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Cube-octameric silsesquioxane-mediated cargo copper Schiff base for efficient click reaction in aqueous media

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Dedicated to the memory of Professor Ali Akbar Entezami who passed away in the summer of 2015.

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ABSTRACT

The azide–alkyne cycloaddition reaction was investigated under catalytic conditions involving a copper(II)—polyhedral oligomeric silsesquioxane (POSS)—bridged Schiff base. This material demonstrated a high catalytic activity in organic synthesis of 1,4-triazoles. No additive such as a base or a reductant was required. Finally, recoverability and reusability of the POSS-bridged Schiff base–Cu(II) catalyst was analyzed.

1. Introduction

The copper-catalyzed azide–alkyne cycloaddition (CuAAC) is one of the most attractive synthetic tools for convenient and reliable construction of 1,2,3-triazole derivatives, whose subunits are often found in biologically active molecules [1–7]. In recent years, due to higher stability and dispersibility of nanoparticles as well as the demand for higher activity and recyclability of catalysts, heterogeneous nano-catalysis has emerged as a sustainable and competitive alternative to conventional catalysis [6–14].

Silsesquioxanes, the three-dimensional oligomeric compounds with the general formula (RSiO1.5)2n, where R can be any functional group (alkyl, hydrogen, halogen, aryl, etc.), show unique properties. A number of silicon-based compounds have recently been developed as substrates for catalyst immobilization in a wide range of biochemical reactions [15–17]. Among them, polyhedral oligomeric silsesquioxane (POSS) cage molecules, $(RSiO_{1.5})_8$, have received a great deal of attention for the synthesis of organic–inorganic hybrid materials with precise control of nanoarchitecture [18,19]. The Si—O—Si backbone and the chemically and thermally stable network of POSS make these compounds a promising precursor for the synthesis of new hybrid materials [20–22].

Recently, there has been a strong interest in the synthesis of functional polysilsesquioxanenano-building blocks as a substrate for immobilization of organo-metallic catalysts, thereby building a bridge between homogeneous and heterogeneous catalysts [23–27]. The formation of stable bonds between metal ions of the catalyst and functionalized silsesquioxanes prevents catalyst leaching [28]. Therefore, several ligands bearing a silsesquioxane moiety have been synthesized and utilized as precursors to the preparation of heterogeneous catalysts with transition metal complexes [29] or nanoclusters [30–34]. Recently, there has been interest in functionalization of POSS with heteroatom ligands as chelating agents for metal ions such as thiourea [35], 3-amino-1,2,4-triazole [36], 2-amino-1,3,4-thiadiazole [37], and 2,2-dipyridylamine [38].

In this work, the application of POSS as a nano-platform for the synthesis of POSS-bridged Schiff base ligands is explored by functionalizing the cage containing eight propylammonium chloride pendant arms with salicylaldehyde. The heterogeneous POSS-bridged Schiff base-Cu(II) complex is obtained by the reaction between POSS-bridged Schiff base ligand and the metal precursor $Cu(OAc)_2{\cdot}H_2O$. To the best of our knowledge, POSS has not been used as a catalyst for the azide–alkyne cycloaddition reaction. Therefore, the produced POSS–SAL–Cu was tested for the first time as a catalyst to carry out the cycloaddition reaction. The two

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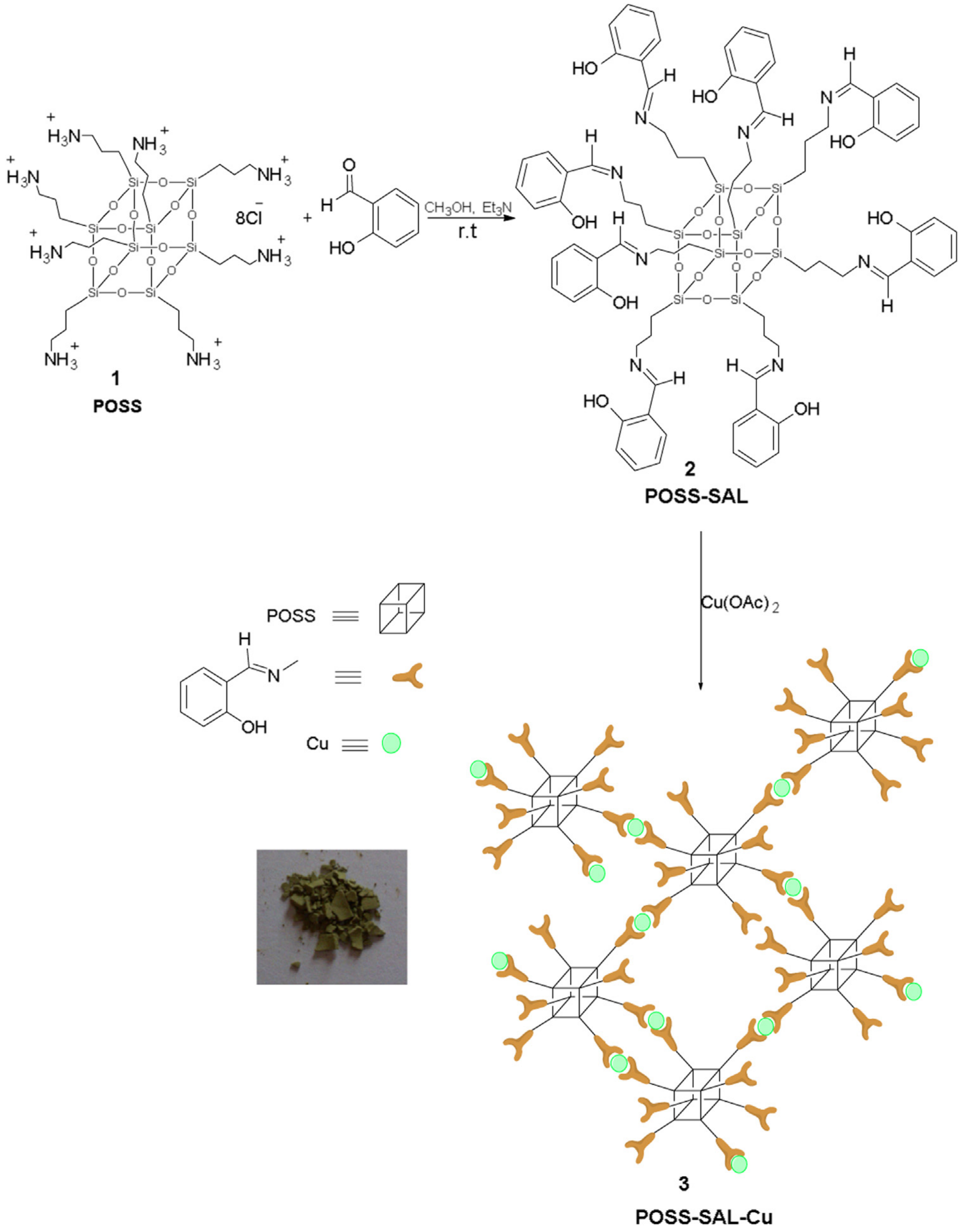


