



Accepted Article

Title: On Water Cu@g-C3N4 Catalyzed Synthesis of NH-1,2,3-Triazoles Via [2+3] Cycloadditions of Nitroolefins/Alkynes and Sodium Azide

Authors: Subhash Banerjee, Soumen Payra, and Arijit Saha

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemCatChem 10.1002/cctc.201801524

Link to VoR: http://dx.doi.org/10.1002/cctc.201801524



WILEY-VCH

www.chemcatchem.org

WILEY-VCH

On Water Cu@g-C₃N₄ Catalyzed Synthesis of NH-1,2,3-Triazoles *Via* [2+3] Cycloadditions of Nitroolefins/Alkynes and Sodium Azide

Dr. Soumen Payra,^[a] Dr. Arijit Saha^[a] and Dr. Subhash Banerjee^{*,[a]}

Abstract: Here, we have reported fabrication of graphitic polymeric C_3N_4 supported $CuCl_2$ ($Cu@g-C_3N_4$) and characterized by powder X-ray diffraction, field emission scanning electron microscopy, high resolution transmission electron microscopy, X-ray photoelectron spectroscopy studies. An efficient and regioselective protocol for the on water synthesis of 4-aryl-NH-1,2,3-triazole derivatives via 1,3-diipolar cycloaddition reactions of nitroolefins/phenylacetylenes to sodium azide were demonstrated by using $Cu@g-C_3N_4$ as robust and reusable catalyst.

Development of sustainable protocols for the synthesis of 1,2,3triazole scaffolds have emerged one of the thrust area of research for organic chemist due to their exclusive pharmaceutical [1-6], agrochemical [7], medicinal [8-13] and many other applications [14-21]. Several strategies have been reported for the synthesis of 1,2,3-triazoles [22-32] and Huisgen's dipolar cycloaddition of organic azides and alkynesis the most straightforward route [33] Subsequently, transition metal catalyzed alkyne-azide cycloaddition (MAAC; M = Cu [34-38]/Ag [39-40]/Ru [41-43]/Ir [44-45]/Al [46]) have been developed for the synthesis of 1,4 or 1,5-disubstitutedor 1,4,5trisubstituted triazoles [34-46]. Among these, CuAAC perhaps is most powerful method which mostly produce 1,4-disubstituted-1,2,3-triazoles. Again, NH-1,2,3-triazole is one of the important class of 1,2,3-triazoles with numerous applications. Particularly, these moieties can further be modified synthetically with alkyl/aryl/acyl-functionality with choice to yield N2-substituted 1,2,3-triazoles [47-49]. Few pharmaceutically active drugs containing NH-1,2,3-triazole scaffold were shown in Figure 1 [50-54].

However, the synthesis of *NH*-1,2,3-triazoles is fairly challenging compared to the direct synthesis of substituted triazoles [55-61]. *NH*-1,2,3-triazoles were prepared by the CAAC reaction of alkyne and TMSN₃ followed by deprotection of the TMS [55,59], Pd-catalyzed reactions of alkenyl bromides and sodium azide [60], or *via* multicomponent reactions [62-66], or through alkynes with NaN₃ in DMSO [67]. It is noteworthy, that the condensation of nitroalkanes and NaN₃ is a popular method for the synthesis of *NH*-1,2,3-triazoles or N1 substituted triazoles. Such type of condensation has been carried out by using *p*-TsOH/DMF [68], Amberlyst-15/DMF [69], acetic acid/flow chemistry [70], Bi₂WO₆/water [71], Ce(OTf)₃ [24], Cu(OTf)₂ [30].

[a] Dr. S. Payra, Dr. A. Saha, Dr. S. Banerjee Department of Chemistry, Guru Ghasidas Vishwavidyalaya Bilaspur, C.G., India, 495009 Tel: +91-7587401979 Fax: +91 7752 260148 E-mail: ocsb2009@gmail.com



Figure 1. Some bioactive molecules containing NH-1,2,3-triazole unit.

Most of the above protocols for the preparation of *NH*-1,2,3triazoles have their own advantages. However, the practical/industrial use of those protocol were limited by low yields, potential substrate polymerization (cyclotrimerization), use of environmentally polluting heavy-metal ions which cannot be regenerated/reused [72]. Heterogenization of the existing homogeneous catalysts could be an attractive solution to circumvent these problems. The design of heterogeneous catalysts has to take into account of high efficiencies, selectivities, stability and most essentially environmental acceptability.

