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Homogeneous and noncovalent immobilization of NHC-Cu catalyzed azide-alkyne cycloaddition reaction

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ARTICLE INFO	A B S T R A C T
Keywords: NHC-Cu Carbon nanotube Azide-alkyne cycloaddition reaction Noncovalent immobilization Recyclability	A series of new pyrene tagged nitrogen heterocyclic carbene copper (NHC-Cu) molecular complexes were syn- thesized and characterized by ¹ H- and ¹³ C-NMR, high resolution ESI-mass spectrometry (HR-MS). The corre- sponding NHC-Cu complex was immobilized onto the surface of multi-walled carbon nanotubes (MWNTs) by using π - π stacking interaction, the noncovalent immobilization catalytic material MWNTs@NHC-Cu were char- acterized by FT-IR, XRD, XPS, thermogravimetry (TGA) and TEM. The new NHC-Cu complexes were tested both in the homogeneous phase and once immobilized onto multi-walled carbon nanotubes support for the azide- alkyne cycloaddition reaction. Both were active in the two-component click cycloaddition reaction of terminal alkynes and organic azides and three-component cycloaddition reaction that employs various terminal alkynes, NaN ₃ and organic halides with the advantage of excellent yields, low catalyst dosage, short reaction time. The

another catalytic cycle, but with loss of product yield.

1. Introduction

The 1,3-dipolar cycloaddition between an azide and alkyne is a prime example of a click chemistry reaction as a concept postulated by Sharpless [1], which has been applied to the various field including medicinal chemistry, materials, and biology [2-6]. Copper (I) is widely used in azide-alkyne cycloaddition reaction as a catalyst because it has several advantages, such as excellent regioselectivity, milder reaction condition, usage of inexpensive and green reaction solvent including aqueous, alcoholic, neat, etc [7,8]. However, the catalytic activity of single copper salt is relatively low. So, various ligands are used in order to improve the activities of the systems catalyzed by Cu (I) [8-14]. Among the various ligands, N-heterocyclic carbenes (NHCs) shows excellent catalytic activity under mild conditions [15–17]. Because of its special electronic structure, it can be used as both a σ electron donor and a π electron acceptor, which can make it coordinate with various metals and maintain considerable stability compared to phosphine ligands [18]. Therefore, NHC-Cu is widely used to accelerate the azide-alkyne cycloaddition reaction [8,19–21]. Despite the high activity and selectivity of carbene complexes in terms of catalyzing various types of reactions, separating the catalyst from the product is a bottleneck restricting its industrial application [22]. Undoubtedly, the simple separation of catalyst and product will bring more economic benefits in industrial production. Therefore, the immobilization of homogeneous catalysts has been a hot issue of research [23,24].

MWNTs@NHC-Cu catalyst could be separated from the reaction system at the end of the reaction and reused in

As an excellent supporting material, carbon nanotubes (CNTs) have good optical, mechanical, chemical, electrical, and functional properties [25–29]. One of the most commonly used functionalization methods for carbon nanotubes is to use covalent bonds to achieve the heterogeneity of homogeneous catalysts by using carboxylic acid groups or hydroxyl groups, etc [30–33]. Despite this method achieving effective grafting, it has obvious drawbacks. First, the modification of the covalent bond leads to the destruction of the structure and properties of the CNTs. In addition, the method will also lead to changes in the structure of the catalyst resulting in potentially impaired activity. So an alternative way was chosen-noncovalent interactions, although this interaction is weak, the catalyst can also be recycled after being immobilized under appropriate methods and fitting reaction conditions. Thus, it has become a trend to immobilize homogeneous catalysts on carbon nanotubes through π - π interaction to achieve the same and even enhanced catalytic effect of homogeneous catalysts. People usually use aromatic small molecules or some polymers to achieve π - π bond stacking with carbon

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Scheme 1. Homogeneous pyrene tagged NHC-Cu molecular complexes and noncovalent immobilization of NHC-Cu onto multi-walled carbon nanotubes.

nanotubes to achieve immobilization [34–36]. Initial carbon nanotubes have a large number of sp2 hybridized carbon atoms and the stacking of π - π bonds provides enough convenience. Among them, pyrene, as a smaller aromatic group, is widely used because of its simple modification method [37-42]. A lot of work on the immobilization of the homogeneous catalyst through the π - π bond conjugation and the realization of multiple cycles of the catalyst has been developed. Liu and co-workers successfully synthesized a pyrene-tagged ruthenium carbene and immobilized on carbon nanotubes via π - π stacking and discovered that this π - π stacking is severely affected by temperature and solvent polarity, which leads to the "boomerang effect" during the reaction [41]. Besides, carbon nanotubes can be easily recovered by using tetrahydrofuran to wash off the complex when it loses activity. Charles et al. prepared a pyrene-tagged gold complex. The author successfully realized the recycling of gold complexes through the influence of temperature on the stacking effect of π - π bonds. At low temperature, the desorbed gold complex was re-adsorbed to the carbon nanotubes [39]. In addition to the π - π stacking effect by immobilizing pyrene-modified

complexes on carbon nanotubes, people have also successfully achieved immobilization of pyrene-modified complexes on reduced graphene oxide. Cuni and Sabater synthesized pyrene-modified NHC-Pt, NHC-Pd and NHC-Ru, respectively, then, loaded it onto reduced graphene oxide, which can be reused several times in various organic transformations [37,42]. In the heat filtration experiment, Researchers did not find detectable leaching or boomerang effect to reveal the nature of heterogeneity. These evidences show that the homogeneous catalyst supported by the π - π stacking effect can fully realize the recycling of the catalyst.

