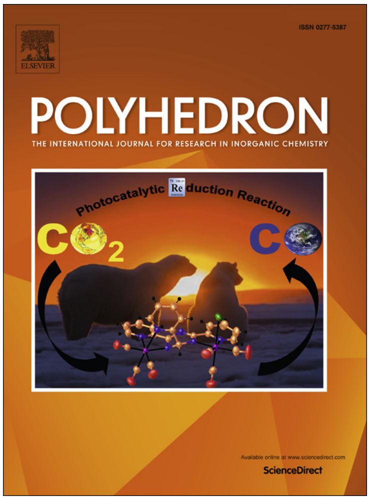

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Ali Zarnegaryan, Majid Moghadam, Shahram Tangestaninejad, Valiollah Mirkhani, Iraj Mohammadpoor–Baltork

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Synthesis and characterization of a novel polyoxometalate–Cu(II) hybrid catalyst for efficient synthesis of triazols

Ali Zarnegaryan, Majid Moghadam,* Shahram Tangestaninejad, * Valiollah Mirkhani,* Iraj Mohammadpoor–Baltork

Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan 81746–73441, Iran

Abstract– A new hybrid complex based on covalent interaction between 1,2–bis(*p*–aminophenylthio)– ethane, (BAPTE), and a Lindqvist type polyoxometalate, $Mo_6O_{19}{}^{2-}$, was prepared. This new hybrid catalyst, $Cu^{II}(BAPTE)Cl_2–[n–Bu_4N]_4[Mo_6O_{18}]_2$, was characterized by ^1H NMR, FT– IR, and UV–vis spectroscopic methods and cyclic voltammetry. The catalytic activity of $Cu^{II}(BAPTE)Cl_2–[n–Bu_4N]_4[Mo_6O_{18}]_2$ hybrid material was investigated in the three component reaction of sodium azide, phenylacetylene and benzyl halides and the corresponding triazoles were produced in good to excellent yield. The reusability of this catalyst was also investigated.

Keywords. *Polyoxometalate; Inorganic–organic compound; Click reaction; Hybrid copper(II) catalyst.*

1. Introduction

Polyoxometalate (POM) anions represent an important class of nanosized polynuclear clusters consisting of d–block transition metals and oxygen atoms. The tunability of their size, structure and elemental composition, and hence of their chemical and electronic properties, render them

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*Corresponding authors: Tel: +98-31-37934920; Fax: +98-31-36689732; E-mails: moghadamm@sci.ui.ac.ir (M. Moghadam); stanges@sci.ui.ac.ir (S. Tangestaninejad); mirkhani@sci.ui.ac.ir (V. Mirkhani).

particularly interesting both for fundamental and applied science, especially for catalysis, materials science and medicine [1−5].

Modification of POMs is very important for their subsequent research and application. An effective way to achieve this goal is to modify the POMs with organic materials to obtain organic–inorganic hybrids. Organic components can dramatically influence the microstructure of hybrid materials. In addition, the synergic interactions between organic and inorganic components may be exploited in the preparation, which make hybrid materials exhibit composite properties [6]. Thus, construction of such hybrid materials involves the selection and design of organic and inorganic building units as well as the control of synergic interactions between the counterparts [7, 8].

Lindqvist hexamolybdate cluster, $[Mo_6O_{19}]^{2-}$ (Fig. 1), as a unique class of metal oxide clusters, is an ideal building block for constructing the organic–inorganic hybrid assemblies [9−11].

Two coordination approaches for the assembly of POMs into macrostructures are as following: (i) Transition metal−substituted POMs are chosen as subunits and organic ligands as intermolecular linkers through coordinating with transition metal ions [12, 13]. (ii) Preformed organic derivatives of POMs, that is POM−functionalized organic ligands, are utilized as building blocks, and transition metal ions as linkers via a well−defined coordination mode [14−18].

Copper(II) containing complexes have been widely used as linking units for construction of hybrid compounds due to their relatively strong coordination abilities with both S and N donor atoms of organic ligands, as well as due to their capacity to adopt various coordination numbers [19].

The copper−catalyzed azide−alkyne cycloaddition (CuAAC) has received much attention in recent years [20−24]. In this reaction, a terminal azide is co pled with an alkyne to produce 1, 2,3−triazoles via a [3+2] Huisgen cycloaddition. This reaction is an excellent example of “click” chemistry because of its selectivity and tolerance to a variety of reaction conditions. It is well known that the best catalyst for this reaction is Cu (I) species [25,26]. The most advantages of these copper catalyzed reactions are wide−ranging scope, using readily available reagents, and insensitivity to oxygen and water [27−30]. Recent studies have shown that highly efficient reactions generically known as "click" reactions provide a versatile route toward highly functional surfaces [31−33].

In recent years, we reported the application of different hybrid materials in catalysis. The [MoO_2 (*N,N′*–(salicylidene)ethylenediamine)−$K_8(SiW_{11}O_{39})$], [MoO_2(acac)–$K_8(SiW_{11}O_{39})$], [Fe(III)(*N,N′*–(salicylidene)ethylenediamine)−$K_8(SiW_{11}O_{39})$], [nickel(*N,N′*–bis(salicylidene)ethylenediamine)−K_8 $(SiW_{11}O_{39})$] and [cobalt(*N,N′*–bis(salicylidene)ethylenediamine)−$K_8(SiW_{11}O_{39})$] systems have been studied in the oxidation of olefins or benzyl halides [14−18]. Recently, we prepared metalloporphyrins–polyoxometalate hybrid compounds and investigated their catalytic activity in the in the epoxidation of alkenes and acetylation of alcohols and phenols [34, 35].

The goal of this research was to prepare a new hybrid material based on the covalent attachment of Lindqvist $Mo_6O_{19}^{2-}$ to copper complex of 1,2−*bis*(*p*−aminophenythio)ethane, BAPTE. This new heterogeneous catalyst, Cu^{II}(BAPTE)Cl_2−[*n*−Bu_4N]$_4$[Mo_6O_{18}]$_2$, was applied in the synthesis of 1,2,3−triazoles by the reaction of phenylacetylenes with benzyl halides in the presence of sodium azide (Scheme 1).