Very recently, graphitic carbon nitride (g-C₃N₄) material has being emerged as an appealing and fascinating material, and attracted a great deal of attention in a wide community [72-78]. The unique features of C_3N_4 are that highest thermal and chemical stability, abundant nitrogen functionalities on the surface sites acts as strong Lewis base sites, while the β bonded planar layered configurations are utilized to anchor desired metal which allows its direct use as heterogeneous catalysts [72]. Pristine $g-C_3N_4$ used for Friedel-Crafts reaction [73], oxidation of benzene to phenol [79], cycloaddition of CO₂ to propylene oxide to propylene carbonate [80]. Few g-C₃N₄ composites have also been developed. For example, Fe-g-C₃N₄ has been developed for degradation of methylene blue, water splitting [81], photo oxidation of benzene to phenol [82-83] and decomposition of nitric oxide [84]. BiVO₄-g-C₃N₄ nanocomposites was used for oxidation of alcohol/amines, VO-g-C₃N₄ was employed for the oxidative esterification of alcohols [78], graphene/C₃N₄ composites have used for visible-light H₂-production [85], g-C₃N₄/N-doped photocatalvtic graphene/NiFe-layered double hydroxide used for solar-driven

ChemCatChem

photoelectrochemical water oxidation [86], Pd-g-C₃N₄ was developed for Sonogashira reactions [72]. However, to the best of our knowledge, g-C₃N₄ supported copper chloride (Cu@g-C₃N₄) material has not been reported in the literature. As a part of continuous interest in the development of heterogeneous synthetic methodologies using nanomaterials [87-92], here, we have developed Cu@g-C₃N₄ for the [3+2]cycloaddition of nitroolefins/alkynes with sodium azide leading to *NH*-1,2,3-triazoles (Scheme 1).



Scheme 1. Fabrication of $Cu@g-C_3N_4$ for the synthesis of 4-aryl-*NH*-1,2,3-triazoles from β -nitrostyrenes/phenylacetylens.

At the outset, we have prepared the catalyst simply by the calcination of urea followed by immobilization of CuCl₂ under sonication. The reaction mixture was then centrifuged, washed with ethanol and dried up at 60 °C under vacuum for 16 h to provide CuCl₂@g-C₃N₄ as off-white bluish solid (Scheme 1). The as prepared material was characterized by using analytical techniques. Figure 2 represents the powder X-ray diffraction (XRD) of g-C₃N₄ (black line) and CuCl₂@g-C₃N₄ (red line).



Figure 2. Powder XRD pattern of g-C₃N₄ and Cu@g-C₃N₄.

On the other hand, the EDAX spectrum of Cu@C₃N₄ (Figure 3d) confirms the presence of carbon, nitrogen, copper and chlorine in the sample. This suggested that the CuCl₂ remained stable during immobilization process on the surface of C₃N₄. On the other hand, as expected only peaks for elemental carbon and nitrogen were observed in the EDAX spectrum of pure g-C₃N₄ and no peak for CuCl₂ was observed (Figure 3c). As seen in Figure 2 both the material showed a broad peak at 2θ 28.1° which suggested the presence graphite-like interlayer stacking of the aromatic systems in C₃N₄ (JCPDS 87-1526) [78]. The

weaker one at 2θ 13.1° is related to in-plane tris-s-triazine structural packing. Thus, the interlayer stacking and in plane packing were remained intact after the immobilization of Cu on C₃N₄ polymer. However, no additional peak corresponding to Cu was observed in the powder XRD pattern of Cu@g-C₃N₄. This could probably be due to the high dispersion of CuCl₂ in the support [78]. The field emission scanning electron microscopy (FE-SEM) studies of g-C₃N₄ (Figure 3a) and Cu@g-C₃N₄ (Figure 3b) have clearly demonstrated that the morphology of g-C₃N₄ remained intact after the immobilization of Cu.



Septed Manuscript

Figure 3. FE-SEM images of (a) $g-C_3N_4$ and (b) $Cu@g-C_3N_4$; EDAX pattern of (c) $g-C_3N_4$ and (d) $Cu@g-C_3N_4$.



 $\label{eq:Figure 4.} \mbox{ (a) HR-TEM image of $Cu@g-C_3N_4$; (b) SAED pattern of $Cu@g-C_3N_4$; (c-d) magnified HR-TEM images of $Cu@g-C_3N_4$.}$

The high resolution transmission electron microscopy images of g-Cu@g-C₃N₄ have been presented in Figure 4. As seen from the Figure 4a, Cu@g-C₃N₄ exhibits a sheet-like structure similar to that of g-C₃N₄ with different thickness.

Thus the immobilization does not destroy the basic skeletal of g- C_3N_4 . However, magnified HR-TEM image shows the high dispersion of Cu in the g- C_3N_4 support (Figure 4c-d). Additionally, the ICP-AES analysis also confirmed the presence of copper in the immobilized material.

The X-ray photoelectron spectroscopy (XPS) was performed, to check the composition on the surface of the materials and oxidation states of the materials (Cu@g-C₃N₄). The full survey of XPS spectrum (Figure 5e) displays that C, N, Cu and Cl elements presence in the material, which is also well accordance with the SEM-EDAX (Figure 3d). The peak at 283.10 eV in C 1s is attributed to the surface adventitious carbon and other peak allocated at 286.8 eV is due to the sp³-hybridized carbon bonded with N-C=N of polymeric graphitic g-C₃N₄ (Figure 5a) [93]. For N 1s, four distinguished peaks were observed. The peak at 397.10 eV has assigned for the nitrogen (N-C-N), like pyridinium-nitrogen and peak corresponding to 398.6 eV is due to the nitrogen N-(C)₃ (Figure5b) [93].