Scheme 1. Synthetic route and the proposed chemical structure for POSS–SAL–Cu complex.

step synthetic pathway for POSS–SAL–Cu is depicted in Scheme 1. POSS (1) was prepared via hydrolyses and condensation reactions using 3-aminopropyltriethoxysilane (ATPES) as the sol–gel precursor in acidic condition [39]. The temperature was increased to 90 °C to reduce the reaction time from one week to 16 h [40]. Imine bonds were readily formed via condensation of salicylaldehyde with POSS (1) in the presence of triethylamine in methanol to yield POSS–SAL (2) in nearly quantitative yield. Finally POSS–SAL–Cu (3) was synthesized as a green solid by the reaction of POSS–SAL with $Cu(OAc)_2 \cdot H_2O$ in ethanol.

2. Experimental

2.1. Materials and analyses

All chemicals and solvents were purchased from Merck and Fluka and were used without further purification. Benzyl azides were prepared according to a previously reported procedure

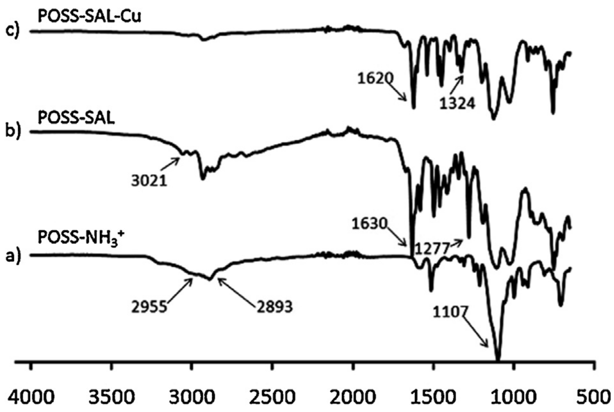


Fig. 1. FT-IR spectra of POSS (a), POSS–SAL (b) and POSS–SAL–Cu (c).

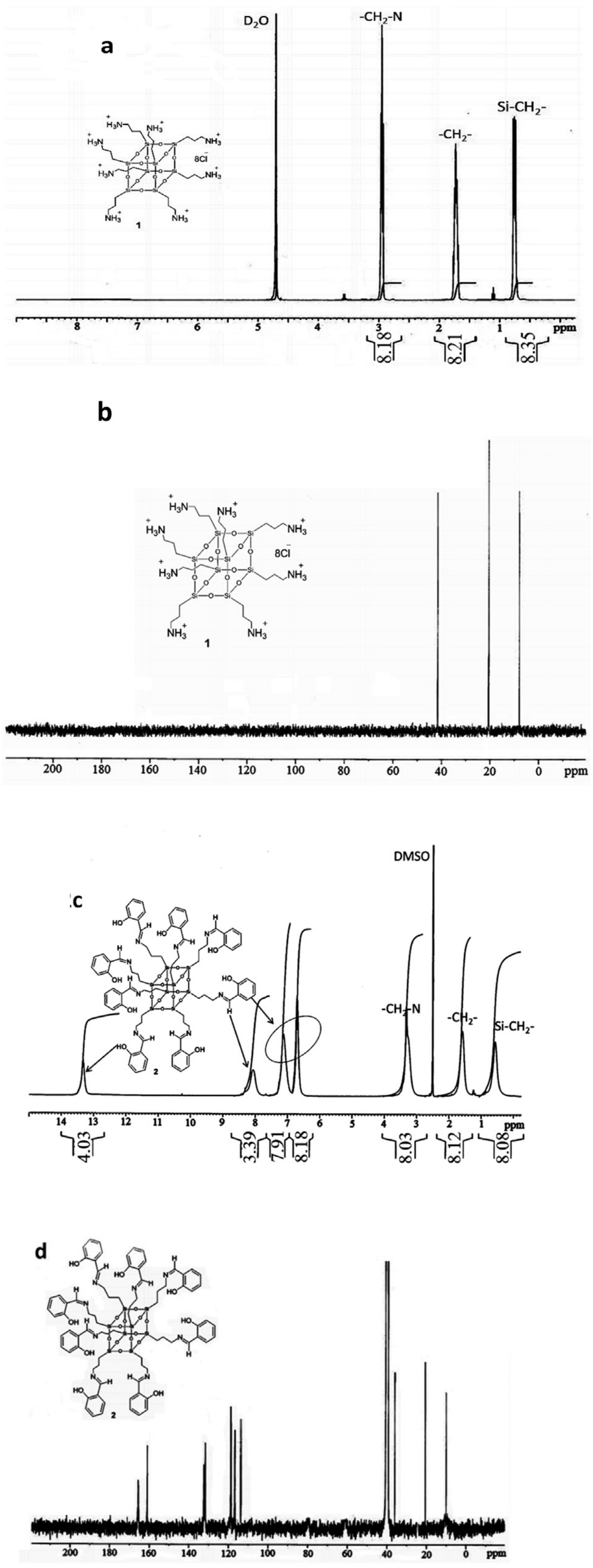
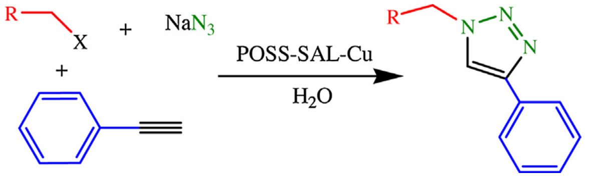


