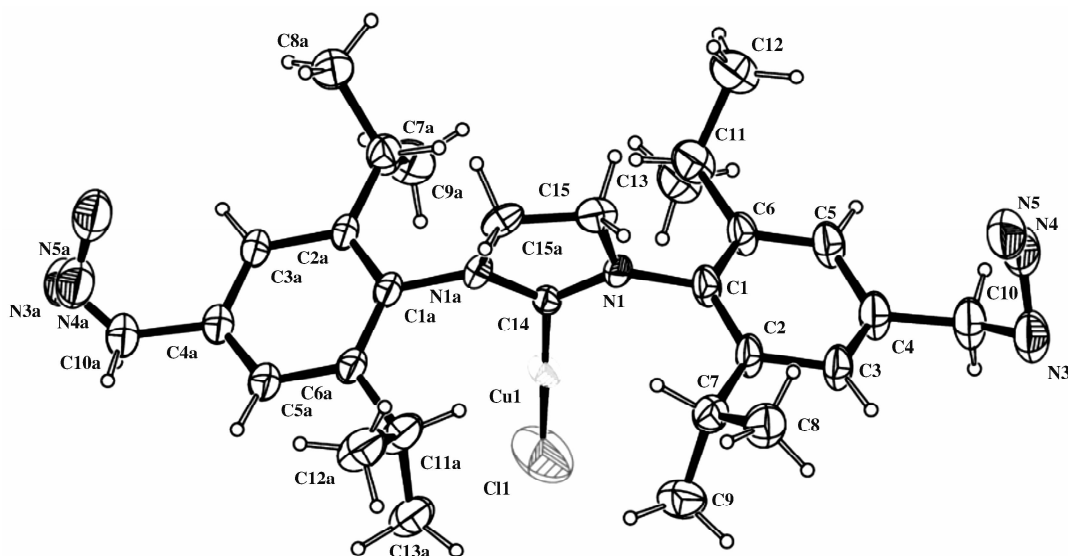
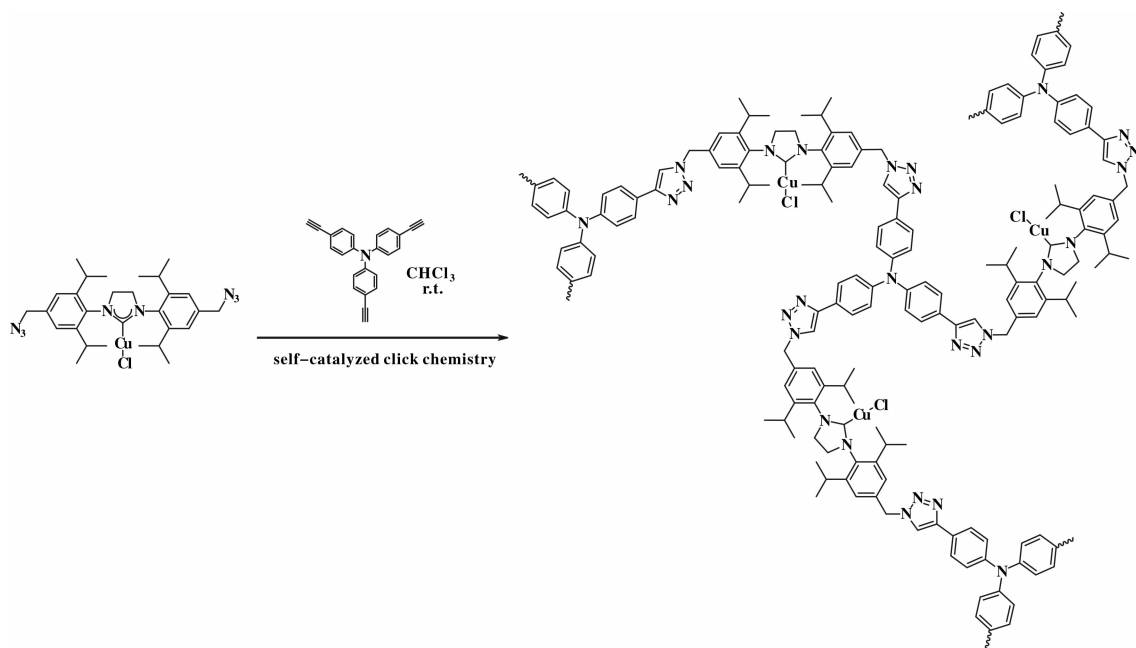