 $\label{eq:Figure 5. XPS analysis of (a) core level spectra C 1s; (b) core level spectra N 1s; (c) core level spectra Cu 2p; (d) core level spectra Cl 2p; (e) XPS survey spectrum of Cu@g-C_3N_4.$

The peaks allocated at 402.8 and 404.6 eV are due to amino functionalized hydrogen (C-N-H) and effects of charge densities [94]. In the XPS spectra of Cu^{2+} 2p (Figure 5c) four distinguished peaks were observed.

The resilient peaks at 930.1 eV and 950.2 eV are due to the two types of Cu species, which corresponds to the strong spin-orbit coupling of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ [95]. The other two peaks at 940.7 eV and 970 eV in lower intensity is might be due to Cu-N and Cu-C bond formation in the surface of the catalyst. Figure 5d demonstrated the XPS spectra of Cl (Figure 5d) two stronger peaks were determined at 198.1 eV and 199.8 eV is mainly due to the strong spin orbit coupling of Cl $2p_{3/2}$ and Cl $2p_{1/2}$ respectively. The XPS studies reflect that amine functionalization in g-C₃N₄ offered sufficient stability of CuCl₂ in the surface of the catalyst and could prevent the oxidation of the metal composite.

Next, we have investigated the catalytic activity of $Cu@g-C_3N_4$ in the synthesis of 4-aryl-*NH*-1,2,3-triazole (**3a**) by the reaction of β -nitrostyrene and sodium azide as a model reaction. When a mixture of β -nitrostyrene (1 mmol), sodium azide (3 mmol) and $Cu@g-C_3N_4$ (20 mg) in DMF (2 ml) was heated at 120 °C (Table 1, entry 1) good yield of (82%) of product was observed after 45 min. and no further significant improvement of yield was observed up to 2 h (Table 1, entries 1-2). Water is proved to best solvents (entry 3, Table 1) giving 99% of product in 30 minutes among other tested (entries 4-7, Table 1). Next, we have also screened the reaction using different metal supported g-C_3N_4 catalyst such as, Zn@g-C_3N_4, Ni@g-C_3N_4, Fe@g-C_3N_4, Co@g-C_3N_4 etc.

Among them, only Zn/Fe@g-C₃N₄ could produce moderate yield of product (**3**) (entries 8-9, Table 1) whereas Ni/Co-@g-C₃N₄ could not initiate the reaction event after 2 h (entries 10-11, Table 1). It was also observed that Cu(0)@g-C₃N₄ produced product marginally (entry 13, Table 1). Further, the amount of Cu@g-C₃N₄ was optimized to 15 mg (entries 16-17, Table 1) and varying amounts of sodium azide (NaN₃) it was observed that 2 equiv. of NaN₃ provided maximum yields (entries 18-19, Table 1). We have also checked the reaction condition by using CuCl₂ and Cu (0) nanoparticles, which yielded 23 % and 62 % of the isolated product (entries 20-21, Table 1). Thus, a mixture of β -nitrostyrene (1 mmol), NaN₃ (2 mmol) and Cu@g-C₃N₄ (15 mg) 2 mL of water under refluxing conditions for 30 min. was considered as optimized reaction conditions (entry 18, Table1).

| Table 1. Optimization of the reaction conditions for the synthesis of 4- aryl-NH-1,2,3-triazole. ^a | | | | | | | | | |
|--|------------------------------------|------------------|-----------|--------|------------------------|--|--|--|--|
| $ \underbrace{NO_2}_{HN_3} \xrightarrow{Conditions} \underbrace{H_{HN_N}}_{HN_N} $ | | | | | | | | | |
| 1 | | 2 | 2 3 | | | | | | |
| Entry | Catalyst | Solvent | Temp (°C) | Time | Yield (%) ^b | | | | |
| | | | | | | | | | |
| 1 | Cu@g-C ₃ N ₄ | DMF | 120 °C | 45 min | 82 % | | | | |
| 2 | Cu@g-C ₃ N ₄ | DMF | 120 °C | 2 h | 85 % | | | | |
| 3 | $Cu@g-C_3N_4$ | H ₂ O | 100 °C | 30 min | 99 % | | | | |
| | | | | | | | | | |

