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Free-radical-mediated copper-catalyzed triazole formation under UV-irradiation

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Kaushik Mallick, Department of Chemistry, University of Johannesburg, P. O. Box 524, Auckland Park 2006, South Africa. Email: kaushikm@uj.ac.za Methoxy-polyethylene glycol (MPEG)-doped Cu (I)-polyaniline acts as an efficient catalyst for the 1,2,3-triazole formation reaction. The catalyst shows excellent performance when the reaction was carried out under ultraviolet irradiation conditions due to the photo-induced free-radical formation from the MPEG. A detailed mechanistic discussion on the free-radical generation, free-radical-mediated hydrogen abstraction and triazole formation has been outlined in this manuscript. The catalyst system is equally active for one-pot multi-component strategies for the title reaction.

KEYWORDS

Cu (I) catalyst, free-radical, triazole formation, ultraviolet irradiation

1 | INTRODUCTION

The conversion of light energy to chemical energy through a catalytic process is a relatively modern approach for organic transformation reactions.^[1] The reaction between aryl iodide and arylboronic acid with the formation of the corresponding coupling product has been reported under light irradiation conditions using a palladiumcarbon nitride-based Mott-Schottky photocatalyst.^[2] The Mott-Schottky effect results in a higher Schottky barrier that enhances the charge separation at the contacting interface of metal and carbon nitride. The abovementioned catalyst system was also efficient in facilitating the photochemical hydrogenation of nitrobenzene using formic acid as hydrogen source at room temperature.^[3] A gold-palladium bimetallic system was reported as a catalyst for Suzuki coupling reactions under visible^[4] and visible-to-near-infrared light^[5] irradiation where the plasmonic component gold was used for light absorption and the palladium acts as the catalyst. The in situ formation of the Cu (I) catalyst from the Cu (II) species in the presence of ultraviolet (UV) or sunlight irradiation for the Cu (I)-catalyzed azide-alkyne cycloaddition reaction has been reported using graphitic carbon nitride as a heterogeneous photocatalyst.^[6] Electronic properties of the catalyst or the

support materials play significant roles in the trapping of light energy, which was converted to chemical energy for the construction of the desired organic molecules. The presence of light shifts the reaction towards a kinetically favorable direction by avoiding the introduction of hazardous chemicals and thermal energy, which make the photochemical reaction both environmentally and economically viable. Several initiatives have been undertaken for the utilization of the conduction band electron of the semiconductor photocatalysts for the light-induced organic reactions. Semiconductor metal oxides with large band gaps demonstrate as efficient photocatalysts under UVirradiation, and the photocatalytic activity is usually associated with free-radical reaction processes for the photo-degradation of organic pollutants.^[7] The band gap of the metal oxides can be manipulated by taking advantage of the various kinds of synthesis approaches. It is reported that rutile TiO₂ nanorods have been used for the aerobic oxidation of benzyl alcohols to benzaldehydes, vielding a high selectivity of 99% under visible light irradiation.^[8] Metal oxide-supported gold nanoparticle, plasmonic photocatalyst, is an excellent example of heterogeneous catalysis for the aerobic oxidation of alcohols in toluene under the irradiation of natural sunlight.^[9] Cerium oxide-supported gold particles have been reported

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for the selective oxidation of 4-aminobenzyl alcohol to 4aminobenzaldehyde through the photo-induced Au–H intermediate under UV and visible light irradiation.^[10] The free-standing gold particles could also act as a photocatalyst for the oxidation of alcohols to the corresponding carbonyl compounds in the presence of peroxide under LED irradiation (530 nm).^[11]