2. Experimental

All chemicals were used as received from the suppliers. Solvents were used as received or distilled and dried using the standard procedures. Tetrabutylammonium hexamolybdate, [(*n*−$C_4H_9)_4N]_2[Mo_6O_{19}]$ was prepared according to the literature method [36].The ligand, 1,2−*bis*(*p*−aminophenylthio)ethane (BAPTE) was synthesized according to a reported procedure [37].All the synthetic procedures were performed protected from light. ^1H NMR spectra were recorded on a Bruker−Avance AQS 400 MHz NMR spectrometer using DMSO as solvent. Elemental analyses were measured by a Perkin Elmer 2400 instrument. The amount of Mo was measured by a Leaman inductively coupled plasma (ICP) spectrometer. Atomic absorption analysis was carried out on a Shimadzu 120 spectrophotometer. The electronic spectra of the compounds in the UV−vis region were recorded in DMF solution using a Shimadzu 160 UV−vis or a Varian Cary NIR spectrophotometer. FT−IR spectra were obtained as potassium bromide pellets in the range

400–4000 cm^{-1} with a Jasco 6300D instrument. Redox potentials of the compounds (10^{-3} $molL^{-1}$) in DMF containing tetrabutylammonium bromide (TBAB, 0.1 $molL^{-1}$) as a supporting electrolyte were determined at room temperature by cyclic voltammetry with a PGSTAT30 (Eco Chemie, Utrecht, The Netherlands) electrochemical analyzer. A three−electrode cell was used, including glassy carbon electrode as working electrode, together with an Ag/AgCl (saturated KCl) and a platinum wire as reference and counter electrode, respectively.

2.1. Synthesis of 1,2−bis(p−aminophenylthio)ethane, BAPTE

In a round−bottom flask, 4−aminothiophenol (2.5 g, 20 mmol) was added to absolute EtOH (20 ml) containing Na (0.46 g, 20 mmol). Then, 1,2−dibromoethane (0.86 ml, 10 mmol) in EtOH (5 ml) was added dropwise with constant stirring to the refluxing solution. The mixture was cooled and poured into H_2O (300 ml). The solid was filtered off, washed with H_2O and dried. The product was recrystallized from EtOH, and a yellowish residue was obtained. Yield: 68%, m.p. 79 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.19 (2H, d), 7.21 (2H, m), 6.60 (2H, m), 6.62 (2H, d), 3.73 (4H, m), 2.89 (4H, m). FT−IR (KBr) (cm^{-1}): 3416(s), 2932 (w), 2280 (w), 1630 (w), 1592 (m), 1493(s), 1283 (s), 1176 (m), 1117 (m), 819 (s).

2.2. Synthesis (BAPTE)−[n−Bu$_4$N]$_4$[Mo$_6$O$_{18}$]$_2$

In a round−bottom flask, BAPTE (69 mg, 0.25 mmol), $[(n-C_4H_9)_4N]_2[Mo_6O_{19}]$ (690 mg, 0.50 mmol) and *N,N′*−dicyclohexylcarbodiimide (DCC, 0.15 g, 0.72 mmol) were dissolved in anhydrous DMSO (10 mL) and heated at 100 °C under a dry atmosphere for 8 h. The reaction was cooled to room temperature and filtered under vacuum (to remove the dicyclohexylcarbodiurea) into a flask containing dry ether (100 mL) and dry methanol (20 mL). A precipitate was formed and washed several times with acetone and ether. Yield: %57, ^1H NMR (400 MHz, DMSO−d_6): δ=7.19 [d, 4H, protons aromatic], 6.60 [d, 4H, protons aromatic], 3.32 [t, 32 H, $(CH_3CH_2CH_2\underline{CH_2}N)$], 3.01 [s, 4H, SCH_2CH_2S], 1.57 [m, 32H, $(CH_3CH_2\underline{CH_2}CH_2N)$], 1.31 [q, 32H, $(CH_3\underline{CH_2}CH_2CH_2N)$], 0.94 [t, 48H, $(\underline{CH_3}CH_2CH_2CH_2N)$]; IR ($cm^{-1}$): 710 (C–C), 783 (Mo–O–Mo), 947 (Mo–O), 984 (Mo–N), 1148 (C–S), 1384 (C–N) 1490, 1642 (C=C), 2881, 2952, 3001 (C–H); 3092, 30123 (Ar–H); UV−vis spectrum (in DMF): (λ_{max}= 396 nm). Elemental Anal. calcd for $Mo_{12}O_{36}C_{78}H_{156}N_6S_2$: C, 31.54; H, 5.23; N, 2.85; S, 2.19. Found: C, 31.63; H, 5.16; N, 2.73; S, 2.11.

2.3. Synthesis of $Cu^{II}(BAPTE)Cl_2-[n-Bu_4N]_4[Mo_6O_{18}]_2$

In a round−bottom flask, (BAPTE)−$[n-Bu_4N]_4[Mo_6O_{18}]_2$ (0.38 g, 0.13 mmol) and $CuCl_2.2H_2O$ (0.02 g, 0.13 mmol) were dissolved in anhydrous DMF (10 mL) and heated to 100 °C under a dry atmosphere for 6 h. The reaction was cooled to room temperature and filtered under vacuum into a flask containing dry ether (100 mL) and dry methanol (20 mL). A precipitate was formed and washed several times with acetone and ether. The dried product was stored in a desiccator.

Yield: %53, IR (cm^{-1}): 448–472 (Cu–S), 708 (C–C), 781 (Mo–O–Mo), 946 (Mo–O), 982 (Mo–N), 1146 (C–S), 1382 (C–N), 1489, 1640 (C=C), 2880, 2950, 3000 (C–H); 3090, 30120 (Ar–H). Elemental Anal. calcd for $Mo_{12}O_{36}C_{78}H_{156}N_6S_2\ CuCl_2$: C, 30.24; H, 5.06; N, 2.75; S, 2.09. Found: C, 30.13; H, 5.03; N, 2.67; S, 2.02.