| 4 | Cu@g-C₃N₄ | DMSO | 120 °C | 2 h | 35 % |
|----|------------------------------------|------------------|--------|--------|-------------------|
| 5 | Cu@g-C ₃ N ₄ | EtOH | 80 °C | 2 h | 31 % |
| 6 | $Cu@g-C_3N_4$ | MeOH | 65 °C | 2 h | 24 % |
| 7 | Cu@g-C ₃ N ₄ | CH₃CN | 65 °C | 2 h | 27 % |
| 8 | Zn@g-C ₃ N ₄ | H ₂ O | 100 °C | 2 h | 49 % |
| 9 | Fe@g-C ₃ N ₄ | H ₂ O | 100 °C | 2 h | 39 % |
| 10 | Ni@g-C ₃ N ₄ | H ₂ O | 100 °C | 2 h | - |
| 11 | Co@g-C ₃ N ₄ | H₂O | 100 °C | 2 h | - |
| 12 | g-C ₃ N ₄ | H₂O | 100 °C | 2 h | - |
| 13 | Nano Cu(0)@ g-CoN | H ₂ O | 100 °C | 2 h | 56 % |
| 14 | Cu@g-C ₃ N ₄ | H ₂ O | R.T. | 2 h | Trace |
| 15 | Cu@g-C ₃ N ₄ | H₂O | 80 °C | 2 h | 91 % |
| 16 | Cu@g-C ₃ N ₄ | H ₂ O | 100 °C | 30 min | 99 % [°] |
| 17 | $Cu@g-C_3N_4$ | H ₂ O | 100 °C | 30 min | 93 % ^d |
| 18 | Cu@g-C₃N₄ | H₂O | 100°C | 30 min | 99 % ^e |
| 19 | $Cu@g-C_3N_4$ | H ₂ O | 100 °C | 30 min | 67 % ^f |
| 20 | CuCl ₂ | H ₂ O | 100 °C | 30 min | 23 % |
| 21 | Cu (0) NPs | H₂O | 100 °C | 30 min | 62 % |

^aReaction conditions: β-nitrostyrenes (0.50 mmol), sodium azide (1.50 mmol), Cu@g-C₃N₄ (20 mg) in 2 mL solvent under air. ^bThe denoted yields corresponds to their pure isolated products. ^c15 mg of Cu@g-C₃N₄, ^d10 mg of Cu@g-C₃N₄, ^e2 equiv. of NaN₃ and ^f1 equiv. of NaN₃.

Next, using optimized reaction conditions and following a simple experimental procedure (see SI) we have explored the scope of the methodology for the synthesis of 4-aryl-NH-1,2,3triazole derivatives. It was established that various β nitrostyrenes with different substituents were well tolerated under the optimized reaction conditions. The results were presented in Table 2. Excellent yields of products (90-99 %) were observed within very short reaction time (30-45 min). Electron donating group like, -Me, -OMe, -OH and withdrawing group like, -NO₂, -Cl, -Ar present in the aromatic ring of at β nitrostyrenes were participated smoothly under the reaction conditions. Moreover, bicycle β -nitrostyrene (**3i**, Table 2) was also participated in the reaction under same conditions. The intrinsic nitrogen skeletal of g-C₃N₄ offers the slightly basic atmosphere in the reaction media to initiate the reaction without the using an external base which is required to complete the conversion. All the reactions listed in Table 2 were very clean and high yielding. The products were purified by simply short column chromatography over silica gel.



Table 2. Substrate scope for the synthesis of 4-aryl-NH-1,2,3-triazoles from β -nitrostyrenes and sodium azide



Next we have investigated the stability and recyclability of the Cu@g-C₃N₄ catalyst by considering the synthesis of 4-phenyl-1H-1,2,3-triazole (3a, Table 2) as a model reaction under optimized conditions. After each cycle, Cu@g-C₃N₄ was recovered simply by filtration, washed thoroughly by ethanol, dried in oven at 80 °C for 2 h and finally reused for the subsequent reactions. It was observed that the Cu@g-C₃N₄ was very stable under the reaction conditions and recycled up to ten times with a minimal lose in yields of the product (Figure 6). This slight decrease in yield was probably due to the leaching of very nominal amount of metal (about 0.08%) after 10th cycle from the g-C₃N₄ support as evident from the inductive-coupled plasma atomic emission spectroscopic (ICP-AES) analysis. However, the graphitic nature of the g-C₃N₄ after 10th cycle remained unchanged as seen in the powder XRD pattern (SI, Figure 1) and HR-TEM image of the recovered catalyst (SI, Figure 2).

WILEY-VCH

WILEY-VCH



Figure 6. Reusability of $Cu@g-C_3N_4$ for the synthesis of 4-phenyl-1*H*-1,2,3-triazole (3a, Table 2).

Motivated by the excellent catalytic activity of Cu@g-C₃N₄ in synthesis of 4-aryl-*NH*-1,2,3-triazoles, we have extended the scope of this methodology by using phenyl acetylenes as substrate under the optimized reaction conditions.

Table 3. Substrate scope for the synthesis of 4-aryl-*NH*-1,2,3-triazoles from phenylacetylenes and sodium azide.





Reaction Conditions: Phenylacetylenes (0.5 mmol), sodium azide (0.75 mmol; 1.5 mmol for **5i**), Cu@g-C₃N₄ (15 mg) in 2 mL water at 100 $^{\circ}$ C for 45 min under air. The yields refer to those of pure and isolated products.