Fig. 2. (a–d) ^{1}HNMR (a,c) and ^{13}CNMR (b,d) spectra of POSS and POSS–SAL.



Scheme 2. Cycloaddition of alkyl halides with phenyl acetylene and NaN_3.

[41]. Fourier transform infrared (FT-IR) spectra was carried out on a Bruker FTIR spectrometer (model Tensor 27) over the range of 500–3500 cm^{-1} using spectroscopic grade KBr powder at room temperature. ^{1}HNMR spectra were recorded on a Varian Mercury-300^{1}H NMR (Varian, Palo Alto, CA) spectrometer. The scanning electron microscopy (SEM) image was taken with Tescan, Kotoutovice, Czech Republic at accelerating voltage of 8 keV. Transmission electron microscopy (TEM) was studied on a Hitachi H-8000 transmission electron microscope. MALDI-MS measurements were performed on Bruker Autoflex III MALDI-TOF MS.

2.2. Synthesis of POSS–NH_3^+, compound 1

Octa (3-aminopropyl) octasilsequioxane octahydro chloride (hereafter named POSS–NH_3^+ for simplicity) was prepared according to the method described in literature [42]. Briefly in 1000 mL two-neck round bottom flask equipped with a reflux condenser and a magnetic stirrer, a solution of 350 mL methanol and concentrated HCl (30 mL, 35–37%) was charged, and then (3-aminopropyl)-triethoxysilane (15 mL, 60 mmol) was added dropwise at 60 °C. The reaction mixture refluxed in oil bath at 90 °C for 16 h with vigorous stirring and then cooled to ambient condition and 300 mL THF was added to precipitate. The white precipitate was collected by filtration and washed three times with THF to obtain POSS–NH_3^+ as a white powder with a yield of 33%. The characterization data are as follows: FT-IR (KBr, cm^{-1}): 3224, 3025, 2920, 1604, 1494, 1125, 1107, 935, 705 cm^{-1}; ^{1}H NMR (300 MHz, D_2O): δ 2.91(t, CH_2NH_3, 16 H), 1.68 (m, $SiCH_2CH_2$, 16 H), 0.68 (t, $SiCH_2$, 16 H). ^{13}CNMR (100 MHz, D_2O): δ 41.04 (s, CH_2NH_3), 20.01 (s, $SiCH_2CH_2$), 8.55 (s, $SiCH_2$).

2.3. Synthesis of POSS–SAL, compound 2

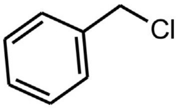
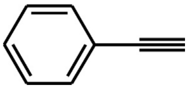
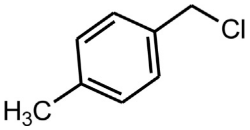
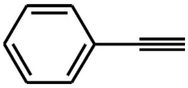
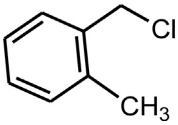
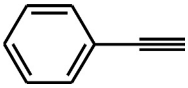
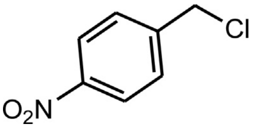
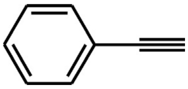
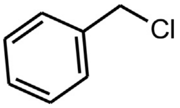
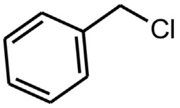
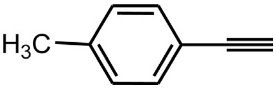
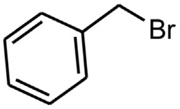
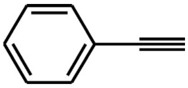
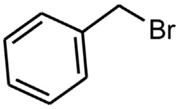
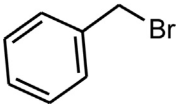
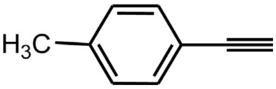
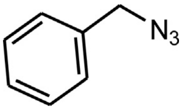
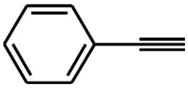
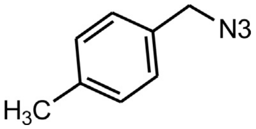
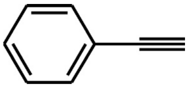
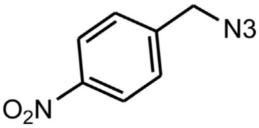
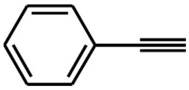
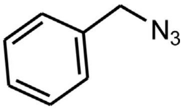
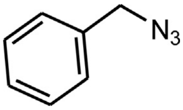
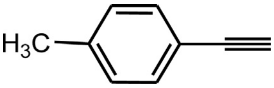
To a solution of POSS–NH_3^+ (1.0 g, 0.85 mmol) and triethylamine (0.97 mL , 0.7 mmol) in methanol (20 mL), salysilaldehyde (4.88 g, 40 mmol) was added, and the reaction mixture was stirred at ambient condition for 2 h and then condensed by evaporation. Then the crude product was washed with diethyl ether (4 × 35 mL) to yield 1.21 g. FT-IR (KBr, cm^{-1}): 3021, 2938, 2883, 1630, 1498, 1277, 1124, 760 cm^{-1}; ^{1}H NMR (300 MHz, DMSO): δ 13.30 (b, OH, 4 H), 8.45 (s, —NCH—, 3.95 H), 6.83–7.30 (b, Aromatic protons, 16 H), 2.91(t, CH_2N, 8 H), 1.68 (m, $SiCH_2CH_2$, 8 H), 0.68 (t, $SiCH_2$, 8 H). ^{13}CNMR