On the basis of the previous reports, As a part of our ongoing efforts to extend the scope of the use of recyclable catalyst in the azide-alkyne cycloaddition reaction [43]. Herein, a series of new pyrene tagged NHC-Cu (nitrogen heterocyclic carbene) molecular complexes and the corresponding multi-walled carbon nanotubes (MWNTs) immobilized NHC-Cu catalytic material by using π - π stacking interaction noncovalent were prepared and applied in the azide-alkyne cycloaddition reaction (Scheme 1). Interestingly, the noncovalent immobilization of NHC-Cu



Scheme 2. The synthesis of pyrene tagged NHC ligand precursors and their copper complexes.

catalyst displayed the same activities with the homogeneous related complexes under solvent-free conditions. Moreover, the noncovalent immobilization of NHC-Cu catalyst could be separated from the reaction system at the end of the reaction and reused in another catalytic cycle, but without significant loss in the catalytic activity.

2. Materials and methods

2.1. Materials and characterizations

Unless otherwise noted, all the reagents were of analytical grade and were used as received. MWNTs (purity >95 %) were purchased from Nanjing Xianfeng Nano Material Technology Co., Ltd. Nitrides were prepared according to the reference [39]. Thermogravimetric analysis (TGA) measurement was measured using NETZSCH STA449F3 under a nitrogen atmosphere at an increased rate of 10 °C/min from room temperature to 800 °C. ¹H NMR and ¹³C NMR spectra were obtained by using a Bruker AvanceTM III 400 MHz spectrometer using CDCl3 or DMSO-D6 containing TMS as the solvent. The chemical shift unit is ppm. The unit of coupling constant J is Hz. High resolution mass spectra (HR-MS) were recorded with Bruker MicroTOF-Q II mass instrument (ESI). ICP analysis was recorded using an Agilent 725-ES spectrometer. FT-IR was performed at VERTEX 70v (Germany). Powder X-ray diffraction (XRD) was characterized by Smartlab-SE (Japan). Fluorescence measurement was performed on F-7000 from Hitachi High-Technologies Corporation. High-resolution transmission electron microscopy images and energy-dispersive X-ray (EDX) mapping were executed at the FEI Tecnai F20 transmission electron microscope.

2.2. Procedure for synthesis of pyrene tagged NHC-Cu (nitrogen heterocyclic carbene) molecular complexes

The pyrene tagged benzimidazolium salts used as NHC precursors and the corresponding NHC-Cu molecular complexes were prepared similarly by using the published procedures [44]. As shown in Scheme 2.

2.2.1. Preparation of 2-(2-bromoethoxy) pyrene (1)

1-Hydroxypyrene (2.18 g, 10 mmol), Cs_2CO_3 (6.5 g, 20 mmol), 1,2dibromoethane (7.48 g, 40 mmol) and acetonitrile (35 mL) were added into a 100 mL round bottom flask, which was stirred and refluxed for 24 h. After cooling, water (50 mL) was added to the reaction mixture, which was extracted with dichloromethane (3 × 30 mL) and dried with magnesium sulfate. Finally, the obtained product was purified by column chromatography (Ethyl acetate: petroleum ether = 1:4) to give yellow solid (2.3 g, 70 % yield). ¹H NMR (400 MHz, DMSO) δ 8.44 (t, *J* =9.9 Hz, 1 H), 8.20 (dq, *J* = 17.1, 8.2 Hz, 4 H), 8.12 – 7.96 (m, 3 H), 7.74 (d, *J* = 8.5 Hz, 1 H), 4.82 – 4.57 (m, 2 H), 4.04 (dd, *J* = 11.7,

Table 1

Screening the solvent for azide-alkyne cycloaddition reaction catalyzed by NHC-Cu^a.

₩N3 +		1 mol% 4c 30 °C 3 h
Entry	Solvent	Isolated yield (%)
1	CH ₃ OH	66
2	PhCH ₃	35
3	CH ₃ CN	15
4	THF	50
5	Neat	93
6	H ₂ O	39

[a] Reaction conditions: 1 mol% 4c, 1 mmol Benzyl azide, 1.2 mmol Phenylacetylene, 3 mL solvent, 30 $^\circ C$, reaction time 3 h.

6.5 Hz, 2 H).¹³C NMR (101 MHz, DMSO) δ 151.8, 131.1, 127.2, 126.4, 125.9, 124.9, 124.5, 124.2, 124.0, 120.7, 119.5, 110.2, 68.7, 31.8.

2.2.2. Preparation of 1-(2-(pyren-2-yloxy) ethyl)-1H-benzo[d]imidazole (2)

A mixture containing benzimidazole (1.18 g, 10 mmol) and potassium hydroxide (1.13 g, 12 mmol) dissolved in acetonitrile (50 mL) was refluxed for 30 min, which was added compound 1 (3.26 g, 10 mmol) and continued to reflux for 24 h. After cooling to room temperature, 20 mL of *n*-hexane was added to the reaction solution and filtered. The filter was washed three times with *n*-hexane and dried in vacuo to obtain a pale yellow solid. (2.7 g, 75 % yield) ¹H NMR (400 MHz, CDCl₃) δ 8.55 (s, 1 H), 8.29 – 8.16 (m, 4 H), 8.04 (ddd, *J* = 26.3, 18.8, 9.3 Hz, 4 H), 7.89 (t, *J* = 8.9 Hz, 1 H), 7.72 (dd, *J* = 21.5, 8.3 Hz, 2 H), 7.40 – 7.32 (m, 1 H), 7.28 – 7.21 (m, 1 H), 5.01 – 4.85 (m, 2 H), 4.73 (t, *J* = 5.0 Hz, 2 H). ¹³C NMR (101 MHz, CDCl₃) δ 157.1, 148.6, 139.2, 136.4, 136.2, 132.4, 131.6, 131.1, 130.1, 129.7, 129.6, 129.3, 129.3, 128.9, 127.5, 126.7, 125.9, 124.6, 124.5, 124.2, 115.9, 114.9, 72.4, 49.1.