When a mixture of phenyl acetylene (0.5 mmol), sodium azide (0.75 mmol) and Cu@g-C₃N₄ (15 mg) was refluxed at 100 °C in water excellent yield (92 %) of 4-aryl-*NH*-1,2,3-triazole (**5a**, Table 3) was obtained within 45 minutes. Next, using standard conditions and following a simple experimental procedure (see SI), we have synthesized various 4-aryl-*NH*-1,2,3-triazole derivatives (**5a-I**, Table 3) using different phenyl acetylene derivatives. Moreover, we observed that 1,4-diethynyl benzene was participated in the reaction smoothly under same reaction conditions and provided two triazole ring (**5i**; Table 3).

Moreover, we have drawn a plausible reaction mechanism for polymeric $Cu@g-C_3N_4$ catalyzed de-nitrative 1,3-dipolar cycloaddition of β -nitrostyrenes and sodium azide leading to formation of 4-aryl-*NH*-1,2,3-triazole scaffolds has been presented in Scheme 2. The catalytic reaction is going via coordination of β -nitrostyrenes in the surface of $Cu@g-C_3N_4$ catalyst followed by nucleophilic addition of sodium azide by triggering of surface Cu. Next step is the elimination of HNO₂ [] followed by the formation of *NH*-1,2,3-triazole.



Scheme 2. Plausible reaction mechanism for the $Cu@g-C_3N_4$ catalyzed 4-aryl-NH-1,2,3-triazole synthesis.

This present methodology for the synthesis of 4-aryl-*NH*-1,2,3-triazoles offered several advantages over previously published protocol (i) broad substrate scope including various β -nitrostyrenes and phenylacetylenes, (ii) excellent yield of products, (iii) shorter reaction time, (iv) use of catalytic amount and reusable Cu@g-C₃N₄, (v) milder reaction condition of heating 100 °C, (vi) use of greener solvent water and (vii) no

JUSC

additives required to furnished the reactions which made the protocol environmental benign in nature.

Conclusions

In summary, Cu@g-C₃N₄ catalyst was prepared by the calcination of urea followed by immobilization of CuCl₂ and characterized by powder XRD, HRTEM, FESEM EDAX, ICP-AES and XPS analysis. The $Cu@g-C_3N_4$ catalyst showed excellent activity for the regioselective synthesis of 4-aryl-NH-1,2,3-triazole derivatives via denitrative 1,3diipolar cycloaddition reactions of nitroolefins and sodium azide in good to excellent yields (90-99%) within short reaction time (0.5 h). This methodology was also applied for the synthesis of 4-aryl-NH-1,2,3-triazole derivatives from phenyl acetylene derivatives. The present protocol offered several advantages such as: (i) use of very stable and novel Cu@g-C₃N₄ as catalyst, (ii) wide range of substrate scope including nitroolefins and phenyl acetylenes, (iii) short reaction time (0.5 h), (iv) excellent yields of 4-aryl-NH-1,2,3-triazole derivatives, and finally, (v) use of water as reaction medium and reusability of catalyst made the protocol environmental-friendly in nature. To the best of our knowledge this is the first report of preparation of polymeric g-C₃N₄@Cu composite and its applications in useful "click reactions".

Supporting Information Summary

Preparation procedures and characterizations of the catalysts, reusability of the catalyst and representative NMR copies will be available in the supporting information.

Acknowledgements

We are pleased to acknowledge funding agency CCOST, Raipur (ENDT No 2096/CCOST/11[RP/2017). Special thanks to Prof. B. C. Ranu and his research group for their help in NMR and powder XRD, FT-IR, FE-SEM, HR-TEM studies. We are also highly grateful to IIT Kanpur, for XPS studies.

Keywords: 4-aryl-*NH*-1,2,3-triazole • Heterogeneous catalysis • polymeric $g-C_3N_4@Cu$ composite • Click reactions • Green protocol

- [1] F. Yang, S. Kundu, A. B. Vidal, J. Graciani, P. J. Ramirez, S. D. Senanayake, D. Stacchiola, J. Evans, P. Liu, J. F. Sanz, J. A. Rodriguez, *Angew. Chem. Int. Ed.* **2011**, *50*, DOI org/10.1002/ange.201103798.
- [2] R. S. Bohacek, C. McMartin, W. C. Guida, Med. Res. Rev. 1996, 16, 3.
- [3] J. E. Moses, A. D. Moorhouse, Chem. Soc. Rev. 2007, 36, 1249.
- [4] G. C. Tron, T. Pirali, R. A. Billington, P. L. Canonico, G. Sorba, A. A. Genazzani, *Med. Res. Rev.* 2008, 28, 278.
- [5] C. Sheng, W. Zhang, Curr. Med. Chem. 2011, 18, 733.
- [6] S. G. Agalave, S. R. Maujan, V. S. Pore, Chem. Asian J. 2011, 6, 2696.
- [7] P. Thirumurugan, D. Matosiuk, K. Jozwiak, Chem. Rev. 2013, 113, 4905.

