

# Copper (II) immobilized on aminated poly(vinyl chloride) as an efficient and retrievable catalyst for the CuAAC reaction in water under mild conditions

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Abstract Ethylenediamine functionalized poly(vinyl chloride) (PVC–EDA) was conveniently synthesized by treatment of commercially available PVC powder with ethylenediamine solution. This amine-functionalized PVC was subsequently immersed in copper sulfate solution to form the supported copper catalyst [PVC–EDA–Cu(II)]. The as-prepared catalyst was well characterized with FT–IR, SEM, DSC, TGA, and ICP methods. It was found to catalyze efficiently the CuAAC reaction for the regioselective synthesis of 1,4-disubstituted-1,2,3-triazoles from benzyl halides, phenylacetylenes, and sodium azide in the presence of sodium ascorbate in water to give the corresponding products under mild and environmentally benign conditions. Various benzyl halides containing electron-withdrawing groups and electron-donating groups afforded the desired products in up to 98% yield. The present procedure has the merits of short reaction time and simple reaction work-up. Moreover, this catalyst can be recovered by simple filtration and reused for at least five consecutive runs without any loss of its catalytic activity.

Keywords Ethylenediamine  $\cdot$  Poly(vinyl chloride)  $\cdot$  Copper sulfate  $\cdot$  CuAAC  $\cdot$  Triazole

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### Introduction

1,2,3-Triazoles play a very important role in chemistry and medicine for the broad spectrum of their biological and pharmaceutical properties such as antibacterial [1], antiallergic [2], anticonvulsant [3], and anti-HIV activities [4] due to their unique molecular structure. In 1963, Huisgen first reported the un-catalyzed 1,3-diplor cycloaddition of azide and alkyne (known as Huisgen's reaction) under thermal condition to produce the approximate 1:1 mixture of 1,4- and 1,5-disubstituted 1,2,3-triazole without regioselectivity [5]. Following the Huisgen's pioneering work, Sharpless [6] and Meldal [7] independently in 2001 reported the coppercatalyzed azide-alkyne cycloaddition to afford exclusive 1,4-disubstituted triazole with high regioselectivity under mild condition. This copper-catalyzed version of azide-alkyne cycloaddition also is called CuAAC or click reaction. Generally, Cu(I) salts have been used as homogeneous catalytic systems [8]. Although the Cu(I) homogeneous system has been widely used in this reaction, the Cu(I) species are prone to Cu(0) and Cu(II) via disproportionation process, thereby decreasing of their activity. Thus, there is need to protect and stabilize the active catalytic Cu(I) species during the course of CuAAC. Various nitrogen- [9] or phosphorus-[10] based ligands have been documented in the protection of the Cu(I) species from oxidation and disproportionation, as well as enhancing its catalytic activity [11]. Another simple and practical alternative method to generate Cu(I) species is the in situ reduction of copper sulfate with excessive sodium ascorbate (3-10-fold excess) in reaction mixture. The excessive sodium ascorbate can efficiently render the reaction much less susceptible to oxygen and water, and thus such reactions can process smoothly in air conditions. Apart from these, homogeneous catalysis suffers from many drawbacks such as cumbersome separation and recycling of the expensive catalyst, metal contamination of products, and environmental pollution. Alternatively, heterogeneous catalysts can mitigate these problems. In the last few years, a variety of heterogeneous catalytic systems were prepared by immobilization of copper ions onto different solid supports such as silica [12], alumina [13], zeolite [14], polymer [15], and organic/inorganic hybrid [16]. More recently, several articles have thoroughly reviewed the progress on heterogeneous catalysis in CuAAC reactions [17, 18]. Although this class of heterogeneous catalysts has operated well in most cases, they still suffer from one or more disadvantages such as multiple-step tedious preparation of support matrix, low loading amount of catalyst, lower catalytic activity, high leaching of catalyst, and low thermal stability. Therefore, developing a simple and efficient heterogeneous copper catalyst with high stability, low leaching, high loading, low costing, and a cleaner catalytic system is still an interesting challenge.

The increasing attention for environmental protection has led both the modern academic and industrial communities to develop chemical processes using nontoxic reagents, solvents, and catalysts to obtain products with maximum yield and minimal cost. Water used as a reaction media has a strong impact on the rate of some organic transformations due to its hydrophobic, hydrogen-bonding, and polarity effects [19]. Thus, there has been a growing recognition that water is an attractive medium for many organic reactions.