2.2.3. Synthesis of benzimidazole salt (3a, 3b, 3c, 3d)

Compound **2** (2 mmol, 724 mg) in 20 mL of acetonitrile was added 2.2 mmol halogenated hydrocarbon and was refluxed for 24 h. The filter was formed and washed with *n*-hexane, providing the desired product as a yellow solid material (**3a**: 730 mg, 72 % yield; **3b**: 800 mg, 75 % yield; **3c**: 560 mg, 56 % yield; **3d**: 630 mg, 60 % yield).

3a : ¹H NMR (400 MHz, DMSO) δ 10.58 (s, 1 H), 8.40 (t, *J* =7.8 Hz, 1 H), 8.23 (ddd, *J* = 20.2, 13.5, 8.0 Hz, 5 H), 8.13 – 7.93 (m, 6 H), 7.81 – 7.73 (m, 2 H), 7.69 (dd, *J* = 13.4, 5.2 Hz, 1 H), 7.59 (dd, *J* = 6.5, 2.9 Hz, 2 H), 7.32 – 7.26 (m, 3 H), 5.91 (s, 2 H), 5.30 (t, *J* = 4.6 Hz, 2 H), 4.90 (t, *J* = 4.7 Hz, 2 H). ¹³C NMR (101 MHz, DMSO) δ 151.5, 143.2,



Scheme 3. The synthesis of immobilization of NHC-Cu by using π - π stacking interaction of pyrene and multi-walled carbon nanotubes (MWNTs).



Fig. 1. The yield of 4c and MWNTs@NHC-Cu catalyzed click reaction at different time points.

[a] Reaction conditions: 1 mol% 4c, 1 mol% MWNTs@NHC-Cu, 1 mmol Benzyl azide, 1.2 mmol Phenylacetylene, neat, 30 $^\circ \rm C.$

133.90, 131.5, 131.1, 130.9, 130.7, 128.8, 128.7, 128.4, 127.2, 126.7, 126.5, 125.8, 125.0, 124.7, 124.6, 124.3, 123.9, 120.7, 119.1, 114.2, 113, 109.7, 66.2, 49.9, 46.7.

3b : ¹H NMR (400 MHz, DMSO) δ 10.43 (s, 1 H), 8.39 (d, J =8.4 Hz, 1 H), 8.30 – 8.18 (m, 4 H), 8.05 (ddd, J = 25.8, 13.6, 7.6 Hz, 5 H), 7.78 (t, J =7.2 Hz, 2 H), 7.69 (t, J =7.5 Hz, 1 H), 7.57 (dd, J = 6.6, 2.8 Hz, 2 H), 7.33 – 7.25 (m, 3 H), 5.88 (s, 2 H), 5.29 (t, J =4.6 Hz, 2 H), 4.95 – 4.81 (m, 2 H). ¹³C NMR (101 MHz, DMSO) δ 151.5, 143.1, 133.8, 131.5, 131.1, 130.9, 130.7, 128.8, 128.6, 128.3, 127.1, 126.7, 126.4, 125.8, 125.0, 124.7, 124.3, 123.9, 120.6, 119.1, 114.2, 113.9, 109.7, 66.1, 4.8, 46.7.

3c : ¹H NMR (400 MHz, DMSO) δ 10.39 (s, 1 H), 8.39 (t, J =15.2 Hz, 1 H), 8.22 (dd, J = 14.5, 8.5 Hz, 4 H), 8.14 (d, J =8.2 Hz, 1 H), 8.11 – 7.94 (m, 4 H), 7.85 – 7.68 (m, 3 H), 5.28 (d, J =4.3 Hz, 2 H), 5.02 – 4.77 (m, 2 H), 4.58 (t, J =7.0 Hz, 2 H), 1.97 – 1.73 (m, 2 H), 1.43 – 1.10 (m, 2 H), 0.78 (t, J =7.3 Hz, 3 H). ¹³C NMR (101 MHz, DMSO) δ 151.5, 142.9, 131.2, 131.0, 130.8, 127.1, 126.6, 126.4, 125.8, 124.9, 124.7, 124.5, 124.3, 123.9, 120.6, 119.1, 114.1, 113.8, 109.8, 66.3, 46.6, 30.5,

Table 2

Catalytic activity test under different conditions ^a.







Fig. 2. TGA curves of MWNTs, MWNTs@NHC-Cu, NHC-Cu (4c).

19.0, 13.3.

3d: ¹H NMR (400 MHz, DMSO) δ 10.19 (s, 1 H), 8.38 (d, J =8.2 Hz, 1 H), 8.26 – 8.16 (m, 4 H), 8.12 (d, J =8.2 Hz, 1 H), 8.02 (ddd, J = 24.5, 13.0, 6.7 Hz, 4 H), 7.84 – 7.69 (m, 3 H), 5.39 – 5.04 (m, 2 H), 4.84 (dd, J = 22.8, 18.0 Hz, 2 H), 4.54 (t, J =7.1 Hz, 2 H), 1.84 (dt, J = 14.9, 7.3 Hz, 2 H), 1.24 – 1.20 (m, 2 H), 1.14 – 1.04 (m, 2 H), 1.02 – 0.92 (m, 2 H), 0.60 (t, J =7.2 Hz, 3 H). ¹³C NMR (101 MHz, DMSO) δ 151.5, 142.8, 131.3, 131.1, 130.9, 127.2, 126.7, 126.5, 126.4, 125.8, 125.0, 124.8, 124.7, 124.6, 124.3, 124.0, 123.8, 120.6, 119.2, 114.1 113.7, 109.7, 66.2, 46.7, 46.5, 30.4, 28.5, 25.3, 21.6, 13.6.