2.4. General procedure for synthesis of 1,2,3−triazoles

A mixture of $Cu^{II}(BAPTE)Cl_2-[n-Bu_4N]_4[Mo_6O_{18}]_2$ (1%, 30 mg) in H_2O/DMSO (3 mL, 1:10) was stirred for 10 min. Then, the phenylacetylenes (1.3 mmol), benzyl halide (1 mmol), sodium azide (1.1 mmol) and sodium ascorbate (5 mol%) were added, and the resulting mixture was stirred at room temperature. The progress of the reaction was monitored by TLC (eluting with *n*−hexane/ethyl acetate, 1:1). At the end of the reaction, methanol (5 mL) was added to precipitate the catalyst. The catalyst was recovered by centrifugation, washed with methanol and diethyl ether, and dried in vaccuo. The filtrates were concentrated and the pure product was obtained by thin layer chromatography.

3. Results and discussion

3.1. Preparation and characterization of $Cu^{II}(BAPTE)Cl_2-[n-Bu_4N]_4[Mo_6O_{18}]_2$

Usually, the association of a molecular unit to a POM is attained by electrostatic interaction [38]. However, in order to increase the stability of the hybrid material, especially in polar solvents; a covalent linkage was established between POM and dithiol ligand. The reaction between POM and the amines of the ligand was carried out according to the procedure reported for the attachment of hexamolybdate to aromatic amines in the presence of dicyclohexylcarbodiimide (DCC) [39]. Direct coupling of $Mo_6O_{19}^{2-}$ with BAPTE ligand in the presence of triethylamine was unsuccessful [40], but good results were obtained using DCC as coupling agent. The synthetic route for $Cu^{II}(BAPTE)Cl_2-[n-Bu_4N]_4[Mo_6O_{18}]_2$ is demonstrated in Scheme 2.

First, 4−aminothiophenol was reacted with 1,2−dibromoethane to produce BAPTE. Next, this ligand was hybridized with. tetrbutylammonium hexamolybdate in the presence of DCC and $(BAPTE)-[n-Bu_4N]_4[Mo_6O_{18}]_2$ was prepared. Finally, $(BAPTE)-[n-Bu_4N]_4[Mo_6O_{18}]_2$ was reacted with $CuCl_2.2H_2O$ for preparation of hybrid compound.

The hybrid compound is soluble in polar, aprotic solvents such as DMSO and DMF. Several attempts for preparation of single crystals of this hybrid compounds were unsuccessful. Therefore, this new hybrid material was characterized by FT−IR, UV−vis and ^1H NMR spectroscopic methods, and cyclic voltammetric studies. All these techniques provide more details for characterization of this polyoxometalate–copper complex hybrid material.

The FT−IR spectra of ligand and hybrid material are shown in Fig 2. The Lindqvist structure shows characteristic IR bands in the 700–1000 cm^{-1} region assigned to M–O and M–O–M stretching vibrations. The hybrid compound displays similar characteristic bands of the Lindqvist structure. Compared to the parent hexamolybdate anion, the asymmetric $Mo–O_b–Mo$ stretching vibration is bathochromically shifted respectively from 797 to 781 cm^{-1} for hybrid compound. These observations imply that these bonds are weakened to some extent due to the stronger Mo–N bonding interaction than that of Mo–O. In the case of hexamolybdate hybrid compounds, the Mo–O vibration is split into two or more bands as commonly observed in arylimido derivatives of hexamolybdate [39]. In this study, the Mo–O band at 957 cm^{-1} splits to three bands at 946, 933 and 915 cm^{-1}. Such splitting has been ascribed to the reduction in symmetry of the hexamolybdate framework from O_h to C_{4v} upon the substitution of Mo_tO by Mo_tNAr. The less intense band, a shoulder at 982 cm^{-1}, might associate principally with the Mo−N vibration. The vibrational bands at around 2900 cm^{-1} are assigned to the stretching vibrations of the methyl and methylene groups in the tetrabutylammonium cations. The bands at 1382 and 1146 can be attributed to the υ(C–N) of the arylimido group and ν(C–S), respectively. Upon attachment of Cu to the (BAPTE)−[n−$Bu_4N]_4[Mo_6O_{18}]_2$, a band was appeared in the range of 448–472 cm^{-1} due to ν_{as}(Cu–S) vibration.

The ^{1}H NMR spectra of BAPTE and (BAPTE)−[n−$Bu_4N]_4[Mo_6O_{18}]_2$ hybrid compound are shown in Fig. 3. These spectra clearly show resolved signals that can be unambiguously assigned. The signals correspond to the aromatic protons present at 6.60–7.21 ppm for BAPTE. In addition, the well−resolved signal at 3.73 ppm is attributed to the NH_2 protons of the ligand (Fig. 3A). Upon hybridization of ligand organic with hexamolybdate, all these signals exhibited downfield chemical shifts compared to the parent BAPTE. This can be attributed to the shielding effect of the POM cluster which is weaker than that of the amino group. This is due to the electron−withdrawing nature of the hexamolybdate moiety. In the (BAPTE)−[n−$Bu_4N]_4[Mo_6O_{18}]_2$ hybrid compound, the aromatic protons signals present at 7.21 and 7.09 ppm and the signal corresponding to the $–NH_2$ protons was disappeared in the hybrid compound.

The electronic properties of the POM, BAPTE, (BAPTE)−[n−$Bu_4N]_4[Mo_6O_{18}]_2$ and hybrid compound were also studied by UV−vis spectrophotometry (see Fig. S1−S4). The maximum absorption wavelength of the parent hexamolybdate is 325 nm, which is derived from the charge−transfer transition from the oxygen π−type HOMO to the molybdenum d−type LUMO. The strong band at 396 nm originates from the charge−transfer transition of the coordinated N atom to the molybdenum atom (LMCT) [41, 42]. The weak absorption peak in the UV−vis spectrum of $Cu^{II}(BAPTE)Cl_2$−[n−$Bu_4N]_4[Mo_6O_{18}]_2$ at 620 nm is attributed to the *d*−*d* transitions of the Cu(II) which is a good indication of complexation of hybrid compound.