PVC is one of the most versatile polymers with good flexibility, chemical resistance, film forming property, and cost effectiveness; it is also easy to modify. PVC functionalized with a functional group can be easily achieved by a displacement reaction without chloromethylation, which makes it a low cost and practical application as new materials for heterogeneous catalysts. As part of our continuing interest in heterogeneous palladium catalyzed carbon-carbon crosscoupling reactions, our group recently demonstrated that the Pd nanoparticles immobilized on functionalized PVC is an efficient catalyst for Heck [20] and Suzuki [21] couplings. However, as far as we know, no CuAAC reaction catalyzed by a functionalized PVC-anchored Cu(II) complex has yet been reported. In order to improve further the practicality and efficiency of the CuAAC reaction, we report here the preparation and characterization of a new ethlylenediamine-functionalized PVC anchored Cu(II) complex [PVC-EDA-Cu(II)], and its performance on CuAAC in water under aerobic conditions. Compared with other supported copper catalysts, the ease of preparation, low cost, its stability toward air and moisture, its compatibility with various substrates, and high catalytic activity make it an ideal catalyst for these reactions.

### **Experimental section**

### Chemicals and characterizations

FT–IR spectra were recorded on a Bruker Equinox-55 spectrometer as KBr pellets in the range of 4000–400 cm<sup>-1.<sup>1</sup>H NMR spectra were obtained with a 300 MHz Bruker Avance instrument with CDCl<sub>3</sub> as solvent and TMS as internal standard. The elemental palladium content of polymeric catalysts was determined by Perkin Elmer Optima 2000DV inductively coupled plasma (ICP). Shimadzu AA6680 atomic absorption spectrometer (AAS) was used to measure residual metal ion concentrations. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed with a Philips XL 30ESEM instrument. Thermogravimetric analysis (TGA) was operated on a Netzsch STA449F3 in the range of 25–700 °C under nitrogen atmosphere.</sup>

Poly(vinyl chloride) powder (MW 4800) is industrial grade. All chemicals are commercial available and used as received without further purification.

### Preparation of PVC-EDA-Cu(II) catalyst

PVC powder (20 g, 310 mmol Cl) and EDA (80 mL, 1200 mmol) were added into a round-bottomed flask equipped with a magnetic stirrer bar and stirred at 80 °C for 48 h. The resulting solid was separated from the mixture and washed thoroughly with deionized water then dried in air to constant weight.

The resulting reddish-brown PVC–EDA powder (2 g) was immersed completely in  $CuSO_4$  aqueous solution (20 mL, 2 mmol), and the resulting mixture was stirred for

48 h at rt. The resulting black powder anchored copper was filtered and successively washed with deionized water and ethanol to afford the PVC–EDA–Cu(II) as black powder. The Cu content was determined to be 1.692 mmol/g by ICP-AES.

### Experimental procedure for copper sorption

Twenty grams of copper solution (0.1 mmol/mL) at neutral condition was mixed with 2.0 g of PVC–EDA in an agitated system at room temperature. Five milliliter samples were withdrawn at specified times and filtered through a 1.2 mm filtration membrane. The  $Cu^{2+}$  concentration was determined with AAS.

### General procedure for the catalytic CuAAC reactions

A mixture of sodium azide (1.2 mmol), sodium ascorbate (0.1 mmol), alkyne (1.1 mmol), benzyl compound (1.0 mmol), PVC–EDA–Cu(II) (0.015 g, mol%), and water (3 mL) was vigorously stirred at 70 °C under for specific time under aerobic condition. The reaction process was monitored by TLC. Upon completion of the reaction, the mixture was filtered to recover the catalyst. The catalyst was washed with water and ethanol, dried, and stored for subsequent runs. The filtrate was extracted with ethyl acetate (10 mL  $\times$  3) and washed with brine. After removing the organic solvent using a rotary evaporator, the crude product was further purified by recrystalization using ethanol as the solvent to afford the pure product. All of the products were characterized by <sup>1</sup>H NMR and melt point, which are consistent with those data reported in the literature.

## **Results and discussion**

## Equilibrium time for the preparation of catalyst

The time needed to reach the equilibrium was evaluated for Cu(II) after impregnating 2.0 g of PVC–EDA in aqueous solutions of the copper sulfate (0.1 mmol/mL), and the metal remaining in the aqueous phase at different times was measured by AAS. The results are presented in Fig. 1. The process can be divided into three phases: (a) a very fast sorption within the 4 h (almost linear plot), (b) a slower mass transfer step (between 4 and 40 h), and (c) the equilibrium step (after 40 h). This results suggested that the specific time (48 h) for the preparation of PVC–EDA–Cu(II) ensures the adsorption equilibrium of Cu<sup>2+</sup> can be reached.