Organic coupling reactions with high activation barriers of the substrates are mostly dependent on relatively high temperatures for activation.^[12] Reports have also been published regarding the formation of the C-C bond at room temperature over the heterogeneous palladium catalysts by light-mediated catalyst activation.^[2] Bimetallic goldpalladium systems showed remarkable performance for the Suzuki coupling reaction of bromo-/iodo-benzenes and aromatic boronic acids to biphenyls under light irradiation conditions.^[4,5] It was also reported that the size of the catalyst has an effect on the reaction performance. Due to the presence of light, the conduction electron of the gold produces energetic electrons on the palladium surface that enhance the intrinsic catalytic activity of the palladium and promote the coupling reaction.^[13] Metal-catalyzed cycloaddition reactions are another important protocol in synthetic organic chemistry, as these reactions are vital to the modern synthesis of natural products and biologically active substances. The copper-catalyzed azide-alkyne cvcloaddition or the click reaction for the triazole formation continues to be of much interest^[14] as it offers an opportunity for chemists to connect two potentially complex building blocks under mild conditions.^[15] The Cu (I) catalysts could facilitate the cycloaddition between an azide and a terminal or internal alkyne in a regiospecific manner to give only 1,4-disubstituted triazole,^[14] and have attracted significant attention due to their potential application in the fields of pharmaceutical, agrochemical, dye, corrosion inhibitor, biochemical, polymer and other functional materials.^[16]

A photochemical protocol has been developed^[17] to catalyze the reaction between azides and alkynes by *in situ* generation of Cu (I) from Cu (II) complex in the presence of UV light, whereas a photolithographic technique has been employed for the comprehensive spatial and temporal control of the Cu (I)-catalyzed azide-alkyne cycloaddition reaction by photochemical reduction of Cu (II).^[18] Fullerene-containing macromolecule network also applied for the visible-light-induced Cu (I)-catalyzed azide-alkyne cycloaddition via an electron transfer mechanism.^[19] Apart from those, an important review article highlighted some fundamental aspects of light-induced click reactions and discussed the potential for this methodology for the study of biomolecular systems.^[20]

In association with our ongoing research on the development of efficient catalysts for the azide-alkyne

cycloaddition reaction,^[21–23] we have found the crucial role of light energy on the yield of the reaction.^[24,25] Due to the light excitation, the conduction band electron of the Cu (I) sulfide quantum dot acts as a scavenger of the terminal proton of the alkyne in the presence of organic azide with the formation of 1,4-disubstituted 1,2,3-triazoles, where the Cu (I) species of Cu₂S acts as a catalyst for the reaction.^[24] We also have demonstrated that the composite of copper nanoparticles and carbon nitride performs as an effective system for the cycloaddition reaction between azide and alkyne molecules under UV-radiation conditions where copper nanoparticles serve as active catalyst and the photoactive support material (carbon nitride) plays the role of a promoter.^[25]

In this current work, we like to report the effect of UV-irradiation on the triazole formation in the presence of methoxy-polyethylene glycol (MPEG; CH_3O - $[OCH_2C_2H]_n$ -OH), a dopant, within the Cu (I)-polyaniline, Cu-PA, catalyst system. In our earlier work, we reported a single-step synthesis route of Cu (I)-polyaniline composite and showed its potential application as a catalyst for the click reaction under ambient^[21] and also under microwave irradiation^[22] conditions. The introduction of MPEG as a dopant to the Cu (I)-polyaniline system, Cu-PA-MPEG, shows a substantial impact on the amount of product formation for the title reaction in the presence and absence of UV-irradiation.

2 | RESULTS AND DISCUSSION

The transmission electron microscopy (TEM) studies were carried out at an accelerated voltage of 200 kV using a Philips CM200 TEM equipped with a LaB₆ source. The UV–Vis spectra were recorded using a Shimadzu UV-1800 spectrophotometer with a quartz cuvette. Infrared spectra, in the region 4000–500 cm⁻¹, were obtained from a Perkin-Elmer 2000 FT-IR spectrometer operating at a resolution of 4 cm⁻¹.

The TEM images (Figure 1) of (a) the Cu (I)polyaniline and (b) the MPEG doped Cu (I)-polyaniline composite show no evidence of the formation of copper nanoparticles. Figure 2A shows the UV–Vis spectra of Cu (I)-polyaniline and MPEG-doped Cu (I)-polyaniline. Both the samples have identical features, with the highintensity absorption peak at 315 nm, and this corresponds to the π - π * transition centered on the benzenoid unit.^[26] There is also a broad absorption band within the range 350–600 nm with the absorption maxima at 395 nm that has also been observed for both samples, and could be assigned for polaron- π * transition for polyaniline.^[27] Xray photoelectron spectroscopy (Figure 2B) for Cu2p shows that the binding energies of the photoelectron



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FIGURE 1 The transmission electron microscopy (TEM) image of the Cu (I)polyaniline (A) and 10 wt% of methoxypolyethylene glycol (MPEG)-doped Cu (I)polyaniline (B) composites