The electrochemical properties of the BAPTE, POM and $Cu^{II}(BAPTE)Cl_2$−[n−$Bu_4N]_4[Mo_6O_{18}]_2$ were studied in degassed DMF containing tetrabutylammonium bromide (TBAB) (0.1 mol L^{-1}) as supporting electrolyte. All potentials are quoted relative to an Ag/AgCl (saturated KCl) electrode

[43]. The cyclic voltammogram (see Fig. S5–S7) of the hybrid compound showed a reduction wave (II) at −1.35 V. This remarkable cathodic shift in the reduction potential of this compound may be associated to the more difficult reduction of the polyoxometalate due to the electron–donating properties of the ring ligand toward the polyoxometalate. This is a similar behavior which has been reported in the attachment of 2, 2′–bipyridine (bipy) and 1,10–phenanthroline to hexamolybdate [44, 45]. One couple of redox peaks (I–I′) located at E_p= –0.75 V and E_p = –0.88 V is observed. These peaks correspond to reduction steps involving Mo atoms, which are similar to analogous compounds reported in the literature [46]. The CV of the parent hybrid compound showed a shift to positive potentials upon attachment of polyoxometalate. This can be attributed to the relatively facile reduction of the copper complex of 1,2−*bis*(*p*−aminophenythio)ethane moiety due to the very strong electron–withdrawing effect of the polyoxometalate. However, the oxidation peak of copper centers is not observed for hybrid compound, perhaps due to their weak signals embedded in the redox peaks of Mo [47–51].

3.2. Catalytic studies

$Cu^{II}(BAPTE)Cl_2-[n-Bu_4N]_4[Mo_6O_{18}]_2$ was used as catalyst in synthesis of triazoles. Initially, for screening experiments, the three−component reaction between phenylacetylene (1 mmol), 4−bromobenzyl bromide (1 mmol), and sodium azide (1.1 mmol) in H_2O/DMSO (1:10) was chosen as a model reaction (Table 1). In the absence of catalyst no appreciable amount of product was produced (Table 1, entry 1). The presence sodium ascorbate is necessary for reduction of Cu^{II} to Cu^{I} species. In the absence of sodium ascorbate only 10% of the corresponding triazole was produced (entry 2). While in the presence of sodium ascorbate and 1 mol% (30 mg) of $Cu^{II}(BAPTE)Cl_2-[n-Bu_4N]_4[Mo_6O_{18}]_2$, the highest yield was obtained (entry 4). As mentioned in the literature, the in the synthesis of unhybridized complex using $PhSCH_2CH_2SPh$ or *p*-H_2N-$PhSCH_2CH_2SPh$-NH_2 as ligand, polymeric materials were produced [52]. Therefore, to show the effect of hybridization on the catalytic activity of Cu^{II} (BAPTE), we refer to our recently published papers in the click reaction. In these two papers, we used a very similar ligand, 1,2-*bis*(4-

pyridylthio)ethane, immobilized on polystyrene and silica nanoparticles. The copper chloro complex was inactive in these reactions. Therefore, the chlorides were exchanged with OTf anions to increase the electron deficiency of copper center [53, 54]. But upon hybridization with POM, the catalytic activity of $Cu^{II}(BAPTE)Cl_2-[n-Bu_4N]_4[Mo_6O_{18}]_2$ increases. This can be attributed to the increasing the electron−deficiency of POM on the Cu^{II}(BAPTE). This shows the synergistic effect of hexamolybdate on the catalytic activity of Cu^{II} (BAPTE) Cl_2. The reaction was also performed in H_2O or DMSO and the results were less than using H_2O/DMSO (1:10) as reaction media (entries 6 and 7). The catalyst is soluble in this media and acts as a homogeneous catalyst in the click reaction. The $CuCl_2$ salt was less efficient in this reaction (entry 8). On the other hand, the catalytic activity of hexamolybdate (1 mmol) was also investigated in the model reaction. The results showed that the amount of the produced triazole was as same as blank experiments (Table 1, entry 9). These results clearly indicated that the [Cu^{II} (BAPTE) Cl_2] is the catalytic active site.

To further investigate the catalytic activity of this catalyst in the synthesis of triazoles, under the optimized reaction conditions, different benzyl bromides were reacted efficiently with phenylacetylene and sodium azide in the presence of $Cu^{II}(BAPTE)Cl_2-[n-Bu_4N]_4[Mo_6O_{18}]_2$, and the corresponding 1,4−disubstituted 1,2,3−triazoles were obtained in good to excellent yield (79−98%). Under the same conditions, the reactions of phenylacetylene with butyl bromide and 4−nitrobenzyl chloride proceeded efficiently to provide the desired 1,4−disubstituted 1,2,3−triazoles in 95% and 81% yield, respectively (entries 4 and 5). The reaction of substituted pheneylacetylenes such as 3−methoxy and 4−chlorophenylacetylene with substituted benzyl bromides was successfully performed and the desired 1,2,3−triazoles were produced in high yields (entries 7 and 8).

The stability of the Cu^{II} $(BAPTE)Cl_2-[n-Bu_4N]_4[Mo_6O_{18}]_2$ catalyst was monitored using multiple sequential reaction of 4−bromobenzyl bromide with phenylacetylene and sodium azide in the presence of sodium ascorbate. At the end of the reaction, the catalyst was separated as described in the experimental section. Then, the recovered catalyst was used in the next run with fresh

4−bromobenzyl bromide, phenylacetylene and sodium azide. The catalyst was consecutively reused five times without detectable catalyst leaching or significant loss of its activity (Table 3). The nature of recovered catalyst was investigated by FT-IR spectroscopy. As can be seen, the FT-IR spectrum of the reused catalyst is similar to fresh catalyst which shows the stability of the reused catalyst during the catalytic cycles (Fig. 1).

4. Conclusions

In summary, a new copper (II) complex–POM hybrid material was prepared via covalent interaction of 1,2−bis(*p*−aminophenylthio)ethane (BAPTE), and a Lindqvist type polyoxometalate, $Mo_6O_{19}^{2-}$. This new hybrid material was characterized and used as catalyst for efficient preparation of various 1,2,3−triazoles under mild conditions. The influence of the polyoxometalate on the catalytic activity of the catalyst was investigated. Short reaction times, excellent yields, easy work−up and reusability and stability of the catalyst are noteworthy advantages of this method.

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References:

[1] A. Dolbecq, E. Dumas, C. R. Mayer, P. Mialane, Chem. Rev. 110 (2010) 6009–6048.