Table 1
The effect of reaction conditions on the azide–alkyne cycloaddition.

Entry	Amount of Cu in nanocatalyst (mmol)	Temperature (°C)	Time (h)	Yield (%)[a]
1	–	70	12	0
2	0.002	70	12	34
3	0.004	70	12	45
4	0.006	70	12	69
5	0.008	70	12	81
6	0.01	70	12	95 (37)[b]
7	0.008	r.t.	12	8
8	0.008	40	12	16
9	0.008	50	12	33
10	0.008	60	12	87
11	0.008	70	2	29
12	0.008	70	6	53
13	0.008	70	8	80

[a] Isolated yield.
[b] In the presence of 0.02 mmol of $Cu(OAc)_2{\cdot}H_2O$ as a catalyst.

Table 2
Cycloaddition of alkyl halides with terminal alkynes in the presence of POSS–SAL–Cu.

Entry	Substrate	Alkyne	Yield (%)[a]
1			95
2			95
3			89
4			94
5			91
6			93
7			96
8			92
9			90
10			95
11			95
12			96
13			91
14			93

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[a] Isolated yield.

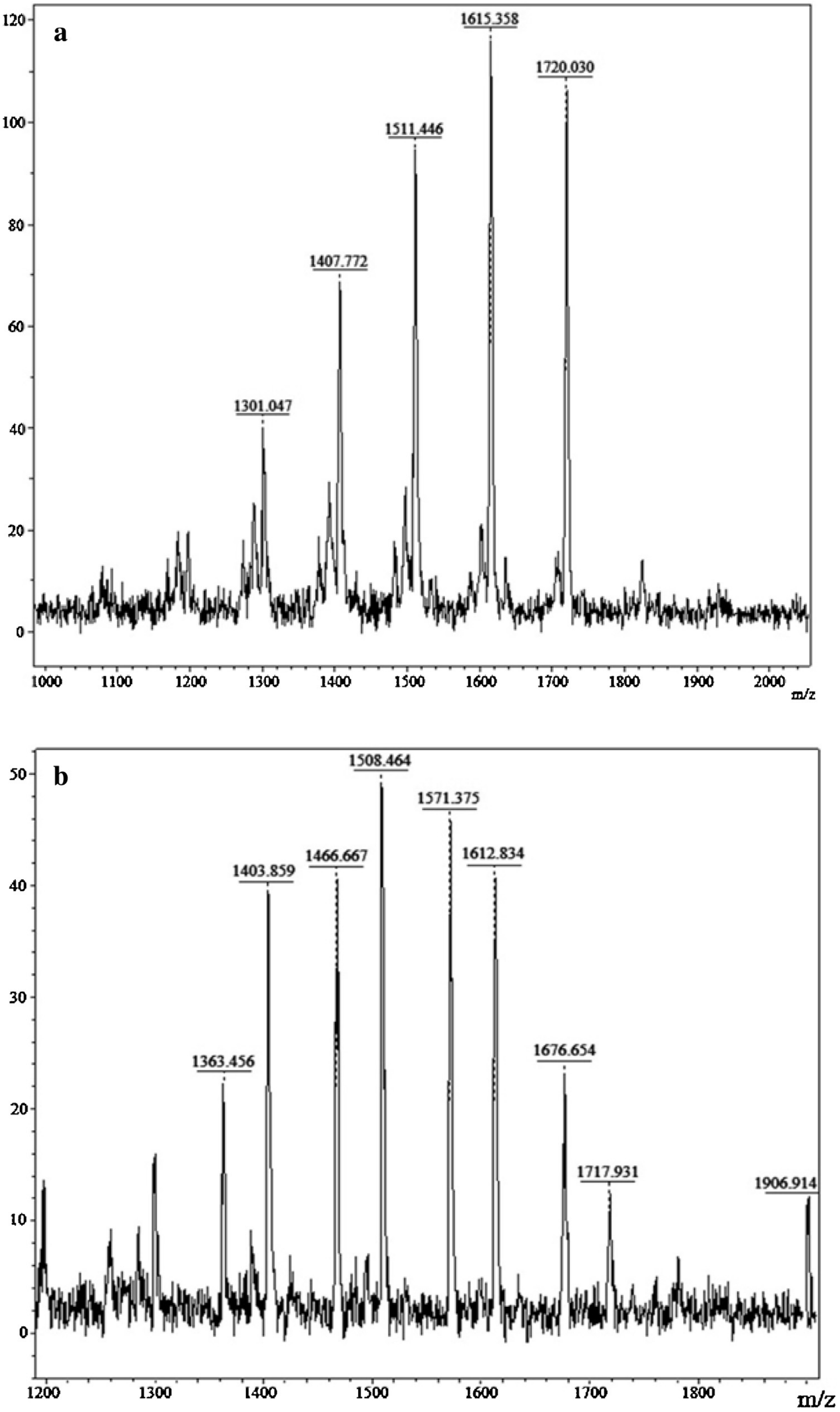

Fig. 3. MOLDI-TOF of POSS–SAL (a) and POSS–SAL–Cu (b).