FIGURE 2 (a) Ultraviolet (UV)-visible spectra of (a) Cu (I)polyaniline and (b) methoxy-polyethylene glycol (MPEG)-doped Cu (I)-polyaniline composites, and (b) X-ray photoelectron spectroscopy for Cu-2_p core-level binding energy. (c) Fourier transform-infrared (FT-IR) spectra of (a) the Cu (I)-polyaniline and (b) the MPEG-doped Cu (I)-polyaniline composites

peaks of $2p_{3/2}$ and $2p_{1/2}$ are 932.7 eV and 952.2 eV, respectively, for the Cu-PA-MPEG sample, indicating copper exists in the form of Cu (I).^[28] The molecular structures of the resulting (a) Cu (I)-polyaniline and (b) MPEG-doped Cu (I)-polyaniline were further characterized by the Fourier transform-infrared (FT-IR) spectroscopy technique (Figure 2C). The characteristic bands of (a) at wavenumber of 1627 and 1501 cm^{-1} are assigned for the C=C stretching of the quinoid and benzenoid rings, respectively. The shifting of the band responsible for C=C stretching of the quinoid rings at 1602 cm^{-1} was noticed for the MPEG-doped Cu (I)-polyaniline (a). The C-N stretching of the secondary aromatic amine was observed at the wavenumbers of 1273 and 1260 cm^{-1} for (a) and (b), respectively. The vibrational peak at about 1115 cm^{-1} is associated with -N=Q=N-(Q refers to the quinoid ring), and observed only in the MPEG-doped sample.^[29] In the spectrum (b), a characteristic peak at 1027 cm⁻¹ represents the vibration of -C-O-C- in MPEG-doped Cu (I)-polyaniline. The detailed characterization of the Cu (I)-polyaniline system is available elsewhere.^[21-24]

The UV-Vis spectra show identical peak positions for both spectra, but the intensity of the Cu (I)-polyaniline spectrum is higher compared with the Cu-PA-MPEG spectrum. The FT-IR spectra shows the high-intensity spectrum of the Cu-PA-MPEG as compared with Cu (I)polyaniline spectrum. The shifting and formation of some of the vibrational bands have also been observed in the FT-IR spectra of the Cu-PA-MPEG sample, which indicates the successful doping of MPEG in the Cu (I)polyaniline sample. The inductively coupled plasma mass spectrometry technique was used to determine the copper concentration within the MPEG-doped Cu (I)-polyaniline hybrid system.

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2.1 | Mechanism of formation of Cu (I)polyaniline composite

Copper sulfate-mediated synthesis of polyaniline is an example of the 'in situ polymerization and composite formation' (IPCF) technique, where the organic component (aniline) and the metal salt (CuSO₄, 5H₂O) were chosen to facilitate this type of reaction, and copper sulfate acts as an oxidizing agent for this type of oxidative polymerization process. The mechanism of the IPCF type of polymerization involves the release of electrons during the reaction between monomer and metal salt (oxidizing agent). In general, the released electrons reduce the metal ions, such as, gold, silver and palladium, with the formation of their corresponding nanoparticles.^[30–32] However, in the present experiment we found the reaction between aniline and copper sulfate evidences the partial reduction of metal salt with the formation of Cu (I) and polvaniline.^[21-23] Aniline has several amine as well as imine moieties that can act as a macro ligand,^[33] that coordinate with the Cu (I) species. The example of the partial reduction of palladium^[34] and copper^[35] is also available in the literature.