[2] J. Zhang, F. Xiao, J. Hao, Y. Wei, Dalton Trans., 41(2012) 3599-3615.

[3] M. P. Santonia, G. S. Hanana, B. Hasenknopf, Coord. Chem. Rev. 281 (2014) 64–85.

[4] D. Y. Du, J. S. Qin, S. L. Li, Z. M. Su, Y. Q. Lan, Chem. Soc. Rev**.** 43 (2014) 4615−4632.

[5] D. Y. Du , L. K. Yan, Z. M. Su, S. L. Li, Y. Q. Lan, E. B. Wang, Coord. Chem. Rev. 257 (2013) 702–717.

[6] C. P. Pradeep, D. L. Long, G. N. Newton, Y. F. Song, L. Cronin, Angew. Chem. 120 (2008) 4460−4463; Angew. Chem. Int. Ed. 47 (2008) 4388−4391.

[7] J. Li, I. Huth, L. M. Chamoreau, B. Hasenknopf, E. Lacôte, S. Thorimbert, M. Malacria, Angew. Chem. 121 (2009) 2069−2072; Angew. Chem. Int. Ed. 48 (2009) 2035−2038.

[8] K. Pamin, M. Prończuk, S. Basg, W. Kubiak, Z. Sojka, J. Poltowiks, Inorg. Chem. Commun. 59 (2015) 13−16.

[9] H. R. Allcock, E. C. Bissell, E. T. Shaw, Inorg. Chem. 12 (1973) 2963–2968.

[10] X. Yang, T. Waters, X. B. Wang, R. A. J. O'Hair, A. G. Wedd, D. A. Dixon , L. S. Wang, J. Phys. Chem. A 108 (2004) 10089–10093.

[11] S. Bank, S. Liu, S. N. Shaikh, X. Sun, J. Zubieta, P. D. Ellis, Inorg. Chem. 127 (1988) 3535–3543.

[12] A. Dolbecq, C. M. Draznieks, P. Mialane, J. Marrot, G. Férey, F. Sécheresse, Eur. J. Inorg. Chem. 15 (2005) 3009−3018.

[13] S. T. Zheng, J. Zhang, G. Y. Yang, Angew. Chem. Int. Ed. 47 (2008) 3909−3913.

[14] M. Moghadam, V. Mirkhani, S. Tangestaninejad, I. M. Baltork and M. Moshref Javadi, Polyhedron 29 (2010) 648–654.

[15] M. Moghadam, V. Mirkhani, S. Tangestaninejad, I. M. Baltork, M. Moshref Javadi, Inorg. Chem. Commun. 13 (2010) 244–249.

[16] V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor−Baltork, N. Rasouli, Inorg. Chem. Commun. 10 (2007) 1537−1540.

[17] V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor−Baltork, N. Rasouli, Appl. Catal. A: Gen. 334 (2008) 106−111.

[18] V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor−Baltork, N. Rasouli, Catal. Commun. 9 (2008) 219−223.

[19] Z. Qu, K. Yu, Z. Zhao, Z. Su, J. Sha, C. Wang , B. Zhou, Dalton Trans. 43 (2014) 6744−6751.

[20] L. Liang, D. Astruc, Coord. Chem. Rev. 255 (2011) 2933–2945.

[21] Y. Xing, N. X. Wang, Coord. Chem. Rev. 256(2012) 938–952.

[22] B. Schulze, U.S. Schubert, Chem. Soc. Rev. 43 (2014), 2522–2571.

[23] W. Tanga, M. L. Becker, Chem. Soc. Rev.43 (2014) 7013–7039.

[24] K. Kempe, A. Krieg, C. R. Becer, U. S. Schubert, Chem. Soc. Rev, 41(2012) 176–191.

[25] C. E. Hoyle, A. B. Lowe, C. N. Bowman, Chem. Soc. Rev. 39 (2010) 1355−1387.

[26] Y. Zhang, S. Luo, Y. Tang, L. Yu, K.–Y. Hou, J.–P. Cheng, X. Zeng, P. G. Wang, Anal. Chem. 78 (2006) 2001–2008.

[27] V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, Angew. Chem. Int. Ed. 41 (2002) 2596–2599.

[28] C. W. Tornøe, C. Christensen, M. J. Meldal, Org. Chem. 67 (2002) 3057−3064.

[29] J. F. Lutz, Z. Zarafshani, Adv. Dru. Deliv. Rev. 60(2008) 958–970.

[30] A. B. Lowe, Polym. Chem. 1 (2010) 17−36.

[31] R. E. Ruther, M. L. Rigsby, J. B. Gerken, S. R. Hogendoorn, E. C. Landis, S. S. Stahl, R. J. Hamers, J. Am. Chem. Soc.133 (2011) 5692–5694.

[32] A. Devadoss, C. E. D. Chidsey, J. Am. Chem. Soc.129 (2007) 5370−5371.

[33] J. E. Hein, V. V. Fokin, Chem. Soc. Rev. 39 (2010) 1302−1315.

[34] M. Araghi, V. Mirkhani, M. Moghadam, S. Tangestaninejad I. Mohammdpoor−Baltork, Dalton Trans. 41 (2012) 3087−3094.

[35] M. Araghi, V. Mirkhani, M. Moghadam, S. Tangestaninejad I. Mohammdpoor−Baltork, Dalton Trans. 41 (2012) 11745−11752.

[36] N. H. Hur, W. G. Klemperer, R. C. Wang, Inorg.Synth. 27 (1990) 77–78.

[37] G. Mukherjee, S. N. Poddar, Transition Met.Chem. 35 (1988) 58−63.

[38] Y. Wei, B. Xu, C. L. Barnes, Z. Peng, J. Am. Chem. Soc. 123 (2001) 4083–4084.

[39] Y. Zhu, L. S. Wang, J. Hao, Z. C. Xiao, Y. G. Wei , Y. Wang, Cryst. Growth Des. 9 (2009) 3509 –3518.

[40] D. Tasis, N. Tagmatarchis, A. Bianco, M. Prato, Chem. Rev. 106 (2006) 1105−1136.

[41] R. S. Mülliken, W. B. Person, Molecular complexes**,** Wiley−VCH, New York, 1969.