(100 MHz, DMSO): δ 165.68 (s, phenolic —OH), 161.01 (s, —CH=NH), 132.44–116.75 (s, Aromatic carbons), 39.57 (s, CH_2NH_3), 24.39 (s, $SiCH_2CH_2$), 9.53 (s, $SiCH_2$).

2.4. Synthesis of POSS–SAL–Cu, compound 3

A solution of $Cu(OAc)_2 \cdot H_2O$ (8 mmol) in 10 mL C_2H_5OH was added to a solution of 1.0 mmol POSS–SAL in 10 mL CH_2Cl_2. The

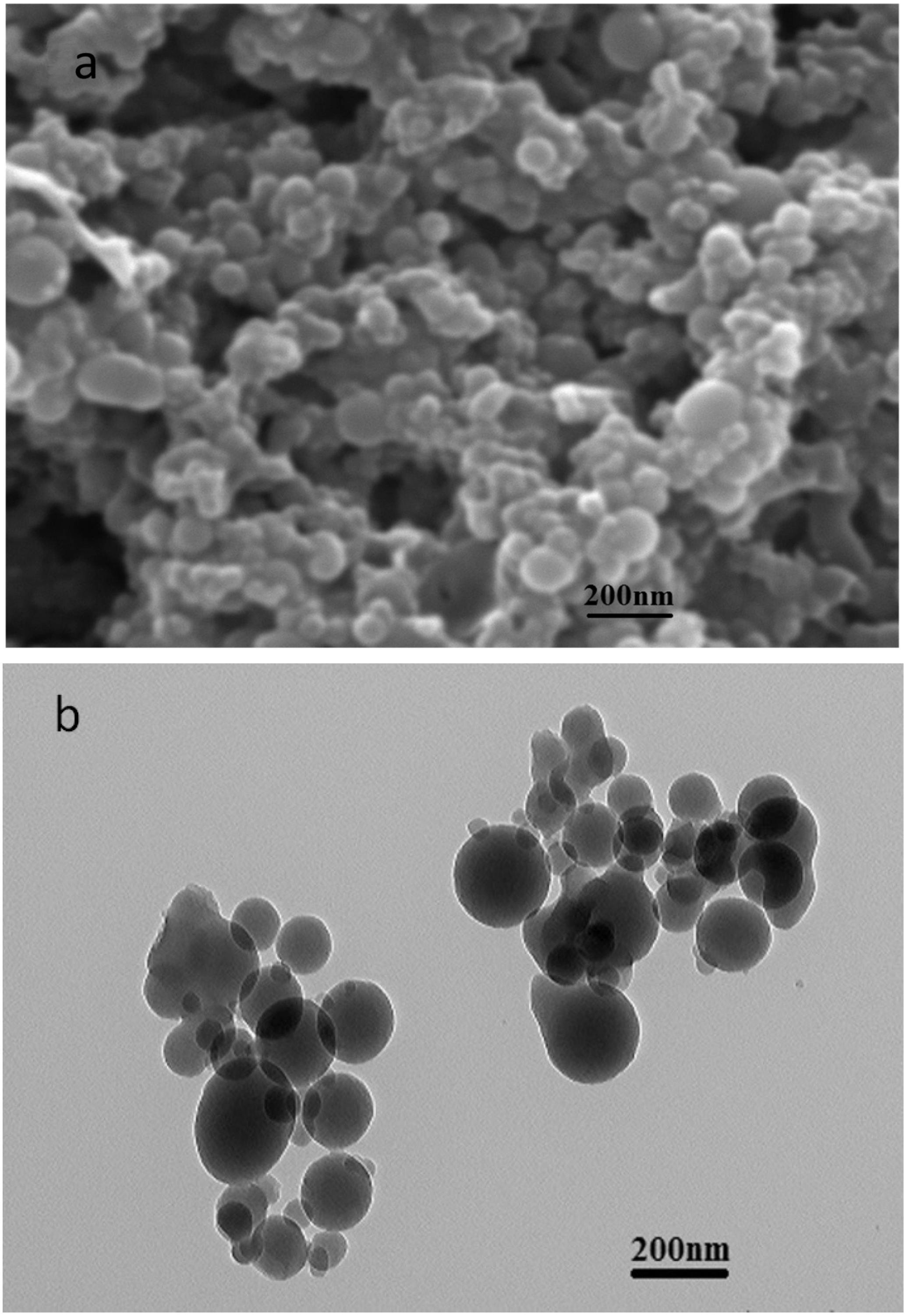

Fig. 4. SEM (a) and TEM (b) images of POSS–SAL–Cu.

mixture was stirred for 24 h at ambient condition to form a green solid. The solid was filtered off, washed with ethanol and finally with diethyl ether and dried in vacuum. Elemental analysis for POSS–SAL–Cu (by the weight percentage): C 51.48%, N 5.57%, and H 5.47%, and the loading amount of Cu in the catalyst POSS–SAL–Cu is calculated to be about 16.7%.