## Synthesis and characterization of PVC-EDA-Cu(II)

PVC-supported ethylenediamine (PVC-EDA) was prepared by treatment of commercially available PVC, which was reported by us previously [21]. Complexation of the as-prepared PVC-EDA with copper sulfate solution provide the desired PVC-EDA-Cu(II) catalyst, respectively. The synthetic pathway is depicted as Scheme 1.



Fig. 1 Sorption kinetic of copper(II) ion



Scheme 1 Schematic route for preparation of PVC-EDA-Cu(II)

To verify formation of the ethylenediamine-functionalized PVC and its corresponding Cu(II) complex, more detailed characterization of the catalyst is conducted by FT–IR, ICP–AES, SEM, EDS, TGA, and DSC techniques (Scheme 2).

FT–IR spectroscopy is an important tool to investigate the polymer structure. Figure 2 shows the FT–IR spectra for the PVC, PVC–EDA, and PVC–EDA–Cu(II). As can be seen from curve (A), the adsorption peaks at 608 and 688 cm<sup>-1</sup> was attributed to the C–Cl stretching vibration. By comparing with the FT–IR spectra of curve (A) and curve (B), the characteristic peaks of C–Cl become weaker in the spectra of PVC–EDA owing to the introduction of EDA. As can be seen from FT–IR of curve (B), the adsorption at 3236 cm<sup>-1</sup> is assigned to the stretching vibration of N–H, the adsorption at 1639.6 cm<sup>-1</sup> is assigned to the stretching vibration of N–



Scheme 2 Proposed mechanism for the PVC-EDA-Cu(II) catalyzed CuAAC reaction



Fig. 2 FT-IR spectra of PVC (a), PVC-EDA (b), PVC-EDA-Cu(II) (c)

H of secondary amine, and 1106 cm<sup>-1</sup> is assigned to the bending vibration of N–H of primary amine, respectively, which negatively shifts to 1627 cm<sup>-1</sup> and 1091 cm<sup>-1</sup>, respectively, in curve (C). This is probably caused by the coordination of Cu(II) with the nitrogen atoms of amine.

SEM images of the fresh catalyst and reused catalyst are shown in Fig. 3. They clearly show that the fresh catalyst has a rough surface, which facilitates the contact



Fig. 3 SEM images of fresh catalyst (left) and recovered catalyst (right)

of catalyst and substrates. It is obvious that the surface of the recovered catalyst after the 3rd run is not as rough as the fresh catalyst.

To examine the existence of elements in the catalyst, the energy-dispersive X-ray spectroscopy (EDS) was also conducted. The presence of Cu is clearly shown in the EDS spectrum, together with other elements including carbon and chloride (Fig. 4) associated with SEM analysis. As a result, it is reasonable to assume that Cu(II) species is anchored on the PVC–EDA matrix.

We conducted thermogravimetric analysis (TGA) of PVC–EDA–Cu(II) to characterize the thermostability of the catalyst (Fig. 5). The initial weight loss happened around 100 °C, which probably was due to the loss of water. As the temperature increased, the second weight loss of catalyst occurred at 280 °C due to decomposition, leaving a residue of 60% of the initial weight of the sample. This result showed that the catalyst had good stability up to 280 °C. The curve of DSC





Fig. 5 TGA and DSC of PVC-EDA-Cu(II)

also indicated that the two strong peaks at around 100 and 280 °C were related to the loss of water and the decomposition, respectively.

#### Performance of catalyst for the CuAAC reactions

To obtain optimal conditions, the influence of the amount of catalyst and temperature on the CuACC reaction was explored using the model reaction of phenylacetylene, benzyl bromide, and sodium azide. The results are list in Table 1.

The catalyst has a significant effect on the product yields. The model reaction was explored with the amount of catalyst ranging from 1.5 to 7.0 mol% (Table 1). It was found that this reaction could be conducted efficiently even with a low amount of the catalyst (1.5 mol% Cu) with 75% yield at 70°C (Table 1, entry 1). The yields increased from 75 to 94% by increasing the amount of catalyst from 1.5 to 5.0 mol% (Table 1, entries 1–4). Further increasing the amount of catalyst to 7.0 mol% had no apparent effect on the product yield (Table 1, entry 5). Therefore, 2.5 mol% of the catalyst was enough to push the reaction to completion. The reaction temperature has great influence on the model reaction. It can be seen from Table 1 that decreasing the temperature from 70 to 25 °C led to lower yields and prolonged time (Table 1, entries 6–7).