[42] B. Xu, Y. Wei, C. L. Barnes and Z. Peng, Angew. Chem., Int. Ed. 40 (2001) 2290–2292.

[43] K. Izutsu, Electrochemistry in Nonaqueous Solutions, Wiley−VCH Verlag GmbH & Co. KgaA, 2002, p. 223, Ch. 8.

[44] A. B. P. Lever, Inorg. Chem. 30 (1991) 1980–1985.

[45] A. B. P. Lever, Inorg. Chem. 29 (1990) 1271–1285.

[46] G. S. Yang, H. Y. Zang, Y. Q. Lan, X. L. Wang, C. J. Jiang, Z. M. Su and L. D. Zhu, CrystEngComm, 13 (2011) 1461–1466.

[47] Z. Y. Shi, X. J. Gu, J. Peng, X. Yu, E. B. Wang, Eur. J. Inorg. Chem. 2006 (2006) 385-388.

[48] Z. Y. Shi, X. J. Gu, J. Peng, Y. H. Chen, J. Solid State Chem. 178 (2005) 1988-1995.

[49] Z. Y. Shi, J. Peng, C. J. Gomez-Garcia, S. Benmansour, X. J. Gu, J. Solid State Chem.179(2006) 253-265.

[50] X. J. Gu, J. Peng, Z. Y. Shi, Y. H. Chen, Z. G. Han, E. B. Wang, J. F. Ma, Inorg. Chim. Acta, 358 (2005) 3701-3710.

[51] Y. Yu, H. Ma, H. Pang, L. Zhang, S. Li, C. Zhao, Z. Zhang, RSC Adv. 4 (2014) 61210–61218.

[52] P. S. Braterman, V.A. Wilson, j.organometal. chem. 31(1971)131-135.

[53] M. Tavassoli, A. Landarani−Isfahani, M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor−Baltork, Appl. Catal. A: Gen. 503 (2015) 186–195.

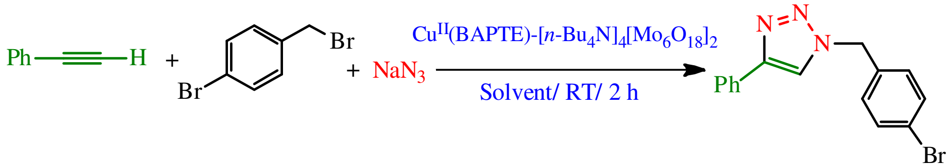
[54] M. Tavassoli, A. Landarani−Isfahani, M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor−Baltork, ACS Sust. Chem. Eng. (2016) DOI: 10.1021/acssuschemeng.5b01432.

Fig. 1. The structure of hexamolybdate ion $[(n\text{−}C_4H_9)_4N]_2[Mo_6O_{19}]$.

Fig . 2. The FT−IR spectra of POM, BAPTE, hybrid compound and recycled hybrid compound.

Fig. 3. ^{1}H NMR spectrum of: (a) BAPTE and (b) (BAPTE)−$[n\text{−}Bu_4N]_4[Mo_6O_{18}]_2$

Table 1. Copper–catalyzed cycloaddition reaction of 4–bromobenzyl bromide and phenylacetylene catalyzed by $Cu^{II}(BAPTE)Cl_2–[n–Bu_4N]_4[Mo_6O_{18}]_2$.[a]



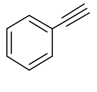
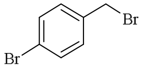
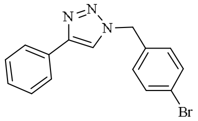
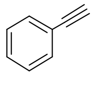
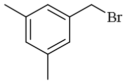
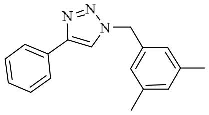
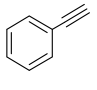
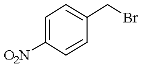
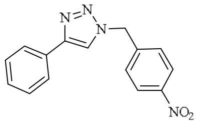
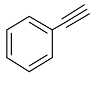
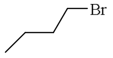
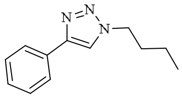
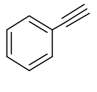
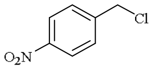
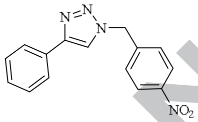
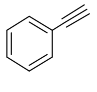
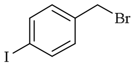
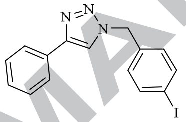
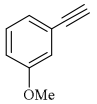
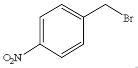
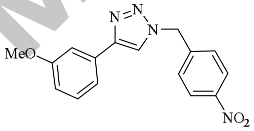
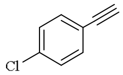
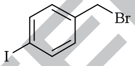
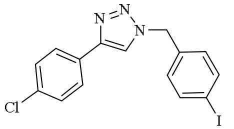
Entry	Cu (mol%)	Solvent	Yield(%)[b]
1	0	H_2O/DMSO (1:10)	5
2[c]	1	H_2O/DMSO (1:10)	10
3	0.5	H_2O/DMSO (1:10)	51
4	1	H_2O/DMSO (1:10)	98
5	1.5	H_2O/DMSO (1:10)	98
6	1	H_2O	28
7	1	DMSO	76
8	$CuCl_2$	H_2O/DMSO (1:10)	23
9	$(n–Bu_4N)_2[Mo_6O_{19}]$	H_2O/DMSO (1:10)	Trace

[a] Reaction conditions: Phenylacetylene (1.3 mmol), 4–bromobenzyl bromide (1 mmol), sodium azide (1.1 mmol), sodium ascorbate (5 mol%), solvent (3 mL) under air atmosphere.

[b] Isolated yields.

[c] Without sodium ascorbate.

Table 2. $Cu^{II}(BAPTE)Cl_2-[n-Bu_4N]_4[Mo_6O_{18}]_2$ catalyzed three−component synthesis of 1,4−disubstituted 1,2,3−triazoles from benzyl halides.[a]

Entry	Phenylacetylene	Benzyl halide	Product	Time (min)	Yield (%)[b]
1				90	98
2				80	94
3				150	83
4				100	95
5				165	81
6				185	79
7				90	98
8				100	94

[a] Reaction conditions: Phenylacetylenes (1.3 mmol), benzyl halide (1 mmol), sodium azide (1.1 mmol), sodium ascorbate (5 mol%), catalyst (1 mol%, 0.03 g), solvent (3 mL) under air atmosphere.