2.5. *General procedure for Cu(II) POSS-bridged Schiff base azide–alkyne cycloaddition*

Alkyne (0.5 mmol), the organic halide (0.55 mmol), and NaN_3 (0.55 mmol) were added to a suspension of POSS–SAL–Cu (5 mg) in H_2O (2 mL). The reaction mixture was heated to 70 °C and monitored by TLC until total conversion of the starting

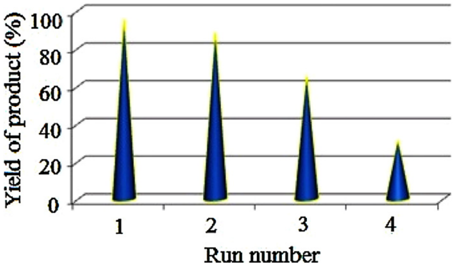

Fig. 5. Product yield with recycling of the catalyst POSS–SAL–Cu in the azide–alkyne cycloaddition reaction.

materials. Water (5 mL) was added to the resulting mixture, the catalyst was recovered by filtration and the product was extracted with EtOAc (2 × 10 mL). The collected organic phases were dried with anhydrous Na_2SO_4 and the solvent was removed under vacuum to give the corresponding triazoles, which did not require any further purification. The catalyst was washed with ethanol and dried in vacuum in order to use the next run without the addition of any fresh catalyst.

3. Results and discussion

3.1. Complex characterization

The two step synthetic pathway for POSS–SAL–Cu is depicted in Scheme 1. POSS–NH_3^+ was prepared via hydrolyses and condensation reaction by using 3-aminopropyltriethoxysilane (ATPES) as the sol–gel precursor in acidic condition [43]. The reaction was carried out at 90 °C to reduce the reaction time (one week at ambient condition) to 16 h [42]. Imine bonds were readily formed via condensation of salicylaldehyde with POSS–NH_3^+ in the presence of triethylamine in methanol and produced the POSS–SAL, compound 2, in nearly quantitative yield. Finally POSS–SAL–Cu, compound 3, was prepared as a green solid. All compounds were characterized by ^{1}HNMR, ^{13}CNMR, FT-IR, MOLDI-TOF, SEM and TEM. The resulting solid catalyst was insoluble in common organic solvents, such as THF, DMF, ethanol, acetonitrile, and chloroform, thus the synthesized catalyst is a good candidate with respect to solubility for heterogeneous catalysis. FT-IR was used for structure elucidation. Fig. 1 illustrates the FT-IR spectra of POSS (a), POSS–SAL (b) and POSS–SAL–Cu (c). Fig. 1a shows the most prominent bands of the POSS cage, Si—O—Si asymmetric stretching absorption between 1107 and 1125 cm^{-1} and deformation of Si—O—Si bridges at 705 cm^{-1} [44]. In addition, the peaks at 2893 and 2955 cm^{-1} in the FT-IR spectra confirmed the presence of propyl chains in POSS. After the reaction of POSS with salicylaldehyde, the structure of the new compound, POSS–SAL, as a free ligand exhibited many new absorption peaks including those at 1630 and 1277 cm^{-1} which were attributed to C—N azomethine and C—O phenolic vibrations, respectively. After complexation with copper, the azomethine vibration of the free ligand at 1630 cm^{-1} was moved to a lower frequency, i.e., 1620 cm^{-1}. Additionally, the C—O phenolic vibration at 1277 cm^{-1} in the free ligand was shifted to a higher frequency by 47 cm^{-1} after complexation. These shifts confirmed the formation of POSS–SAL–Cu by coordination of azomethine nitrogen and phenolic oxygen with copper ions.

We have characterized the POSS–NH_3^+ and POSS–SAL by NMR spectroscopy (^{1}HNMR and ^{13}CNMR) as shown in Fig. 2a–d. Based on the ^{1}HNMR spectrum in Fig. 2c, the ratio of the peaks for methylene groups of POSS, as the base with integral value of 8 protons, to that of the imine protons (8.45 ppm, 3.95 H) was 2.02. As a result, 8 ammonium groups of POSS were successfully reacted with salicylaldehyde and converted to imine groups.

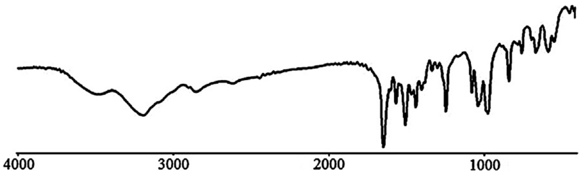

Fig. 6. IR spectrum of the reused catalyst POSS–SAL–Cu.

We also characterized the new products POSS–SAL and POSS–SAL–Cu by MOLDI-TOF mass spectrometry. In both cases, the observed mass was lower than the calculated mass. According to Fig. 3a and b, the observed mass for POSS–SAL (calculated $m/z = 1664$) and POSS–SAL–Cu (calculated $m/z = 2072$) were $m/z = 1615.35$ and 1906.91, respectively. The discrepancy can be attributed to the partial cleavage of imine bonds of the Schiff bases in the structure of the products by high-energy laser with acid as the matrix. The same results were observed previously by Wu et al. [45].

Fig. 4a and b shows the SEM and TEM images of POSS–SAL–Cu (3). These images show spherical aggregate of nanoparticles with average size of 100 nm. It was not possible to image the individual POSS nanoparticles (1–3 nm) because of the complexation of copper metals with POSS–SAL–Cu.