2.2.4. Synthesis of NHC-Cu-X' (4a, 4b, 4c, 4d, 4e)

To a Schlenk tube under nitrogen was introduced **3a** (0.2 mmol, 98 mg), copper(I) chloride (0.2 mmol, 20 mg) and sodium *tert*-butoxide (0.2 mmol, 20 mg) followed by 5 mL dry THF. The mixture was stirred at room temperature for 4 h. A suspension was filtered through a short pad of Celite and the pad was washed with methylene chloride (3×10 mL). Then the filtrate was concentrated by vacuum rotary evaporation to a saturated solution, which was added *n*-hexane (30 mL) to generate white solid washed with pentane (3×10 mL) to afford pure complex **4a** as off-white solid (46 mg, 42 % yield). Other complexes were obtained by similar methods.



Fig. 3. XRD patterns of MWNTs (a) and MWNTs@NHC-Cu (b).



Fig. 4. FT-IR spectra of NHC-Cu (4c), MWNTs and MWNTs@NHC-Cu.

4a: off-white, 45 % yield, ¹H NMR (400 MHz, DMSO) δ 8.25 – 8.14 (m, 1 H), 7.95 (dddd, J = 28.6, 21.0, 17.0, 8.1 Hz, 7 H), 7.77 (d, J = 8.9 Hz, 1 H), 7.71 (q, J = 8.6 Hz, 1 H), 7.43 (t, J = 7.9 Hz, 2 H), 7.34 – 7.22 (m, 3 H), 7.12 (dt, J = 14.4, 7.0 Hz, 3 H), 5.54 (s, 2 H), 5.09 (d, J = 11.5 Hz, 2 H), 4.70 (d, J = 11.4 Hz, 2 H). ¹³C NMR (101 MHz, DMSO) δ 193.6, 151.5, 136.4, 134.0, 133.1, 130.9, 130.7, 128.4, 127.59, 127.32, 127.1, 126.9, 126.3, 126.2, 125.9 125.5, 124.7, 124.3, 124.2, 124.1, 124.0, 123.7, 123.3, 122.7, 121.9, 120.75, 119.00, 111.86, 111.61, 109.12, 67.2, 50.9, 47.2. HRMS (ESI): calcd for C₆₄H₄₈CuN₄O₂ [2M–2Cl–Cu]⁺: 967.3073, found 967.2991

4b: white soild, 42 % yield, ¹H NMR (400 MHz, DMSO) δ 8.13 – 7.82 (m, 7 H), 7.75 (dd, J = 26.7, 9.1 Hz, 2 H), 7.40 (t, J = 8.1 Hz, 3 H), 7.30 (d, J = 5.6 Hz, 3 H), 7.11 (dd, J = 14.5, 7.0 Hz, 3 H), 5.59 (d, J = 27.7 Hz, 2 H), 5.09 (s, 2 H), 4.70 (s, 2 H). ¹³C NMR (101 MHz, DMSO) δ 191.6, 151.5, 136.3, 134.0, 133.1, 130.9, 130.7, 128.4, 127.6, 127.1, 126.9, 126.2, 125.9, 125.5, 124.8, 124.3, 124.0, 123.7, 123.3, 120.7, 119.0, 111.8, 111.6, 109.1, 67.2, 50.8, 47.1. HRMS (ESI): calcd for C₆₄H₄₈CuN₄O₂ [2M–2Br–Cu]⁺: 967.3073, found 967.3068

4c: off-white, 48 %yield, ¹H NMR (400 MHz, DMSO) δ 8.07 (dd, J = 14.0, 7.4 Hz, 4 H), 8.00 – 7.86 (m, 3 H), 7.80 (t, J = 8.5 Hz, 2 H), 7.60 (d, J = 8.6 Hz, 1 H), 7.43 (dd, J = 13.9, 7.3 Hz, 2 H), 7.35 – 7.23 (m, 3 H), 7.20 – 7.10 (m, 3 H), 5.48 (s, 2 H), 5.08 (t, J = 8.5 Hz, 2 H), 4.78 (t, J = 4.5 Hz, 2 H). ¹³C NMR (101 MHz, DMSO) δ 194.6, 151.6, 136.4, 134.3, 133.2, 130.9, 130.7, 128.4, 127.5, 127.3, 127.1, 126.9, 126.2, 125.9, 125.5, 124.7,124.5, 124.2, 124.0, 123.7, 123.2, 120.7, 118.9, 111.8, 111.5, 109.2, 67.4, 50.8, 47.0. HRMS (ESI): calcd for C₆₄H₄₈CuN₄O₂ [2M–2I–Cu]⁺: 967.3073, found 967.3043