2.2 | Optimization of the reaction conditions

The optimization study was performed based on the amount of product formation, 1-benzyl-4-(4methoxyphenyl)-1*H*-1,2,3-triazole, **3aa**, (Table 1), in terms of yield percentage, during the reaction between 1,3-dipolar compound, azidomethyl benzene (1a) and dipolarophile, 1-ethynyl-4-methoxybenzene (2a) under different conditions in the presence of MPEG-doped Cu (I)-polyaniline, Cu-PA-MPEG (5 mol% of copper). When the above reaction was performed in the presence of triethylamine (Et₃N) and methanol (solvent) under both daylight and dark conditions, about 65% of the isolated yield of the desired product, 3aa, was obtained after 3 hr, for both experiments. A yield of 98% of 3aa was obtained when the reaction was performed under UVirradiation (UV-C) in the absence of Et₃N for 3 hr. With the addition of base, in the presence of UV-irradiation, the above reaction did not show any further positive impact, in terms of the speed of the reaction as well as the amount of yield obtained. It is important to mention that the Cu (I)-polyaniline (5 mol% of copper) system (without MPEG) produced a yield of 65% of 1-benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole in triethylamine and methanol as solvent under UV-irradiation, and also under daylight and dark conditions. For both Cu-PA-MPEG and Cu (I)-polyaniline systems, the above reaction showed less than 10% of yield in the absence of base (Et₃N) under daylight and also under dark conditions.

From the above optimization reaction, it is evident that MPEG has a distinct positive role on the title reaction under UV-irradiation conditions. We also have checked the current reaction with various solvents, such as dichloromethane, chloroform, tetrahydrofuran and water, and concluded that methanol was the best

TABLE 1 Substrate scope for Cu-PA-MPEG catalyzed cycloaddition reaction under different reaction conditions



Reaction conditions: (i) azide (1.0 mmol), alkyne (1.0 mmol), MeOH (4.0 mL) and Cu-PA-MPEG (5 mol% of Cu); (ii) isolated yields (%): (a) = UV (absence of Et₃N), (b) = daylight + Et₃N (1.0 mmol), (c) = dark + Et₃N (1.0 mmol), (d) = daylight (absence of Et₃N) and (e) = dark (absence of Et₃N).

performer as a solvent. A series of organic as well as inorganic bases, such as, diethylamine, triethylamine (Et₃N), di-isopropylamine, hydrazine monohydrate, potassium carbonate and potassium hydroxide have been tested, and Et₃N was determined as the most successful base for the reaction. We found that 5 mol% of copper was the optimum amount of catalyst for the title reaction in this current experiment. Below that amount a lesser yield% was obtained and above that amount no substantial improvement, either in terms of yield% or the velocity of the reaction, was noticed. A doping concentration of 10 wt% of MPEG produced the optimum result for the reaction.

2.3 | Substrate scope and comparative study under different optical conditions

In this section, we compared the performance of the Cu-PA-MPEG catalyst due to the effect of UV-irradiation and daylight conditions on the amount of product formation, in the absence and presence of base, respectively. The optimized reaction condition has now been explored for various substituted 1,3-dipolar molecules and dipolarophile to test the feasibility of the reaction and the substrate scope. The summarized data have been presented in Table 1. A graphical representation (Figure 3) shows the comparative yields for the cycloaddition products under the event of base-free UV-irradiation and base (Et₃N)-mediated daylight reaction conditions.

Benzylazide (**1a**), 1-(azidomethyl)-4-methylbenzene (**1b**), 1-azidonaphthalene (**1c**) and *ortho*bromobenzylazide (**1d**) as 1,3-dipolar counterpart



FIGURE 3 Graphical representation showing the comparative yields for the cycloaddition products under base-free ultraviolet (UV)-irradiation and base-mediated daylight conditions