3.2. Catalytic effects

To optimize the reaction conditions, a series of experiments were carried out with varying catalyst loading, temperature and time for representative reaction of benzyl chloride, phenyl acetylene and NaN_3 to synthesize 1-benzyl-4-phenyl-1,2,3-traizole with POSS–SAL–Cu as the catalyst (Scheme 2). Water was used as the standard "green" solvent. All reactions were performed in air without any additive. In a typical reaction, alkyne, organic halide and NaN_3 in a ratio of 1:1.1:1.1 were mixed in a flask, followed by the addition of water and catalyst. The mixture was heated to 70 °C for a certain period (Table 1). The organic product was isolated by extraction and analyzed by elemental analysis and ^{1}H NMR. Results are summarized in Table 1.

When the amount of catalyst was increased from 0 to 5 mg, the product yield increased sharply from 0 to 95%. No product was obtained in the absence of catalyst. As indicated in Table 1, the reaction did not initiate at ambient temperature with magnetic stirring for 12 h, but the product yield increased significantly at higher temperatures. Also, the yield increased significantly from 29% to 95% with increasing reaction time from 2 to 12 h. Catalytic activity of the reaction system decreased dramatically when POSS–SAL–Cu was replaced by $Cu(OAc)_2$, as shown in Table 1 (entry 6).

A wide range substituted phenyl acetylenes were reacted with the mixture of benzyl bromides/chlorides and sodium azide using this procedure to produce the corresponding 1,4-disubstituted-1,2,3-triazoles. The results are summarized in Table 2. The substitution of electron withdrawing or electron donating groups on the phenyl ring of benzyl halides and phenyl acetylenes did not have an appreciable effect on the reaction outcome (entries 2–6). Furthermore, steric hindrance of the *ortho* substituents on benzyl chlorides affected progress of the reaction. The benzyl chloride substituted with methyl group at the *ortho* position was less reactive toward the cycloaddition reaction than the *para* derivative (entries 2 and 3). However, the cycloaddition of benzyl bromide had a lower yield under similar reaction conditions (entries 7–9). The results of Cu(II)-catalyzed cycloaddition of various terminal alkynes with benzyl azide are summarized in Table 2. The reactions of substituted phenyl acetylenes and benzyl azides in water with 5 mg of POSS–SAL–Cu resulted in 91–96% products (entries 10–14), while a blank experiment under similar conditions provided no product.

Higher reaction conversions compared to the blank experiments clearly demonstrated the activity of POSS–SAL–Cu catalyst in the reactions.

Finally, a set of experiments were carried out to test the heterogeneity and reusability of POSS–SAL–Cu catalyst in the azide–alkyne cycloaddition reaction of benzyl chloride, phenyl acetylene and NaN_3 at 70 °C for 12 h. For each cycle, the catalyst was recovered from the reaction mixture by filtration, washed with distilled water and ethyl ether repeatedly, dried at 50 °C for 1/2 h, and reused in the next cycle. As shown in Fig. 5, the reaction yield slightly decreased due to the loss of catalyst activity after recycling the catalyst three times. A comparison of the IR data for the fresh and recycled catalyst (Fig. 6) revealed changes in the spectra for the two materials. Thus, structural changes maybe responsible for the reduction in catalytic activity of the catalyst upon repeated use.

To address the leaching of copper species into solution, the catalyst was removed by ultracentrifugation at half the reaction time (6 h) in a separate experiment. The reaction did not proceed significantly upon further treatment of the residual mixture under similar reaction conditions for 6 h (second half of the reaction). Therefore, it can be concluded that the leaching of the copper catalyst was negligible. The Cu content of the residual mixture, measured by atomic absorption spectroscopy, was below the detection limit which confirmed negligible leaching of the catalyst.

4. Conclusions

All eight propylammonium side chains of POSS 1 reacted with salicylaldehyde, producing the new compound 2 (POSS–SAL) with eight salicylaldehyde arms. Further, the reaction of compound 2 with the metal precursor $Cu(OAc)_2$ produced the new derivative POSS–SAL–Cu (3). Based on the SEM and TEM images, the derivative 3 contained an aggregate of spherical nanoparticles. The synthesized POSS-bridged copper Schiff base was a highly efficient catalyst for azide–alkyne cycloaddition in aqueous media. Superior catalytic activity, easy recovery and reusability are the advantages of compound 3. To our knowledge, this is the first POSS cage functionalized with eight salicylaldehydes as a ligand for coordination with copper metal to produce model nano-platforms in heterogeneous catalysis. The application of POSS–SAL as a Schiff base free ligand catalyst in coordination with other metals for organic synthesis is in progress.