- [8] C. Y. Chen, P. H. Lee, Y. Y. Lin, W. T. Yu, W. P. Hu, C. C. Hsu, Y. T. Lin, L. S. Chang, C. T. Hsiao, J. J. Wang, M. I. Chung, Bioorg. *Med. Chem. Lett.* **2013**, *23*, 6854.
- [9] R. Alvarez, S. Velazquez, A. S. Felix, S. Aquaro, E. De Clercq, C. F. Perno, A. Karlsson, J. Balzarini, M. J. Camarasa, J. Med. Chem. 1994, 37, 4185.
- [10] A. Tam, U. Arnold, M. B. Soellner, R. T. Raines, J. Am. Chem. Soc. 2007, 129, 12670.
- [11] A. Carta, M. Palomba, G. Paglietti, P. Molicotti, B. Paglietti, S. Cannas, S. Zanetti, *Bioorg. Med. Chem. Lett.* 2007, *17*, 4791.
- [12] D. K. Mohapatra, P. K. Maity, M. Shabab, M. I. Khan, *Bioorg. Med. Chem. Lett.* **2009**, *19*, 5241.
- [13] M. O. Anderson, J. Zhang, Y. Liu, C. Yao, P. W. Phuan, A. S. Verkman, *J. Med. Chem.* **2012**, *55*, 5942.
- [14] M. Galibert, P. Dumy, D. Boturyn, Angew. Chem., Int. Ed. 2009, 48, 2576.
- [15] W. Q. Fan, A. R. Katritzky, In Comprehensive Heterocyclic Chemistry II; A. R.Katritzky, C. W. Rees and E. F. V. Scriven, *Eds.; Elsevier Science: Oxford, U.K.* **1996**; *4*, 1.
- [16] B. Chattopadhyay, V. Gevorgyan, Angew. Chem., Int. Ed. 2012, 51, 862.
- [17] D. Urankar, B. Pinter, A. Pevec, F. DeProft, I. Turel, J. Košmrlj, Inorg. Chem. 2010, 49, 4820.
- [18] H. Struthers, T. L. Mindt, R. Schibli, *Dalton. Trans.* **2010**, *39*, 675.
- [19] T. C. Johnson, W. G. Totty, M. Wills, Org. Lett. 2012, 14, 5230.
- [20] F. Saleem, G. K. Rao, A. Kumar, G. Mukherjee, A. K. Singh, Organometallics, 2013, 32, 3595.
- [21] C. Chu, R. Liu, *Chem. Soc. Rev.* **2011**, *40*, 2177.
- [22] J. E. Hein, V. V. Fokin, Chem. Soc. Rev. 2010, 39, 1302.
- [23] C. O. Kappe, E. V. D. Eycken, Chem. Soc. Rev. 2010, 39, 1280.
- [24] Y. C. Wang, Y. Y. Xie, H. E. Qu, H. S. Wang, Y. M. Pan, F. P. Huang, J. Org. Chem. 2014, 79, 4463.
- [25] D. Sahu, S. Dey, T. Pathak, B. Ganguly, Org. Lett. 2014, 16, 2100.
- [26] L. Wu, Y. Chen, J. Luo, Q. Sun, M. Peng, Q. Lin, *Tetrahedron Lett.* 2014, 55, 3847.
- [27] L. Hong, W. Lin, F. Zhang, R. Liu, X. Zhou, Chem. Commun. 2013, 49, 5589.
- [28] J. Li, D. Wang, Y. Zhang, J. Li, B. Chen, Org. Lett. 2009, 11, 3024.
- [29] F. C. Jia, C. Xu, Z. W. Zhou, Q. Cai, D. K. Li, A. X. Wu, Org. Lett. 2015, 17, 2820.
- [30] Y. Chen, G. Nie, Q. Zhang, S. Ma, H. Li, Q. Hu, Org. Lett. 2015, 17, 1118.
- [31] Q. Hu, Y. Liu, X. Deng, Y. Li, Y. Chen, Org. Lett. 2016, 18, 6034.
- [32] J. Thomas, S. Jana, J. John, S. Liekens and W. Dehaen, *Chem. Commun.* 2016, *52*, 2885.
- [33] R. Huisgen, In 1,3-Dipolar Cycloaddition Chemistry; Padwa, A., *Ed.; Wiley: New York*, **1984**.
- [34] H. C. Kolb, M. G. Finn, K. B. Sharpless, Angew. Chem., Int. Ed. 2001, 40, 2004.
- [35] V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, Angew. Chem., Int. Ed. 2002, 41, 2596.
- [36] C. W. Tornøe, C. Christensen, M. Meldal, J. Org. Chem. 2002, 67, 3057.
- [37] K. Kamata, Y. Nakagawa, K. Yamaguchi, N. Mizuno, J. Am. Chem. Soc. 2008, 130, 15304.
- [38] J. E. Hein, J. C. Tripp, L. B. Krasnova, K. B. Sharpless, V. V. Fokin, Angew. Chem., Int. Ed. 2009, 48, 8018.
- [39] J. McNulty, K. Keskar, Eur. J. Org. Chem. 2012, 2012, 5462.
- [40] J. McNulty, K. Keskar, R. Vemula, Chem. Eur. J. 2011, 17, 14727.