4d: light-pink, 40 % yield, ¹H NMR (400 MHz, DMSO) δ 8.08 – 7.94 (m, 5 H), 7.90 (t, *J* =7.6 Hz, 1 H), 7.76 (dt, *J* = 13.2, 9.1 Hz, 3 H), 7.61 (dd, *J* = 16.9, 8.3 Hz, 2 H), 7.47 (t, *J* =7.5 Hz, 1 H), 7.40 (t, *J* =7.6 Hz, 1 H), 5.11 (s, 2 H), 4.84 (d, *J* = 4.4 Hz, 2 H), 4.27 (t, *J* =7.1 Hz, 2 H), 1.85 – 1.70 (m, 2 H), 1.21 (dd, *J* = 14.5, 7.5 Hz, 3 H), 0.78 – 0.65 (m, 3 H). ¹³C NMR (101 MHz, DMSO) δ 191.5, 151.5, 133.6, 133.2, 130.9, 130.8, 130.6, 126.8, 126.2, 125.9, 125.6, 124.6, 124.3, 124.0, 123.8,123.6, 123.4,123.2, 123.3, 123.1, 120.9, 120.6, 119.1, 111.8, 111.5, 111.3, 109.4, 67.9, 66.2, 47.4, 47.3, 47.1,46.3, 32.0, 19.5, 13.52. HRMS (ESI): calcd for C₅₈H₅₂CuN₄O₂ [2M–2I–Cu]⁺: 899.3386, found 899.3362

4e: light-pink, 47 % yield, ¹H NMR (400 MHz, DMSO) δ 8.13 – 7.90 (m, 6 H), 7.84 (d, *J* =9.0 Hz, 1 H), 7.81 – 7.72 (m, 2 H), 7.63 (d, *J* =7.0 Hz, 2 H), 7.49 (t, *J* =7.6 Hz, 1 H), 7.42 (t, *J* =7.6 Hz, 1 H), 5.08 (s, 2 H), 4.82 (s, 2 H), 4.23 (t, *J* =6.8 Hz, 2 H), 1.81 – 1.63 (m, 2 H), 1.15 (s, 2 H), 1.08 – 0.89 (m, 4 H), 0.72 – 0.48 (m, 3 H). ¹³C NMR (101 MHz, DMSO) δ 191.1, 151.6, 133.7, 133.2, 130.9, 130.7, 127.3,127.0, 126.9, 126.3, 125.9, 125.6, 124.7, 124.3, 124.0, 123.8, 123.3, 120.8, 119.1, 111.9, 111.4, 109.4, 47.5, 46.9, 30.7, 29.9, 25.8, 21.8, 13.6. HRMS (ESI): calcd for C₆₂H₆₀CuN₄O₂ [2M–2I–Cu]⁺: 955.4012, found 955.3996.

2.3. Procedure for immobilization of NHC-Cu complex on MWNTs

The immobilization of NHC-Cu complex on MWNTs catalyst was prepared similarly by using one-step synthesis process [39] which was demonstrated in Scheme 3.

First, 300 mg of carbon nanotubes was dispersed under ultrasonication in 50 mL of methylene chloride for 30 min. Then complex **4c** (120 mg) of dissolved with 50 mL of dichloromethane was added into above mixture for further ultrasonication for 30 min and stirred overnight. The resulting mixture was filtered and then washed with dichloromethane (3×20 mL) to remove unloaded **4c**, marked as MWNTs@NHC-Cu. The loading of the complex measured by ICP-AES is 0.15 mmol/g.



Fig. 5. Cu 2p XPS spectra of a: NHC-Cu(4c) b: MWNTs@NHC-Cu c: MWNTs@NHC-Cu after reaction and the MWNTs@NHC-Cu composite spectra.

2.4. General procedure for homogeneous cycloaddition reaction of azide and alkyne

To a vial fitted with a screw cap, azide (1.0 mmol), alkyne (1.2 mmol) and NHC-Cu complex catalyst were added and stirred at 30 °C. The reaction process was monitored by TLC. After the reaction, the filtered solid product was washed with water and *n*-hexane and dried at 60° C to get the corresponding product (No further purification is required). For three-component click cycloaddition reaction, the reaction was carried out by using organic halide (1.0 mmol), alkyne (1.0 mmol) and NaN₃ (1.2 mmol) as the substrates and 3 mL H₂O as the solvent. The purity of the crude product is more than 95 % by ¹H NMR.

2.5. General procedure for the cycloaddition reaction catalyzed by *MWNTs-supported 4c* and the corresponding recycle

To a vial fitted with a screw cap, azide (1.0 mmol), alkyne (1.2 mmol) and MWNTs@NHC-Cu were added and stirred at room temperature. After the reaction was completed, the mixture was extracted by 10 mL of dichloromethane to give the crude product and was filtered to isolate the catalyst washed with dichloromethane (3×2 mL). The crude product was obtained by rotary evaporation to remove the solvent, washed with water and *n*-hexane and further dried. The purity of the crude product is greater than 95 % by ¹H NMR. The separated catalyst was vacuum dried at 40° C, and then used for the next cycle test.

3. Results and discussions

3.1. Optimization of MWNTs@NHC-Cu reaction conditions

We have successfully synthesized five different types of NHC-Cu with different side chain R groups and coordinating with different halogens, which were characterized by NMR and HR-MS spectroscopy to clarify their structure (Shown in Scheme 2). Due to the instability of NHC-Cu, a large number of [Cu(NHC)₂]⁺ species appear in high-resolution mass spectrometry, which presents a confusion of ligands [45,46]. Therefore, we further verify its structure by measuring the content of copper in the compound by ICP-AES and through the anion mode of high-resolution mass spectrometry to determine its coordinated halogen, indicating that it was formed as NHC-Cu species. Through the activity test, it is found that the conversion rate of azide-alkyne cycloaddition reaction is lower in the presence of the solvent such as THF, CH₃CN, CH₃OH, but pleasantly, there is a noticeable acceleration without solvent (Show in Table 1).