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in the title reaction participated with simple phenylacetylene (2d) or an electron-withdrawing group attached alkyne such as 1-ethynyl-4-nitrobenzene (2b) and 1-ethynyl-4-(trifluoromethoxy) benzene (2e), or an electron-donating group attached alkyne such as 1-ethynyl-4-methylbenzene (2c) to yield the expected product 1-benzyl-4-(4-nitrophenyl)-1*H*-1,2,3-triazole (3ab, 95%) and 73%), 1-(4-methylbenzyl)-4-(4-nitrophenyl)-1H-1,2,3triazole (3bb, 90% and 62%), 1-(4-methylbenzyl)-4-ptolyl-1H-1,2,3-triazole (3bc. 97% and 78%). 1-(naphthalen-1-yl)-4-phenyl-1H-1,2,3-triazole (3cd, 91% and 78%), 1-(2-bromobenzyl)-4-(4-(trifluoromethoxy)phenyl)-1H-1,2,3-triazole (3de, 83% and 50%) and 1-(2bromobenzyl)-4-phenyl-1H-1,2,3-triazole (3dd, 88% and 69%), under two different reaction conditions. Again, bromobenzylazide (1d) underwent reaction with aliphatic alkyne 1-pentyne (2f), six-member lactone attached dipolarophile, i.e. 6-methyl-4-(prop-2-ynyloxy)-2H-pyran-2-one (2g), and cyclic alcohol attached dipolarophile, i.e. 1-ethynylcyclohexanol (2h) for the respective 1,2,3triazole molecules 1-(2-bromobenzyl)-4-propyl-1H-1,2,3triazole (3df, 87% and 51%), 4-((1-benzyl-1H-1,2,3triazol-4-yl)methoxy)-6-methyl-2H-pyran-2-one (3dg, 85% and 58%) and 1-(1-benzyl-1*H*-1,2,3-triazol-4-yl) cyclohexanol (3dh, 80% and 49%). In all cases, an average of 30-40% higher yield was obtained when the reactions were performed under UV-irradiation conditions in the absence of base, as compared with the daylight-driven reaction in the presence of triethylamine. The percentage within the brackets indicates the isolated yield for the reactions performed under the condition of UVirradiation in the absence of triethylamine (a) and daylight in the presence of triethylamine (b).

The unique properties of the carbohydrate moiety have attracted increasing attention in various fields of science, with particular interest to the biological sciences.^[36] The carbohydrate units critically control the specific biological functions of cells and also play an important role in cellto-cell recognition mechanisms.^[37] In the current study we have chosen anomeric β -anzide substituted glucopyranose tetra acetate (1e) and anomeric β -anzide substituted galactopyranose tetra acetate (1f) as 1,3-dipolar molecules to react with both electron-withdrawing and electrondonating groups substituted aromatic alkyne, such as, 1ethynyl-4-nitrobenzene (2b), 1-ethynyl-4-methylbenzene (2c)and di-substituted 1-ethynyl-4-methoxy-2methylbenzene (2i) as dipolarophile. Results of the isolated yields of the products in two different conditions have been summarized in Table 2 and also in Figure 3. Both 1e and 1f successfully react with 1-ethynyl-4-nitrobenzene (2b) to form the products 4-(4-nitro-phenyl)-1-(2,3,4,6-tetra-Oacetyl- β -D-glucopyranosyl)-1*H*-1,2,3-triazole (3eb) and 4-(4-nitro-phenyl)-1-(2,3,4,6-tetra-O-acetyl-β-D-



TABLE 2 Substrate scope for Cu-PA-MPEG catalyzed cycloaddition of sugar azide with alkyne under base-free UV-irradiation and base

 mediated daylight conditions



Reaction conditions: (i) sugar azide (373 mg, 1.0 mmol), alkyne (1.0 mmol), MeOH (4 mL) and Cu-PA-MPEG (5 mol% of Cu); (ii) isolated yields (%): (a) = UV and (b) = daylight + Et_3N (1 mmol).

galactopyranosyl)-1H-1,2,3-triazole (3fb) with 89% and 85% of isolated products under UV-irradiation in the absence of triethylamine, and 57% or 59% of isolated products under daylight in the presence of triethylamine, respectively. In a similar way, 1e reacted with aromatic alkynes 2c and 2i to yield their corresponding 4-p-tolyl-1-(2,3,4,6-tetra-O-acetyl-β-Dclick products glucopyranosyl)-1H-1,2,3-triazole (**3ec**, 96% and 66%) 4-(4-methoxy-2-methyl-phenyl)-1-(2,3,4,6-tetra-Oand acetyl- β -D-glucopyranosyl)-1*H*-1,2,3-triazole (**3ei**, 98% and 64%), respectively. Again, when 1f was reacted with aromatic alkynes 2c and 2i to yield their corresponding click products 4-p-tolyl-1-(2,3,4,6-tetra-O-acetyl-β-Dgalactopyranosyl)-1*H*-1,2,3-triazole (**3fc**, 94% and 63%) 4-(4-methoxy-2-methyl-phenyl)-1-(2,3,4,6-tetra-Oand acetyl- β -D-galactopyranosyl)-1*H*-1,2,3-triazole (**3fi**, 94% and 61%), respectively, were formed.