- [41] L. Zhang, X. G. Chen, P. Xue, H. H. Y. Sun, I. D. Williams, K. B. Sharpless, V. V. Fokin, G. C. Jia, J. Am. Chem. Soc. 2005, 127, 15998
- [42] M. M. Majireck, S. M. Weinreb, J. Org. Chem. 2006, 71, 8680. [43] A. Tam, U. Arnold, M. B. Soellner, R. T. Raines, J. Am. Chem.
- Soc. 2007, 129, 12670.
- [44] S. Ding, G. Jia, J. Sun, Angew. Chem., Int. Ed. 2014, 53, 1877.
- [45] E. Rasolofonjatovo, S. Theeramunkong, A. Bouriaud, S.Kolodych, M. Chaumontet, F. Taran, Org. Lett. 2013, 15, 4698
- [46] Q. Hu, Y. Liu, X. Deng, Y. Li, Y. Chen, Adv. Synth. Catal. 2016, 358. 1689
- H. Aruri, U. Singh, M. Kumar, S. Sharma, S. K. Aithagani, V. K. [47] Gupta, S. Mignani, R. A. Vishwakarma, P. P. Singh, J. Org. Chem. 2017, 82, 1000.
- [48] X. Deng, X. Lei, G. Nie, L. Jia, Y. Li, Y. Chen, J. Org. Chem. 2017, 82, 6163.
- [49] L. L. Zhu, X. Q. Xu, J. W. Shi, B. L. Chen, Z. Chen, J. Org. Chem. 2016. 81. 3568
- L. S. Kallander, Q. Lu, W. Chen, T. Tomaszek, G. Yang, D. Tew, T. [50] D. Meek, G. A. Hofmann, C. K. S. Pritchard, W. W. Smith, C. A. Janson, M. D. Ryan, G. F. Zhang, K. O. Johanson, R. B. Kirkpatrick, T. F. Ho, P. W. Fisher, M. R. Mattern, R. K. Johnson, M. J. Hansbury, J. D. Winkler, K. W. Ward, D. F. Veber, S. K. Thompson, J. Med. Chem. 2005, 48, 5644.
- [51] T. Weide, S. A. Saldanha, D. Minond, T. P. Spicer, J. R. Fotsing, M. Spaargaren, J. M. Frere, C. Bebrone, K. B. Sharpless, P. S. Hodder, V. V. Fokin, ACS Med. Chem. Lett. 2010, 1, 150.
- [52] A. R. Gakovic, J. J. Csanadi, E. A. Djurendic, O. Klisuric, G. Bogdanovic, K. M. P. Gasi, Tetrahedron Lett. 2009, 50, 4107.
- [53] Q. Huang, M. Zheng, S. Yang, C. Kuang, C. Yu, Q. Yang, Eur. J. Med. Chem. 2011, 46, 5680.
- [54] U. F. Rohrig, S. R. Majjigapu, A. Grosdidier, S. Bron, V. Stroobant, L. Pilotte, D. Colau, P. Vogel, B. J. Van den Eynde, V. Zoete, O. Michielin, J. Med. Chem. 2012, 55, 5270.
- [55] D. B. Ramachary, K. Ramakumar, V. V. Narayana, Chem. Eur. J. 2008, 14, 9143.
- J. Thomas, J. John, N. Parekh, W. Dehaen, Angew. Chem., Int. [56] Ed. Engl. 2014, 126, 10319.
- S. S. V. Ramasastry, Angew. Chem., Int. Ed. 2014, 53, 14310. C. G. S. Lima, A. Ali, S. S. van Berkel, B. Westermann, M. W. [58]
- Paixao, Chem. Commun. 2015, 51, 10784. [59] J. John, J. Thomas, W. Dehaen, Chem. Commun. 2015, 51,
- 10797. J. John, J. Thomas, N. Parekh, W. Dehaen, Eur. J. Org. Chem. [60]
- 2015, 4922. [61] J. Thomas, V. Goyvaerts, S. Liekens, W. Dehaen, Chem. Eur.
- J. 2016, 22, 9966. [62] R. C. Cioc, E. Ruijter, R. V. A. Orru, Green Chem. 2014, 16, 2958.
- [63] B. H. Rotstein, S. Zaretsky, V. Rai, A. K. Yudin, Chem. Rev. 2014, 114, 8323.
- B. B. Toure, D. G. Hall, Chem. Rev. 2009, 109, 4439. [64]
- S. Sengupta, H. Duan, W. Lu, J. L. Petersen, X. Shi, Org. Lett. [65] 2008, 10, 1493. B. I. V. Arenas, L. L. Romero, D. Á. Beltrán, G. E. N. Silva, A. G.
- [66] Carrillo, V. H. Lara, J. A. M. Serna, Tetrahedron Lett. 2017, 58, 2690.
- J. L. Tang, L. Ming, X. M. Zhao, J. Heterocyclic Chem. 2016, [67] 53, 1367.