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References

[1] C.W. Tornøe, C. Christensen, M. Meldal, J. Org. Chem. 67 (2002) 3057–3064.
[2] V. Rostovtsev, L.G. Green, V.V. Fokin, K.B. Sharpless, Angew. Chem. Int. Ed. 41 (2002) 2596–2599.
[3] E. Haldón, M.C. Nicasio, P. Pérez, Org. Biomol. Chem. 13 (2015) 9528–9550.
[4] J.E. Hein, V.V. Fokin, Chem. Soc. Rev. 39 (2010) 1302–1315.
[5] D. Bock, H. Hiemstra, J.H. van Maarseveen, Eur. J. Org. Chem. (2006) 51–68.
[6] M. Meldal, C.W. Tornøe, Chem. Rev. 108 (2008) 2952–3015.
[7] C.O. Kappe, E. Van der Eycken, Chem. Soc. Rev. 39 (2010) 1280–1290.
[8] S. Park, M.S. Kwon, Y. Kim, J.S. Lee, J. Park, Org. Lett. 10 (2008) 497–500.
[9] B.S. Lee, M. Yi, S.Y. Chu, J.Y. Lee, H.R. Kwon, K.R. Lee, D. Kang, W.S. Kim, H.B. Lim, J. Lee, H.-J. Youn, D.Y. Chi, N.H. Hur, Chem. Commun. 46 (2010) 3935–3937.
[10] L. Liang, D. Astruc, Coord. Chem. Rev. 255 (2011) 2933–2945.
[11] F. Alonso, Y. Moglie, G. Radivoy, Acc. Chem. Res. 48 (2015) 2516–2528.
[12] F. Alonso, Y. Moglie, G. Radivoyand, M. Yus, Org. Biomol. Chem. 9 (2011) 6385–6395.
[13] Y. Monguchi, K. Nozaki, T. Maejima, Y. Shimoda, Y. Sawama, Y. Kitamura, Y. Kitade, H. Sajiki, Green Chem. 15 (2013) 490–495.
[14] I. Luz, F.X.L. i Xamena, A. Corma, J. Catal. 276 (2010) 134–140.
[15] R.H. Baney, M. Itoh, A. Sabakibara, T. Suzuki, Chem. Rev. 95 (1995) 1409–1430.
[16] E.A. Quadrelli, J.-M. Basset, Coord. Chem. Rev. 254 (2010) 707–728.
[17] D.B. Cordes, P.D. Lickiss, F. Rataboul, Chem. Rev. 110 (2010) 2081–2173.
[18] C. Marcolli, G. Calzaferri, Appl. Organomet. Chem. 13 (1999) 213–226.
[19] H.C.L. Abbenhuis, Chem. Eur. J. 6 (2000) 25–32.
[20] G. Li, L. Wang, H. Ni, C.U. Pittman Jr., J. Inorg. Organomet. Polym. 11 (2002) 123–154.
[21] G. Calzaferri, R. Imhof, K.W. Törnroos, J. Chem. Soc. Dalton Trans. (1993) 3741–3748.
[22] P.G. Harrison, R. Kannengiesser, J. Chem. Soc. Chem. Commun. (1995) 2065–2066.
[23] M. Rattay, D. Fenske, P. Jutzi, Organometallics 17 (1998) 2930–2932.
[24] A.R. Bassindale, T. Gentle, J. Organomet. Chem. 521 (1996) 391–393.
[25] S.G. Kim, J. Choi, R. Tamaki, R.M. Laine, Polymer 46 (2005) 4514–4524.
[26] E.A. Bijpost, M.A. Zuideveld, A. Meetsma, J.H. Teuben, J. Organomet. Chem. 551 (1998) 159–164.
[27] M. Moraín, C.M. Casado, I. Cuadrado, J. Losada, Organometallics 12 (1993) 4327–4333.
[28] N.L. Dias Filho, F.C.M. Portugal, J.M.F. Nogueira, P. Branda˜o, V. Feílix, P.D. Vaz, C.D. Nunes, L.F. Veiros, M.J. Villa de Brito, M. JoseíCalhorda, Organometallics 31 (2012) 4495–4503.
[29] K. Wada, D. Izuhara, M. Shiotsuki, T. Kondo, T. Mitsudo, Chem. Lett. 30 (2001) 734–735.
[30] G. Hornyak, M. Kroll, R. Pugin, T. Sawitowski, G. Schmid, J.O. Bovin, G. Karsson, H. Hofmeister, S. Hopfe, Chem. Eur. J. 3 (1997) 1951–1956.
[31] G. Schmid, R. Pugin, J.O. Malm, J.O. Bovin, Eur. J. Inorg. Chem. (1998) 813–817.
[32] K. Naka, H. Itoh, Y. Chujo, Nano Lett. 2 (2002) 1183–1186.
[33] X. Wang, K. Naka, H. Itoh, Y. Chujo, Chem. Lett. 33 (2004) 216–217.
[34] K. Naka, H. Itoh, Y. Chujo, Bull. Chem. Soc. Jpn. 77 (2004) 1767–1771.
[35] E.G. Vieira, I.V. Soares, G. Pires, R.A.V. Ramos, D.R. Do Carmo, N.L. Dias Filho, Chem. Eng. J. 264 (2015) 77–88.
[36] N.L. Dias Filho, F. Marangoni, R.M. Costa, J. Colloid Interface Sci. 313 (2007) 34–40.
[37] V. Soares, E.G. Vieira, N.L. Dias Filho, A.C. Bastos, N.C. da Silva, E.F. Garcia, L.J.A. Lima, Chem. Eng. J. 218 (2013) 405–414.
[38] E.G. Vieira, I.V. Soares, N.L. Dias Filho, N.C. da Silva, S.D. Perujo, A.C. Bastos, E.F. Garciaa, T.T. Ferreira, L.F. Fraceto, A.H. Rosa, J. Hazard. Mater. 237–238 (2012) 215–222.
[39] M.C. Gravel, C. Zhang, M. Dinderman, R.M. Laine, Appl. Organomet. Chem. 13 (1999) 329–336.
[40] Y.J. Pu, H. Yuan, M. Yang, B. He, Z.W. Gu, Chin. Chem. Lett. 24 (2013) 917–920.
[41] S.G. Alvarez, M.T. Alvarez, Synthesis 4 (1997) 413–414.
[42] Y.-J. Pu, H. Yuan, M. Yang, B. He, Z.-W. Gu, Chin. Chem. Lett. 24 (2013) 917–920.
[43] T. Fouquet, T.N.T. Phan, L. Charles, Rapid Commun. Mass Spectrom. 26 (2012) 765–774.
[44] H. Mori, M.G. Lanzendörfer, A.H.E. Müller, J.E. Klee, Macromolecules 37 (2004) 5228–5238.
[45] X. Wu, G. Yu, C. Luo, A. Maeda, N. Zhang, D. Sun, Z. Zhou, A. Puntel, K. Palczewski, Z.R. Lu, ACS Nano 8 (2014) 153–161.