A single-step reaction is more attractive than a multistep one in terms of overall yield of the target molecule, and is also beneficial for the enlargement of substrate scopes depending on the choice of reaction condition. Also, attention has been given for the development of single-step multi-component reactions, because of the high degree of atom economy, applications in combinatorial chemistry and diversity-oriented synthesis.^[28] Multicomponent strategies for click reaction where inorganic azide salts, such as sodium azide and alkyl halide, may participate in an *in situ* nucleophilic substitution reaction to produce organic azide molecules that further could undergo cycloaddition with the alkyne dipolarophile in a single-step one-pot reaction and similar types of protocol are also evident in the literature.^[38,39]

In this work, we were also interested to implement Cu-PA-MPEG catalyst for the single-step multicomponent reaction using aryl halide, sodium azide and alkyne under different photonic conditions. The results are shown graphically in Figure 3 and also in Table 3. Two aryl halides, such as benzylbromide (**4a**) and *ortho*-

TABLE 3 Substrate scope for Cu-PA-MPEG catalyzed one-pot multi-component cycloaddition reaction under base-free UV-irradiation and base-mediated daylight conditions



Reaction conditions: benzyl bromide (1 mmol), NaN_3 (78 mg, 1.2 mmol), alkyne (1 mmol), MeOH (4 mL) and Cu-PA-MPEG (5 mol% of Cu), (ii) isolated yields (%): (a) = UV, (b) = daylight + Et₃N (1 mmol).

bromobenzylbromide (4b), were used in this experiment for the multi-component reaction. In each separate phenylacetelene (2d). 1-ethvnvl-4-experiment. (trifluoromethoxy) benzene (2e), 3-ethynylthiophene (2j) and propargyl alcohol (2k) reacted with 4a in the presence of sodium azide, and the corresponding products 1benzyl-4-phenyl-1H-1,2,3-triazole (5ad, 90% and 65%), 1benzyl-4-(4-(trifluoromethoxy) phenyl)-1H-1,2,3-triazole (5ae, 88% and 55%), 1-benzyl-4-(thiophen-3-yl)-1H-1,2,3triazole (5aj, 83% and 58%) and (1-benzyl-1H-1,2,3triazol-4-yl) methanol (5ak, 78% and 42%), respectively, were obtained successfully when MPEG-doped Cupolyaniline was used as a catalyst. In a similar way, ortho-bromobenzylbromide (4b) reacted with 1-ethynyl-4-methoxybenzene (2a) to yield 1-((2-bromobenzyl)-4-(4methoxy) phenyl)-1H-1,2,3-triazole (5ba, 88% and 55%). The respective yield% values are mentioned within the bracket, where the higher yields of products were achieved under UV-irradiation conditions in the absence of base, while lower yields of the isolated products were achieved in the presence of triethyl ammine under daylight conditions.

2.4 | Mechanistic discussion of the reaction

The alkyne-azide cycloaddition reaction needs alkaline conditions to initiate the process in the presence of a Cu (I) catalyst,^[14,40] which allows the reaction to proceed at room temperature with an increased rate of reaction.^[22,41] In this report, MPEG-doped Cu (I)-polyaniline (Cu-PA-MPEG) was used as a catalyst for the title reaction.

The mechanism for the copper-catalyzed cycloaddition reaction for triazole synthesis is illustrated in Scheme 1. A π -complex (A), step (I), has been formed between the Cu (I) and alkyne molecule, which results in the lowering of the pKa value of the terminal proton, a typical Lewis acid character. The π -complex facilitated the deprotonation of the alkyne molecule under basic conditions (triethylamine), through step (II) (a) and (III), with the formation of copper-acetylide complex (B). In the presence of the azide molecule, step (IV), the copper-acetylide forms a couple of intermediate complexes that subsequently form the 1,2,3-triazole (C) through protonation along with the elimination of the catalyst. When the reaction was carried out under the exposure of UV-irradiation in the absence of base, a higher amount of yield (triazole product) was obtained. The UV light source, UV-C, within the range of 6.53-4.43 eV and 190-280 nm wavelength, possesses a sufficient amount of energy to produce the free-radicals



SCHEME 1 Mechanism for the triazole formation

through the photolysis of MPEG, doped in the Cu (I)-polyaniline system.