Then, we tested the activity of the five kinds of NHC-Cu prepared without solvent, and found that 4c had a better catalytic performance (Show in Table 1). The substrate is completely converted within three hours at 30 °C. We attribute it to two aspects. On the one hand, it is possible that I was easier to leave the Cu(I)(active center) than Br and Cl to form a copper acetylide intermediate [8,47]. On the other hand, the benzene ring has greater rigidity and less steric hindrance than other straight-chain alkanes, making the alkynyl group closer to the active center. For the above reasons, 4c has better activity than other complexes. Therefore, we choose 4c as the precursor of the load. The content of 4c was determined by ICP to be 0.15 mmol/g.



Fig. 6. a, b: TEM image of the MWNTs. c, d: TEM image of the MWNTs@NHC-Cu. e: STEM images of the MWNTs@NHC-Cu. f, g, h: Corresponding EDS line scan profiles for C, N, and Cu along the line.

We compared the catalytic activity before and after 4c immobilization and found that there was no obvious difference (Show in Fig.1). MWNTs@NHC-Cu has a TOF value of 32.67 h^{-1} when the product is close to complete conversion after three hours under mild conditions. ^a

This shows that the immobilization of the homogeneous catalyst does not significantly affect the activity of the catalyst, which is consistent with our original purpose. NHC-Cu is conjugated on the surface of carbon nanotubes through π - π bonds and plays a catalytic role. By comparing items 10 and 11 (Show in Table 2), we find that the ligand has a significant acceleration effect. During the click reaction, (NHCH)⁺ [(Ph=C⁻)CuX]- are easily formed [47]. Therefore, we believe that 3b (NHCH)⁺ X- may act as a base and reacts with phenylacetylene to remove a molecule of HX to obtain an (NHCH)⁺ [(Ph=C⁻)CuX]-. Then, this intermediate is subjected to the HX removal reaction to obtain acetylide copper ligand Ph=C-Cu-NHC to promote the reaction. The amount of 4c also has a significant effect on the reaction.

3.2. Characterization of MWNTs@NHC-Cu

3.2.1. Discussion of TGA

TGA investigations on the thermal degradation of NHC-Cu, MWNTs, MWNTs@NHC-Cu in nitrogen were the temperature range of r. t. – 800 °C at a heating rate of 10 °C/min. The thermogravimetric experiment showed that the decomposition temperature of the NHC-Cu was between 280 °C and 420 °C (Show in Fig. 2). The MWNTS@NHC-Cu had a more significant weight loss at around 350 °C compared to the original MWNTs. It showed that the NHC-Cu complex was successfully loaded on the MWNTs.

3.2.2. Study of XRD

XRD patterns of the functionalized MWNTs before and after 4c immobilized. Both samples have an obvious diffraction peak at 26.1° (Show in Fig. 3) which is attributed to the (002) planes of crystalline graphite-like materials [48]. We can see that there is a slight decrease in the intensity of the peak after loading. This may be due to the complexes loaded on the surface of the carbon nanotubes increasing the disorder of the crystal lattice. This also confirms the successful loading of the complex from another level. The absence of crystal face peaks of the complex indicates that it does not show an aggregated form but was evenly distributed.

3.2.3. FT-IR analysis

Although the absorption peak of NHC-Cu is mostly curtained off by carbon nanotubes, after careful identification, we can still find the corresponding peak of NHC-Cu. NHC-Cu has a strong infrared absorption peak at 1250 cm⁻¹ (Show in Fig. 4), which is attributed to the stretching vibration of C—O—C, and correspondingly an enhanced absorption peak appears in MWNTs@NHC-Cu.

3.2.4. XPS analysis

Through the above analysis, we confirmed that NHC-Cu was successfully loaded onto MWNTs. Further, we characterized the state of the NHC-Cu on MWNTs. XPS analysis was performed on the solid samples and the complex 4c. The binding energies of a, b, and c are all around 933ev and 953ev (Show in Fig.5), and they are attributed to Cu $2p_{3/2}$ and Cu $3p_{1/2}$, respectively, which are consistent with what is reported in the literature [49], indicating that there was no change during the whole load process. Meanwhile, through composite spectra, we can also see that the existence of the Cu, I, O, N, C, elements confirm the existence of



Fig. 7. i, g: TEM image after four runs of MWNTs@NHC-Cu. k: STEM images of the MWNTs@NHC-Cu after recycling. l, m, n: Corresponding EDS line scan profiles for C, N, and Cu along the line.

Table 3

Cycloaddition reaction of azides and alkynes catalyzed by MWNTs@NHC-Cu a.

R.—N. + P	$= \underbrace{MWNTs_{\mathbb{Q}}NHC-Cu}_{N} \underbrace{K_{1} N}_{N} N}_{N}$				
$K_1 M_3 K_2^-$	neat 30°C	R ₂			
Entry	Azide	Alkyne	Product	Isolated yield (%)	
1	N ₃	\$~~~~		82	
2	₩ ^{N3}	₩=	5b	91	
3	₩ ^N a	$\mathbf{H} = \sqrt{2} \mathbf{H}$	5c	86	
4	₩ ^{N3}			90	
5	N ₃	н-=-	N.N. 5f	87	
6		н-=-{	Sg CJ	90	
7	N ₃	+=-{}	Sh North	84	
0		H-={_}NH_2		94	
10		H-=-{_}-0´	5j	77	
10	N ₃	н-=-		<i>``</i>	
11			SI	89	
12	Br	√→==+	Sm 5m	03	
19	N ₃	< <u> </u> H	5n C	20	
14	Br	Кн		90	
15	CN N3	——н		92	
17	~~~~N ₃	Кн	5p ~~ ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	92 ^b	
18	~~~~N ₃	<_>−н		93 ^b	

[a] Reaction conditions: 1 mol% catalyst MWNTs@NHC-Cu, 1 mmol organic azide, 1.2 mmol alkyne, reaction temperature 30 °C, reaction time 3 h. [b] 3 mol% catalyst MWNTs@NHC-Cu, reaction time 3 h.