Once optimized reaction conditions were reached, the coupling reactions of sodium azide, a variety of benzyl halides, and phenylacetylenes were performed to explore the general effectiveness of the PVC–EDA–Cu(II) catalyst. The results are listed in Table 2. As shown in Table 2, the reaction proceeds well and affords the desired products in good yields. Because of the high reactivity of aryl bromides, the

Br	+ NaN <sub>3</sub> +	PVC-EDA-Cu(II) water, sodium ascorbate	
Entry	Amount of catalyst (mol% of C	u) T (°C) Tin	ne (min) Yield <sup>a</sup> (%)
1	1.5	70 12	20 75
2	2.5	70	70 93
3	3.0	70	50 93
4	5.0	70	50 94
5	7.0	70	50 95
6	2.5	25 >12	20 62
7	2.5	50	90 75

Table 1 Opitimization of reaction conditions

Reaction conditions: benzyl bromide (1.0 mmol), phenylacetylene (1.1 mmol), sodium ascorbate (0.020 g, 0.1 mmol), sodium azide (1.2 mmol), catalytic amount of PVC–EDA–Cu(II), water (3 mL) <sup>a</sup> Isolated violate

<sup>a</sup> Isolated yields

benzyl bromides gave higher yields than that of benzyl chlorides. The reactions of electron-rich benzyl halides proceeded well and gave high yields for the corresponding products compared with electron-deficient ones. However, the substituent effects in phenylacetylene had not obviously influenced the reaction time and the yield of products.

### Heterogeneity of the catalysis

To determine the heterogeneous nature of the catalytic system, we have also performed a hot filtration test using model reaction. During this test, the catalyst was removed from the reaction mixture by filtration after 5 min using a hot filtration, and the filtrate was then allowed to react continually for 2 h under the optimal condition. The results show that after removal of the catalyst, the reaction did not proceed, indicating that no catalytically active  $Cu^{2+}$  remained in the filtrate. This finding suggests that the catalyst is characteristically heterogeneous in nature.

### Recycling of the catalyst for the CuAAC reaction

For practical applications, reusability of catalyst is another important parameter. In order to make this issue clear, catalytic recycling was performed using the model reaction. The results are listed in Table 3. After completion of the reaction, the catalyst was easily recovered by filtering and directly used in the next run after washing with water, ethanol, and drying. The results demonstrated that this catalyst can be reused at least five times with comparative loss of its activity. The SEM of reused catalyst showed that the changes of surface and size of particles of the catalyst, which probably decrease the activity of catalyst.

						N	
	×.		P١	/C-EDA-Cu(II)		$\rightarrow \underbrace{ \bigvee_{R_1}^{N \times N} }_{R_1}$	
R1	X + N	JaN <sub>3</sub> + R₂──	water	, sodium ascorba	ate R <sub>1</sub>		
Entry	R <sub>1</sub>	R <sub>2</sub>	Х	Time (min)	Yield <sup>a</sup> (%)	Product	
1	Н	Ph	Br	70	93	а	
2	Н	Ph	Cl	100	90	а	
3	4-F	Ph	Cl	110	82	b	
4	3-F	Ph	Cl	120	80	c	
5	4-Cl	Ph	Cl	165	86	d	
6	3-C1	Ph	Cl	155	85	e	
7	$4-NO_2$	Ph	Br	240	87	f	
8	$4-CH_3$	Ph	Cl	180	78	g	
9	3-CH <sub>3</sub>	Ph	Cl	210	80	h	
10	$4-CH_3$	Ph	Br	120	84	g	
11	Н	4-Me-C <sub>6</sub> H <sub>4</sub>	Br	120	90	i	
12	4-Br	$4-Me-C_6H_4$	Br	150	89	j	
13	$4-NO_2$	4-Me-C <sub>6</sub> H <sub>4</sub>	Br	270	85	k	
14	$4-CH_3$	4-Me-C <sub>6</sub> H <sub>4</sub>	Br	120	98	1	
15	Н	$4-MeO-C_6H_4$	Br	140	88	m	
16	4-F	4-MeO-C <sub>6</sub> H <sub>4</sub>	Cl	280	81	n	
17	3-F	4-MeO-C <sub>6</sub> H <sub>4</sub>	Cl	210	77	0	
18	Н	$4-MeO-C_6H_4$	Cl	150	86	m	
19	$4-CH_3$	$4-MeO-C_6H_4$	Br	300	94	р	
20	Н	2-Py	Br	120	88	q	
21	4-Br	2-Py	Br	160	85	r	
22	4-CN	2-Py	Br	200	83	s	