[b] Isolated yields.

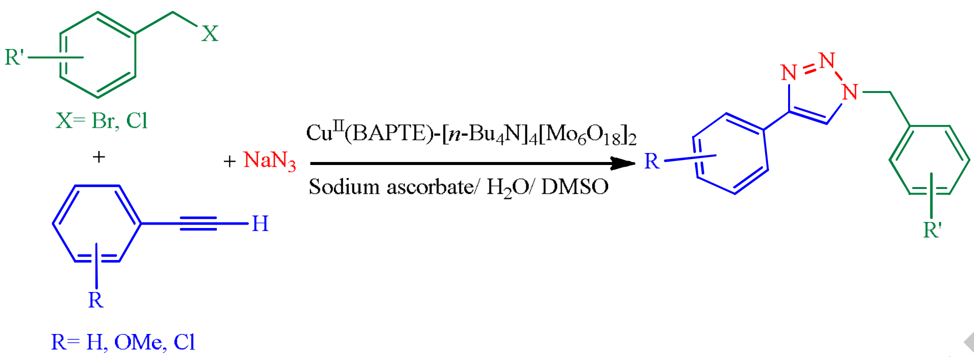
Table 3. Reusability of $Cu^{II}(BAPTE)Cl_2-[n-Bu_4N]_4[Mo_6O_{18}]_2$ in the reaction of 4−bromobenzyl bromide with phenylacetylene and sodium azide.[a]

Run	Yield (%)[b]	Time (min)	Cu leached (%)[c]
1	98	90	0.2
2	95	90	0
3	95	90	0
4	95	90	0
5	95	90	0

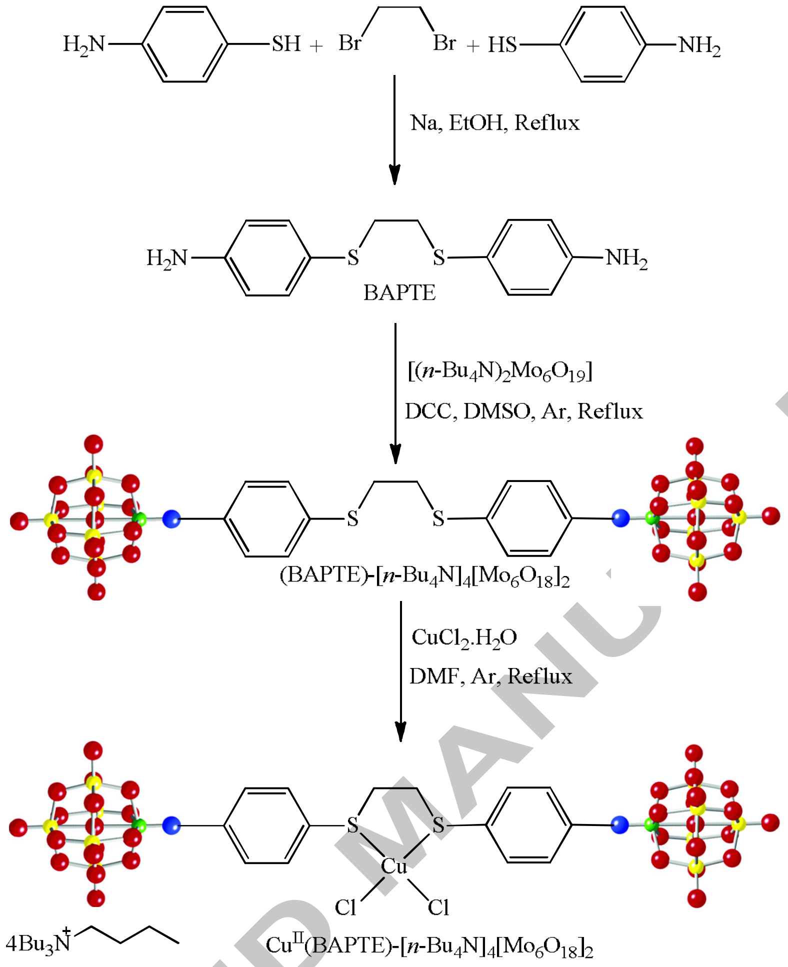
[a] Reaction conditions: Phenylacetylene (1.3 mmol), 4−bromobenzyl bromide (1 mmol), sodium azide (1.1), catalyst (1 mol%), solvent (3 mL).

[b] Isolated yields.

[c] Determined by ICP.



Scheme 1. Synthesis of 1,2,3−triazoles catalyzed by $Cu^{II}(BAPTE)Cl_2$−[*n*−$Bu_4N]_4[Mo_6O_{18}]_2$



Scheme 2. Preparation of $Cu^{II}(BAPTE)Cl_2-[n-Bu_4N]_4[Mo_6O_{18}]_2$

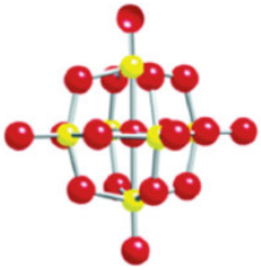


Fig. 1. The structure of hexamolybdate ion $[(n-C_4H_9)_4N]_2[Mo_6O_{19}]$.