5s

4c. There is no change in the binding energy of Cu 2p before and after the reaction, which is consistent with that before loading, indicating that the complex remained intact, and the real catalyst is NHC-Cu which returned to its original position through a completed catalytic cycle. Our catalyst can exist stably throughout the loading and catalytic reaction process without degradation.

3.2.5. TEM analysis

The supported catalyst and multi-walled carbon nanotubes were further studied through TEM and Energy-dispersive X-ray (EDX) mapping. Comparison before (a, b) and after (c, d) loading, there was no obvious difference and we did not found agglomeration of metal particles or complex molecules indicating that the complexes are uniformly distributed on the carbon nanotubes at the molecular level (Show in Fig. 6). But Energy dispersive X-ray (EDX) mapping and line-scan analysis (f, g, h) can obtain the distribution, and Cu on the surface of MWNTs. Due to the low copper content, the response signal value of copper may be lower. However, some enhanced signals can still be seen in the significant range of carbon and nitrogen signals which indicates the presence of copper.

After cycles of MWNTs@NHC-Cu, we conducted a TEM test on the MWNTs@NHC-Cu. Through i and g (Show in Fig. 7), we did not find obvious copper or copper ion aggregates on the surface of the carrier after the reaction. Besides, the scanning transmission electron microscopy (STEM) images and energy disperse spectroscopy mappings of MWNTs@NHC-Cu reveals that the Cu and N components are distributed throughout the catalyst. Although the signal value of copper is low, it still shows a trend similar to that of nitrogen which shows that the NHC-Cu is distributed on the carrier.

3.3. Substrate scope of the azide-alkyne cycloaddition reaction

For cycloaddition reactions of click, we found that the reaction between azide and acetylene, whether it is aliphatic or aromatic, has a good yield under mild reaction conditions (Show in Table 3). The results indicated that our catalyst has broad substrate adaptability, which is consistent with the ideal of azide-alkyne cycloaddition reaction. The reaction has good compatibility with various functional groups and is prompt, convenient and efficient.

3.4. Catalyst recycling

The cyclability of the catalyst is a very important characteristic of heterogeneous catalysts. Therefore, we conducted a cycle test on the



Fig. 9. The effect of catalyst removal on click reaction in ethanol solvent.[a] Reaction conditions: 1 mol% catalyst MWNTs@NHC-Cu, 1 mmol azide, 1.2 mmol alkyne, reaction temperature 70 °C, ethanol as solvent.

MWNTS@NHC-Cu. At the same time, we use the time-yield distribution graph to determine the degree of inactivation. The supported catalyst can be recycled four times without significant loss of activity. But in the fifth cycle, there was an obvious loss of activity (Shown in Fig. 8a). The unchanged binding energy of copper before and after the reaction indicates that the state of copper present in the catalyst has not changed, namely NHC-Cu(I). The resulting loss of activity is not due to changes in the valence of copper. ICP analysis was realized after four runs, it is found that the copper loss is close to 23 %. Therefore, it caused a significant decrease in activity. We assumed that part of the reason for the serious loss of copper is that the product encapsulates the complex loaded on the carbon nanotubes so that it is easily lost with the product during separation.

3.5. Hot filtration experiment

We conducted a hot filtration experiment on the MWNTs@NHC-Cu with ethanol as the solvent ^a. In the early stage of the reaction, a hot filtration experiment was performed on the reaction, and then the reaction solution and the original reaction were monitored (Shown in Fig. 9). It was found that the reaction solution did not react further,



Fig. 8. a: The recycling of the MWNTs@NHC-Cu (1 mol%). b: valid assessment by rates: the consecutive experimental runs 1–3 to examine the extent of deactivation Reaction condition: neat, 30 °C, for 3 h, using a model reaction of phenylacetylene and azide.

Table 4

Three-component cycloaddition reaction catalyzed by 4c.

R ₁ —X + R ₂ —	\equiv + NaN ₃ $\frac{4c}{H_{O}}$	$R_1 N N$		
	1120	R ₂		
Entry	R ₁ -X	Alkyne	Product	Isolated yield(%)
1	Ph Br	Дун	N.N.N.	98 ^a
2	Ph ^A Br	{н	5a N ^N N	90 ^a
3	Ph Br	н	St V	93 ^a
4	Ph Br	_0-{_}-н	59 LL	94 ^a
5	Ph [^] Br	н	5j vo	95 ^a
6	Ph Br	СІН	5d ~~~	93 ^a
7	Ph Br	CN-		96 ^a
8	Ph ^{Cl}	-{_}=-н		90 ^b
9	Ph ^{CI}	—	5t 5t	94 ^b
10	Ph ^{CI}	_0-		92 ^b
11	Ph ^{Cl}	Щ С	N.N.N. 5d	92 ^b
12	Ph ^{Cl}	СІК		95 ^b
13	Ph ^{Cl}	CN-		96 ^b
14	Ph ^{Cl}	Хн		88 ^b
15	Br	————————————————————————————————————	5f N = N N = N Sq	90 ^c
16	∕∕∕~Br	Дун	,,,,,,,, .	92 ^c
17	∕∕∕~_ _{Br}	—— н	5s	94 ^c

[a] Reaction conditions: 3 mol% 4c, 1 mmol benzyl bromide (PhCH₂Br), 1.2 mmol NaN₃, 1.2 mmol alkyne, 3 mL H₂O, reaction temperature 30 °C, reaction time 5 h. [b] Reaction conditions: 3 mol% 4c, 1 mmol benzyl chloride (PhCH₂Cl), 1.2 mmol NaN₃, 1.2 mmol alkyne, 3 mL H₂O, reaction temperature 30 °C, reaction time 20 h. [c] Reaction conditions: 3 mol% 4c, 1 mmol RBr, 1.2 mmol NaN₃, 1.2 mmol phenylacetylene, 3 mL H₂O, reaction temperature 40 °C, reaction time 24 h.