Fig. 1 Crystal structure of monomer **7** azide-tagged SIPr-Cu(I) complex (ellipsoids are drawn at 50% probability level)

## 1.2 Synthesis of novel hyperbranched NHC-Cu(I) complex-based “click polymers”

For preparation of NHC-Cu(I) Complex-based “Click Polymers” (Scheme 2), monomer **7** (1.5 equiv relative to trialkyne) and trialkyne were stirred

in 10 mL  $\text{CHCl}_3$  at room temperature for 3 days. Gradually, a brown precipitate was formed. After washing with  $\text{CHCl}_3$  and dried under vacuum, the resultant solid with a 62% yield.



Scheme 2 Synthesis of novel hyperbranched NHC-Cu(I) complex-based “click polymers”

## 2 Results and discussion

We were interested in hyperbranched NHC-Cu(I) complex-based “click polymers” because they’re new concept polymers. As we know, almost all the organic polymers are constituted of C, H, O, N and S elements and there is scarcely any organic polymer incorporate metal atoms evenly through covalent bonds without the procedure of post-functionalization of metal elements, without post-functionalization procedures. NHC-Cu(I) complexes are definitely air and moisture-stable. In the “click polymers”,  $\text{SiPr-Cu(I)}$  complexes are connected by triazole rings covalently in a repeated and hyperbranched way. Copper is successfully doped into hyperbranched polymers evenly in molecular level, and this will provide a novel methodology regarding to develop covalently metal incorporated organic polymeric materials.

To confirm the chemical structure of hyper-

branched NHC-Cu(I) complex-based “Click Polymers”, solid-state  $^{13}\text{C}$  NMR (Fig. 2) and Fourier transform infrared (FTIR) (Fig. 3) spectroscopic studies were conducted. As shown in Figure. 2, all peaks were clearly assignable to the carbon atoms in the expected structure as shown in Scheme 2. The  $^{13}\text{C}$  NMR peaks from the isopropyl, methylene groups and benzene rings appeared at 24 ~ 29, 48 ~ 54 and 122 ~ 148 ppm respectively. From the FTIR spectra, we can see the  $\equiv\text{C-H}$  and  $\text{N}_3$  group of the monomers have strong absorption bands at around  $3\,268\text{ cm}^{-1}$  and  $2\,076\text{ cm}^{-1}$ , respectively. The almost disappeared absorbance at  $3\,268\text{ cm}^{-1}$  and the very weak absorbance at around  $2\,706\text{ cm}^{-1}$  of hb-NHC-Cu(I) polymer indicates that most of alkyne and azide groups have been consumed during polymerization, TLC and MS analysis showed there were a small quantity of monomers and soluble oligomers in the mother solution. The absorption bands at around  $2\,868 \sim 2\,962\text{ cm}^{-1}$  are attributed

to the characteristic peaks of isopropyl groups.

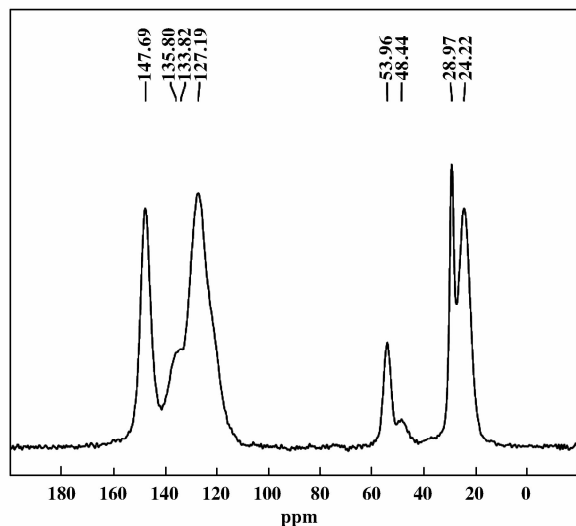


Fig. 2 Solid-phase  $^{13}\text{C}$  NMR spectrum of hyperbranched NHC-Cu(I) complex-based “click polymers”