- [68] X. J. Quan, Z. H. Ren, Y. Y. Wang, Z. H. Guan, Org. Lett. 2014, 16. 5728.
- H. Zhang, D. Z. Dong, Z. L. Wang, *Synthesis*, **2016**, *48*, 131. D. Li, L. Liu, Y. Tian, Y. Ai, Z. Tang, H. Sun, G. Zhang, [69] [70] Tetrahedron, 2017, 73, 3959.
- [71] B. Paplal, S. Nagaraju, V. Palakollu, S. Kanvah, B. V. Kumar, D. Kashinath, RSC Adv. 2015, 5, 57842.
- [72] S. Elavarasan, B. Baskar, C. Senthil, P.Bhanja, A. Bhaumik, P. Selvam, M. Sasidharan, RSC Adv. 2016, 6, 49376.
- F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, Angew. [73] Chem., Int. Ed. 2006, 45, 4467.
- J. M. Notestein, A. Katz, Chem. Eur. J. 2006, 12, 3954
- F. Goettmann, C. Boissiere, D. Grosso, F. Mercier, P. Le Floch, [75] Sanchez, Chem. Eur. J. 2005, 11, 7416.
- [76] Goettmann, P. Le Floch, C. Sanchez, Chem. Commun. F. 2006 2036
- F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, Chem. [77] Commun. 2006, 4530.
- S.Verma, R. B. N. Baig, C. Han, M. N. Nadagouda, R. S. [78] Varma, Green Chem. 2016, 18, 251.
- [79] M. B. Ansari , B. H. Min , Y. H. Mo, S. E. Park, Green Chem. 2011, 13, 1416.
- J. Xu, J. K. Shang, Q. Jiang, Y. Wang, Y. X. Li, RSC Adv. 2016, [80] 6, 55382. [81] J. Gao, Y. Wang, S. Zhou, W. Lin, Y. Kong, *Chem. Cat. Chem.*
- 2017, 9, 1708.
- X. Chen, J. Zhang, X. Fu, M. Antonietti, X. Wang, J. Am. Chem. [82] Soc. 2009, 131, 11658.
- X. Wang, X. Chen, A. Thomas, X. Fu, M. Antonietti, Adv. Mater. [83] 2009. 21. 1609. [84]
- J. Zhu, P. Xiao, H. Li, S. A. C. Carabineiro, ACS Appl. Mater. Interfaces, 2014, 6, 16449. Q. Xiang, J. Yu, M. Jaroniec, J. Phys. Chem. C, 2011, 115, [85]
- 7355. [86] Y. Hou, Z. Wen, S. Cui, X. Feng, J. Chen, Nano Lett. 2016, 16, 2268
- [87] S. Banerjee, S. Payra, A. Saha, G. Sereda, Tetrahedron Lett. 2014, 55, 5515.
- [88] A. Saha, S. Pavra, S. Baneriee, Green Chem. 2015, 17, 2859.
- [89] S. Payra, A. Saha, S. Guchhait, S. Banerjee, RSC Adv. 2016, 6 33462
- [90] S. Payra, A. Saha, S. Banerjee, RSC Adv. 2016, 6, 52495.
- [91] A. Saha, S. Payra, B. Selvaratnam, S. Bhattacharya, S. Pal, R. T. Koodali, S. Banerjee, ACS Sustainable Chem. Eng. 2018, 6, 11345-11352
- [92] S. Payra, A. Saha, S. Banerjee, Chemistry Select, 2018, 3, 7535.
- [93] X. Xu, J. Luo, L. Li, D. Zhang, Y. Wang, G. Li, Green Chem. 2018. 20. 2038.
- [94] X. L. Weng, Q. S. Zeng, Y. L. Zhang, F. Dong, Z. B. Wu, ACS Sustainable Chem. Eng. 2016, 4, 4314.
- [95] N. Fredj, T. D. Burleigh, Journal of The Electrochemical Society, 2011, 158, C104
- [96] S. Payra, A. Saha, S. Banerjee, RSC Adv. 2016, 6, 12402-12407.

WILEY-VCH

COMMUNICATION

Entry for the Table of Contents



Here, we have developed of graphitic polymeric C_3N_4 supported $CuCl_2$ ($Cu@g-C_3N_4$) material for efficient and regioselective on water synthesis of 4-aryl-*NH*-1,2,3-triazole derivatives *via* 1,3-diipolar cycloaddition reactions of nitroolefins/phenylacetylenes to sodium azide.