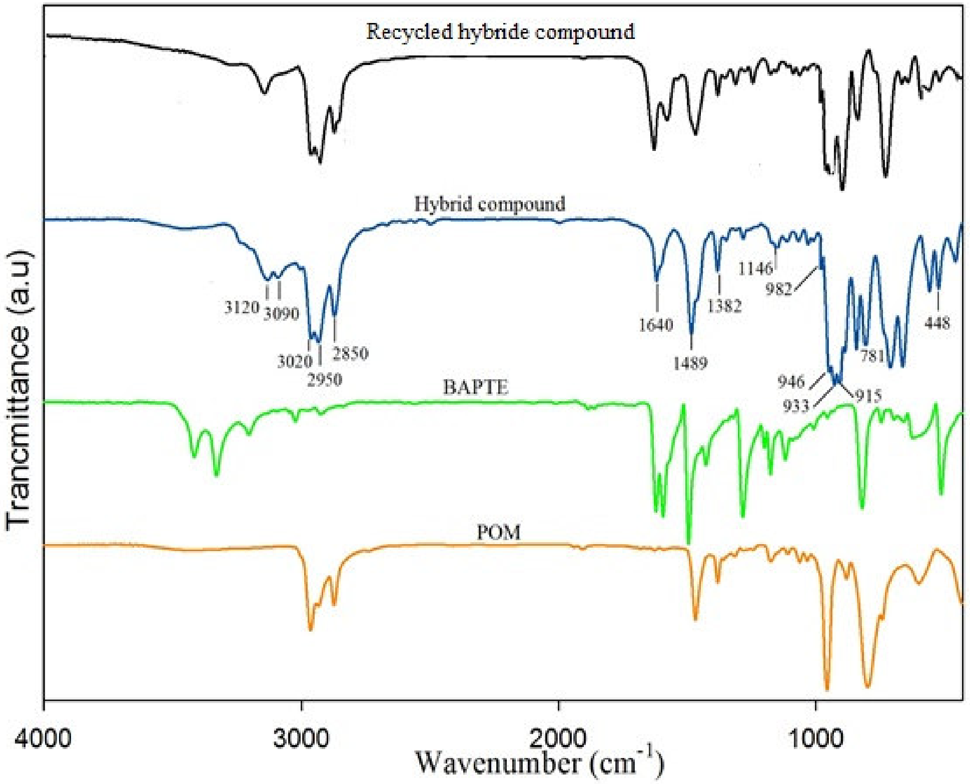
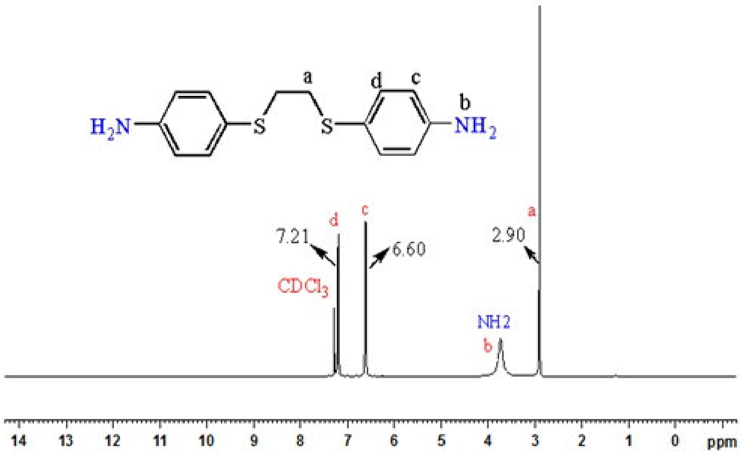
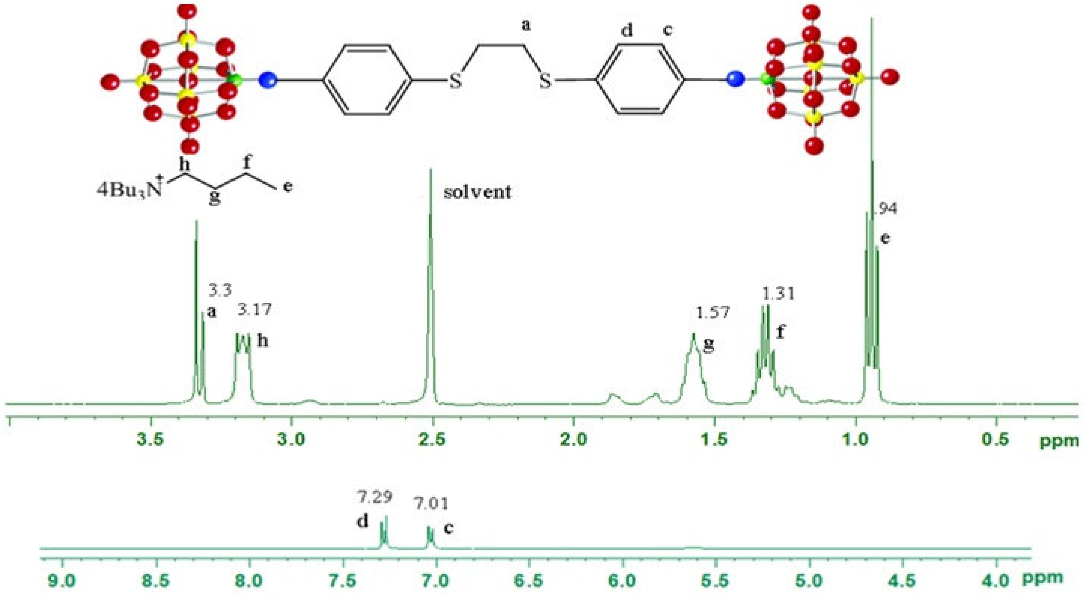


Fig. 2. The FT–IR spectra of POM, BAPTE, hybrid compound and recycled hybrid compound.

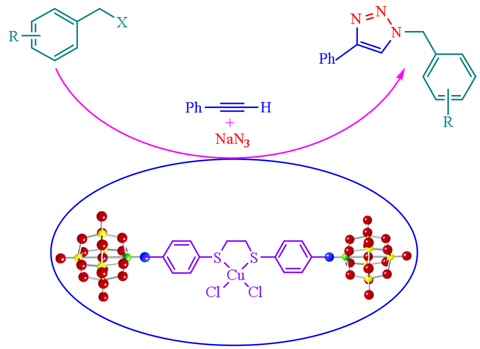


(a)



(b)

Fig. 3. ^{1}H NMR spectrum of: (a) BAPTE and (b) (BAPTE)–[n–Bu$_4$N]$_4$[Mo$_6$O$_{18}$]$_2$



A new copper(II) complex-polyoxometalate hybrid catalyst based on covalent interaction between 1,2–bis(*p*–aminophenylthio)ethane, (BAPTE), and a Lindqvist type polyoxometalate, $Mo_6O_{19}^{2-}$, is synthesized, characterized and used as a highly efficient heterogeneous catalyst for click reaction.