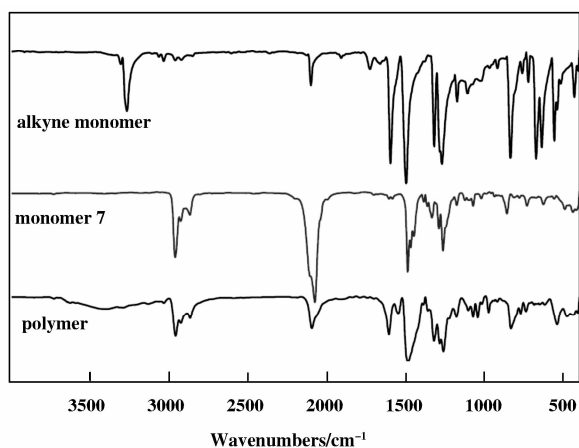


Fig. 3 FTIR spectra of monomers and hyperbranched NHC-Cu(I) complex-based “click polymers”

To acquire information on the chemical components of the “click polymers”, elemental analysis (EA) by combustion and atomic absorption spectroscopy (AAS) were conducted, which clearly supports the formation of the hyperbranched NHC-Cu(I) complex-based “click polymers”. The observed contents of carbon (67.0%), nitrogen (14.8%), hydrogen (6.4%) in the NHC-Cu(I) polymer matched well with the theoretical values for carbon (66.6%), nitrogen (15.0%), hydrogen (6.2%) in the NHC-Cu(I) polymer. The Cu contents of NHC-Cu(I) polymer

were calculated to be 7.3% by the analysis with AAS (atomic analysis spectroscopy) matched well with theoretical values 7.8%.

To further study the valence state information of the “click polymers”, the X-ray photoelectron spectra (XPS) characterization were employed to investigate the variations of binding energy (BE) of Cu between monomer **7** (azide-tagged SIPr-Cu(I) complex) and NHC-Cu(I) polymers. As shown in Figure 4, copper  $2p_{3/2}$  peaks of NHC-Cu(I) polymer and Cu-monomer **7** are observed at 933.0 and 933.3 eV respectively, which strongly confirmed Cu(I) valence state of both NHC-Cu(I) polymer and NHC-Cu(I) monomer. The Cu(I) state of azide-tagged SIPr-Cu(I) complex remained very well after self-catalyzed polymerization process, and the NHC-Cu(I) monomer were successfully doped into the “click polymers”.

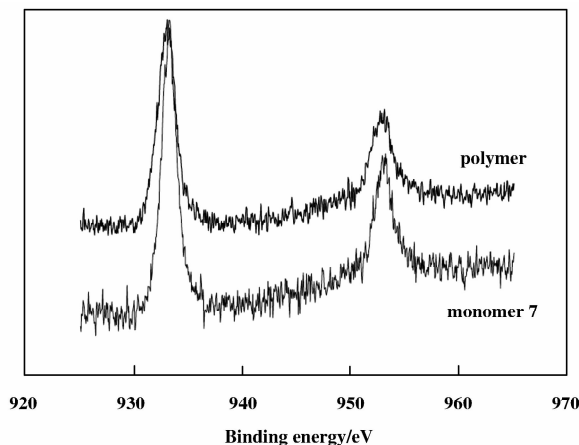


Fig. 4 XPS spectra of Cu-hyperbranched NHC-Cu(I) complex-based “click polymers” and Cu-monomer **7**.

$^1\text{H}$ ,  $^{13}\text{C}$  NMR and HRMS data for new compounds are listed below:

Compound **5**:  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  9.38 (s, 1H), 7.51 (s, 4H), 4.73 (s, 4H), 4.62 (s, 4H), 3.16 (pentet,  $J = 6.8$  Hz, 4H), 1.47 (d,  $J = 6.8$  Hz, 12H), 1.33 (d,  $J = 6.8$  Hz, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  161.5, 147.5, 142.1, 130.0, 125.7, 54.3, 45.3, 29.5, 24.6, 23.1; HRMS  $m/z$  (ESI) calculated for  $\text{C}_{29}\text{H}_{41}\text{Cl}_2\text{N}_2^+ [\text{M}-\text{Cl}]^+$  487.2641, found 487.2645; Anal. calcd for  $\text{C}_{29}\text{H}_{41}\text{Cl}_2\text{N}_2$ : C 66.47, H 7.89%, N 5.35%; found C 66.45%, H 7.93%, N 5.34%.