Fig. 10. The recycling of the MWNTs@NHC-Cu(3 mol%). Reaction condition: 30 °C, for 5 h, using a model reaction of benzyl bromide, phenylacetylene and Sodium azide.

which proved the heterogeneity of the catalyst and no detectable obvious contribution came from the homogeneous catalyst.

Due to the potential dangers of organic azides in the synthesis process, we tested the three-component click cycloaddition reaction that uses organic halides and sodium azide for direct cycloaddition with alkyne and found that our catalyst still has good catalytic activity for this reaction (Table 4).

3.6. Three-component cycloaddition reaction

3.6.1. Catalyst recycling of three-component [3 + 2] cycloaddition reaction

Then, we carried out a catalytic cycle on the MWNTs@NHC-Cu and found that the circularity was short of (Shown in Fig. 10). We performed an ICP measurement on the used catalyst. Nearly 20 % of copper is lost after the first run, which resulted in a significant decrease in catalytic activity. There may be two main reasons for the loss of copper(I) one is the separation process between a product which are attached to the catalyst and catalyst. The other is that NHC-Cu desorbed from carbon nanotubes under the influence of the solvent [57–59]. Based on the above two reasons, Significant copper loss occurred after the first cycle. poor cyclicity occurred in the three-component cycloaddition reaction.

3.7. Possible mechanisms

Based on previous research [47,60–62], a possible reaction mechanisms of cycloaddition reaction of azides and alkynes through NHC-Cu Complexes (Shown in Fig. 11) was proposed. First, acetylide copper ligand is formed by NHC-Cu dissociation and phenylacetylene deprotonation. Then, a stable six-membered ring is formed by reacting with azide, acetylide copper ligand. Finally, this six-membered ring intermediate underwent a rapid ring contraction to form another more stable

five-membered ring which It reacts with phenylacetylene to produce a product and another molecule of acetylide copper ligand entering the next catalytic cycle.

In addition, in comparison with the other recently reported Cu catalyzed cycloaddition reaction for the synthesis of triazoles, MWNTs@NHC-Cu has higher catalytic activity (Table 5).

4. Conclusions

In summary, we have successfully prepared five novel pyrene-tagged NHC-Cu molecular complexes and characterized by ¹H- and ¹³C- NMR, and high resolution ESI-mass spectrometry to clarify their structure. Moreover, MWNTs supported NHC-Cu catalytic material was achieved by via π - π stacking between pyrene and carbon nanotube. Both the NHC-Cu molecular complexes and the immobilized homogeneous catalyst onto carbon nanotube are demonstrated to be highly effective in the two-component click cycloaddition reaction of terminal alkynes and organic azides or three-component click cycloaddition reaction that employs various terminal alkynes, NaN3 and organic halides with the advantage of excellent yields. Especially, the immobilization catalyst displayed competitive advantages, including no need to add other ligands and easy catalyst recycling, allowing several reuses with no significant loss in catalytic activity. This may be due either to a facilitated boomerang effect or to a gradual release of the active species in solution. It nevertheless describes the first use of multi-walled carbon nanotubes as support for such NHC-Cu catalysts by π - π interaction, as far as we know, and its successful use in recycling methodologies for azide-alkyne



Fig. 11. Possible reaction mechanisms of azide-alkyne cycloaddition reaction.

Comparison of MWNTs@NHC-Cu with other reported catalysts for the synthesis of triazoles.

Entry	Catalyst	Solvent	[Cu] (mol%)	Temp.(°C)	Time (h)	Yield (%)	Refs
1	PS[NEt ₃][OAc](CuI)	t-BuOH/H ₂ O	13	R.T	12	100	[50]
2	NRGO/Cu(I)	THF	2	R.T	48	100	[51]
3	TRGO/Cu	water/methanol	2	R.T	24	99	[52]
4	Fe ₃ O ₄ /Si[CuI]	water	0.25	R.T	18	92	[53]
5	CRGO-Ima-CuI	THF	2	40	72	99	[54]
6	Cu NPs	[BMIM][BF ₄]/water	5	R.T	0.3	90	[55]
7	Poly(M1-co-M3)- b-poly(M2)–Cu	water	0.25	R.T	16	53	[56]
8	MWNTs@NHC-Cu	neat	1	30	3	95	Present work

cycloaddition reactions. Further work is being undertaken in order to improve the performance of the immobilized homogeneous catalyst onto carbon materials in other organic transformations.

Declaration of Competing Interest

The authors report no declarations of interest.

CRediT authorship contribution statement

Xiangjie Zhang: Conceptualization, Methodology, Writing - original draft. Bingyang Wang: Conceptualization, Methodology. Yanmei Lu: Validation. Chungu Xia: Supervision. Jianhua Liu: Supervision, Funding acquisition, Writing - original draft, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2021.111452.

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