Table 2 The CuAAC reaction based on the different benzyl halides and alknynes

Reaction conditions: benzyl bromide (1.0 mmol), phenylacetylene (1.1 mmol), sodium ascorbate (0.020 g, 0.1 mmol), sodium azide (1.2 mmol), PVC–EDA–Cu(II) (2.5 mol%), and water (3 mL) at 70  $^{\circ}\mathrm{C}$ 

<sup>a</sup> Isolated yields

### Plausible mechanism for CuAAC reaction

Many explorations on prediction of the mechanism of the CuAAC have been reported. On the basis of a dinuclear copper intermediate reported by Fokin et al. [22], we propose the possible mechanism for the regioselective synthesis of 1,4-disubstituted-1,2,3-triazole from benzyl halide, phenylacetylene, sodium azide, and sodium ascorbate in the presence of PVC–EDA–Cu(II).

Initially, the PVC–EDA–Cu(I) species, generated in situ by reduction of PVC– EDA–Cu(II) and sodium ascorbate, reacts with alkyne to form an acetylide–copper complex (A). Secondly, the Cu(I)-activated intermediate A interacts with the azide activated by PVC–EDA–Cu(I) to produce the dinuclear copper intermediate (B).

Entry	Yield <sup>a</sup> (%)	Time (min)
1	93	70
2	89	90
3	86	95
4	80	100
5	77	120

 Table 3 The reusability of PVC-EDA-Cu(II) for repeat experiments

Reaction conditions: benzyl bromide (1.0 mmol), phenylacetylene (1.1 mmol), sodium ascorbate (0.1 mmol), sodium azide (1.2 mmol), PVC–EDA–Cu(II) (2.5 mol%), and water (3 mL) at 70 °C <sup>a</sup> Isolated violate

<sup>a</sup> Isolated yields

Next, rearrangement of intermediate B leads to the formation of the copper metalated triazolide (C) and releases PVC–EDA–Cu(I). Finally, the intermediate C captures a proton to produce the target triazole and regenerate the PVC–EDA–Cu(I) complex. In addition, PVC–EDA in this catalytic cycle serves as an efficient ligand to coordinate to the Cu species on the catalyst.

#### Conclusions

In conclusion, PVC–EDA–Cu(II) was conveniently synthesized in a simple and efficient way by the treatment of  $CuSO_4$  with PVC–EDA, which was achieved by a substitution reaction of PVC and EDA. It was proven that PVC–EDA–Cu(II) has good performance to catalyze the CuAAC reaction with excellent yields. Moreover, the catalyst can be conveniently separated and recovered from the reaction system, and it can be reused at least five times.

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### References

- N. Nayak, J. Ramprasad, U. Dalimba, P. Yogeeswari, D. Sriram, H.S. Santosh Kumar, S.K. Peethambar, R. Achur, Synthesis of new pyrazole-triazole hybrids by click reaction using a green solvent and evaluation of their antitubercular and antibacterial activity. Res. Chem. Intermed. 42, 3721–3741 (2016)
- D.R. Buckle, D.J. Outred, C.J.M. Rockell, H. Smith, B.A. Spicer, Studies on v-triazoles. 7. Antiallergic 9-oxo-1H, 9H-benzopyrano [2,3-d]-v-triazoles. J. Med. Chem. 26, 251–254 (1983)
- J.L. Kelley, C.S. Koble, R.G. Davis, E.W. McLean, F.E. Soroko, B.R. Cooper, 1-(Fluorobenzyl)-4amino-1H-1,2,3-triazolo [4,5-c] pyridines: synthesis and anticonvulsant activity. J. Med. Chem. 38, 4131–4134 (1995)
- N. Pribut, C.G.L. Veale, A.E. Basson, W.A.L. van Otterlo, S.C. Pelly, Application of the Huisgen cycloaddition and 'click' reaction toward various 1,2,3-triazoles as HIV non-nucleoside reverse transcriptase inhibitors. Bioorg. Med. Chem. Lett. 26, 3700–3704 (2016)
- 5. R. Huisgen, in 1,3-Dipolar Cycloaddition Chemistry, ed. by A. Padwa (Wiley: New York, 1984), pp. 1–176