Compound **6**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.29 (s, 1H), 7.17 (s, 4H), 4.62 (s, 4H), 4.38 (s, 4H), 3.02–2.91 (pentet, 4H,  $J = 6.8$  Hz), 1.36 (d, 12H,  $J = 6.8$  Hz), 1.24 (d, 12H,  $J = 6.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO)  $\delta$  160.1, 146.5, 140.6, 129.7, 125.3, 53.7, 28.3, 24.9, 23.2; HRMS  $m/z$  (ESI) calculated for  $\text{C}_{29}\text{H}_{41}\text{N}_8^+ [\text{M}-\text{Cl}]^+$  501.3449, found 501.3447. Anal. calcd for  $\text{C}_{29}\text{H}_{41}\text{ClN}_8$ : C 64.85, H 7.69%, N 20.86%; found C 64.83, H 7.70%, N 20.88%.

Compound **7**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 (s, 4H), 4.40 (s, 4H), 4.03 (s, 4H), 3.10–3.00 (pentet, 4H,  $J = 6.8$  Hz), 1.37–1.35 (dd, 24H,  $J_1 = 3.2$  Hz,  $J_2 = 6.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO)  $\delta$  147.4, 137.4, 134.2, 124.4, 54.9, 53.8, 29.1, 25.6, 24.0; HRMS  $m/z$  (ESI) calculated for  $\text{C}_{29}\text{H}_{41}\text{ClCuN}_8 [\text{M} + \text{H}]^+$  598.2360, found 598.2356. Anal. calcd for  $\text{C}_{29}\text{H}_{40}\text{ClCuN}_8$ : C 58.08, H 6.72, N 18.69%; found C 58.11, H 6.70, N 18.70.

### 3 Conclusions

In conclusion, we have developed a novel concept about click chemistry: self-catalyzed clickchemistry. Through the methodology of self-catalyzed click chemistry, novel hyperbranched NHC-Cu(I) complex-based “click polymers” were synthesized more fast and efficiently at room temperature without adding extra catalysts compared with generally sluggish click polymerization process. The elaborate designed monomer (azide-tagged SIPr-Cu(I) complex) plays both the roles of catalyst and monomer, and this will provide a new idea and methodology about catalytic polymerization process especially for transition metal catalyzed polymerization process. Furthermore, we have developed a new concept “click polymers” (hyperbranched NHC-Cu(I) complex-based “click polymer”) through one step self-catalyzed click chemistry which is more superior to the multistep post-functionalization. They were characterized by solid-phase NMR, FTIR, EA, AAS and XPS respectively. All the analytical technique supports the following conclusions: in the “click polymer”, air and moisture-stable NHC-Cu(I) com-

plexes are connected by triazole rings covalently in a repeated and hyperbranched way. Copper is successfully doped into hyperbranched polymers evenly in molecular level. This will provide a novel methodology regarding to develop covalently metal incorporated organic polymeric materials.

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## 自催化点击化学:新型基于氮杂卡宾铜配合物的超分枝 “click 聚合物”的合成与表征

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**摘要:** 设计合成和表征了新型叠氮基官能团化的 SIPr(2,6-diisopropylphenyl)imidazolin-2-ylidene) 氮杂卡宾铜配合物。这种氮杂卡宾铜配合物既可作为反应底物又可作为催化剂进行自催化的叠氮炔烃 3+2 环加成反应(CuAAC)。通过这种配合物与炔烃的简单自催化反应, 在常温常压条件下合成出了一种新型的基于氮杂卡宾铜配合物的超分枝“聚合物”, 并通过固体核磁、红外光谱、元素分析、原子吸收光谱和 X 射线光电子能谱对其进行了完整的表征。

**关键词:** 自催化; 点击化学; 聚合物; 氮杂卡宾配合物