- V.V. Rostovtsev, L.G. Green, V.V. Fokin, K.B. Sharpless, A stepwise Huisgen cycloaddition process: copper(I)-catalyzed regioselective "ligation" of azides and terminal alkynes. Angew. Chem. Int. Ed. 41, 2596–2599 (2002)
- C.W. Tornøe, C. Christensen, M. Meldal, Peptidotriazoles on solid phase: 1,2,3-triazoles by regiospecific copper(I)-catalyzed 1,3-dipolar cycloadditions of terminal alkynes to azides. J. Org. Chem. 67, 3057–3064 (2002)
- M. Meldal, C.W. Tornoe, Cu-catalyzed azide-alkyne cycloaddition. Chem. Rev. 108, 2952–3015 (2008)
- T.R. Chan, R. Hilgraf, K.B. Sharpless, V.V. Fokin, Polytriazoles as copper(I)-stabilizing ligands in catalysis. Org. Lett. 6, 2853–2855 (2004)
- F. Perez-Balderas, M. Ortega-Munoz, J. Morales-Sanfrutos, F. Hernandez-Mateo, F.G. Calvo-Flores, J.A. Calvo-Asin, J. Isac-Garcia, F. Santoyo-Gonzalez, Multivalent neoglycoconjugates by regiospecific cycloaddition of alkynes and azides using organic-soluble copper catalysts. Org. Lett. 5, 1951–1954 (2003)
- 11. M. Meldal, C.W. Tornoe, Cu-catalyzed azide–alkyne cycloaddition. Chem. Rev. 108, 2952–3015 (2008)
- T. Shamim, S. Paul, Silica functionalized Cu(I) as a green and recyclable heterogeneous catalyst for the Huisgen 1,3-dipolar cycloaddition in water at room temperature. Catal. Lett. 136, 260–265 (2010)
- N. Mukherjee, S. Ahammed, S. Bhadra, B.C. Ranu, Solvent- free one- pot synthesis of 1,2,3-triazole derivatives by the 'Click' reaction of alkyl halides or aryl boronic acids, sodium azide and terminal alkynes over a Cu/Al<sub>2</sub>O<sub>3</sub> surface under ball-milling. Green Chem. **15**, 389–397 (2013)
- S. Chassaing, M. Kumarraja, A. Sani Souna Sido, P. Pale, J. Sommer, Click chemistry in Culzeolites: the Huisgen [3 + 2]-cycloaddition. Org. Lett. 9, 883–886 (2007)
- A. Taher, D. Nandi, R.U. Islam, M. Choudhary, K. Mallick, Microwave assisted azide–alkyne cycloaddition reaction using polymer supported Cu(I) as a catalytic species: a solventless approach. RSC Adv. 5, 47275–47283 (2015)
- 16. Z. Zhang, P. Song, J. Zhou, Y. Chen, B. Lin, Y. Li, Metathesis strategy for the immobilization of copper(II) onto carboxymethylcellulose/Fe<sub>3</sub>O<sub>4</sub> nanohybrid supports: efficient and recoverable magnetic catalyst for the CuAAC reaction. Ind. Eng. Chem. Res. 55, 12301–12308 (2016)
- E. Haldon, M.C. Nicasio, P.J. Pérez, Copper-catalysed azide–alkyne cycloadditions (CuAAC): an update. Org. Biomol. Chem. 13, 9528–9550 (2015)
- S. Chassaing, V. Bénéteau, P. Pale, When CuAAC 'Click Chemistry' goes heterogeneous. Catal. Sci. Technol. 6, 923–957 (2016)
- R.N. Butler, A.G. Coyne, Water: nature's reaction enforcer—comparative effects for organic synthesis "In-Water" and "On-Water". Chem. Rev. 110, 6302–6337 (2010)
- X.-J. Huang, F. Dong, L. Chen, Y.-Q. Li, Nanopalladium immobilized on aminoethanol-functionalized poly(vinyl chloride): an easily prepared, air and moisture stable catalyst for Heck reactions. Monatshefte Chem. 139, 1447–1451 (2008)
- J. Liu, Y.-Q. Li, W.-J. Zheng, Synthesis of immobilized nanopalladium on polymer- supported Schiff base, and study of its catalytic activity in the Suzuki–Miyaura reaction. Monatshefte Chem. 140, 1425–1429 (2009)
- B.T. Worrell, J.A. Malik, V.V. Fokin, Direct evidence of a dinuclear copper intermediate in Cu(I)catalyzed azide–alkyne cycloadditions. Science 340, 457–460 (2013)