The photo- and thermal-induced free-radical formation of polyethylene glycol is well documented in the literature.^[42,43] A similar kind of photolysis mechanism can also be considered for methoxy polyethylene glycol ($R - [OCH_2CH_2]_n - OH$) with the formation of oxygen-centered ($-OCH_2CH_2 -)$ and carbon-centered ($-OCH_2CH -)$ free-radicals due to the exposure of UV light. The free-radical-mediated hydrogen abstraction route is observed in biological systems, with the specific examples of dehydrogenation of C-H bond of a lipid molecule^[44] and the radical-mediated dehydrogenation of bile salts.^[45] Free-radical-mediated organic transformation reactions are also common in literature.^[43,46]

In the current study, the free-radical-induced hydrogen abstraction from the copper-alkyne π -complex (A) can be proposed with the formation of the copperacetylide complex (B), Scheme 1, step (II) (b) and (III). In the presence of the azide molecule, the rest of the reaction followed the above-mentioned pathway and formed the triazole molecule (C). Free-radicals have more reactive unpaired electrons than lone pairs of electrons and, because of that, the proton abstraction process from the alkyne molecule was faster and consequently produced a higher amount of triazole product for a particular time period.

We found that the triazole product (**3aa**) was also formed, although a very small amount of yield (< 10%), both under daylight as well as dark conditions in the absence of base (Et₃N), indicating that the amine group of polyaniline is mainly responsible for the deprotonation from the alkyne molecule.^[26] It is also reported that the amine moiety in graphitic carbon nitride was also in control for the proton abstraction process.^[28] The Cu-PA-MPEG composite system can act as a heterogeneous 8 of 9 WILEY-Organometallic-Chemistry

catalyst for the current triazole formation reaction. Under UV-irradiation conditions, deactivation of the catalyst is faster compared with daylight and dark environment, which could be the effect of dissolution of MPEG in the presence of solvent with time. The Cu-PA-MPEG catalyst can be recycled five times without considerable deactivation under daylight and dark conditions.

3 | CONCLUSION

This report demonstrates the catalytic role of the MPEGdoped Cu (I)-polyaniline system for the cycloaddition reaction between azide and alkyne molecules under UVradiation conditions, where the polyaniline acts as a support material for both Cu (I) and MPEG. The UVirradiation plays a crucial role in generating free-radicals through the photolytic fission of MPEG for the radicalinduced hydrogen abstraction from the alkyne molecule. Copper serves as a catalyst for the title reaction, whereas MPEG scavenges the free-radicals with the formation of stable carbon-centered free-radicals that abstract the Hatom from the alkyne molecule by means of a hydrogen atom transfer mechanism, and finally proceed for the triazole product in the presence of an azide molecule. In association with our ongoing research on the fabrication of effective catalysts for the cyclo-addition of azide and alkyne molecules,^[21-25] further efforts will undertake in future for the development of new materials as catalyst to perform the similar kind of reactions by involving the heterocycle substituted azide molecules.

4 | EXPERIMENTAL

4.1 | Preparation of Cu-PA-MPEG composite materials

In a typical experiment, 0.093 g of aniline was diluted in methanol. On the other hand, in a separate 25-mL beaker, 0.004 g of MPEG was dissolved in hot water. MPEG solution was added drop-wise to the methanolic solution aniline monomer solution under stirring conditions and allowed to stir for 30 min. A solution of CuSO₄·5H₂O $(10 \text{ mL}, 10^{-2} \text{ mol dm}^{-3})$ was added slowly under continuous stirring conditions to the mixture solution of aniline and MPEG solution. During the addition, the solution took on a green color while, at the end, a greenish precipitation was formed, indicating the formation of Cu (I)polyaniline composite, at the bottom of the conical flask. The ntire reaction was performed under ambient conditions, and the product was dried at 60°C under vacuum conditions. The material was used as a catalyst for the azide-alkyne cycloaddition reaction (5 mol% of Cu).

4.2 | General procedure for the click reaction

In a round-bottomed glass flask (for daylight and dark experiments) or round-bottomed quartz flask (for the UV-irradiation experiment), azide, **1a–1d**, (1 equivalent), alkyne, **2a–2h**, (1 equivalent), were charged in 4 mL of methanol. To this reaction mixture, the catalyst Cu-PA-MPEG was added and stirred under the following conditions.

- a. UV light (in the absence of Et_3N): a 50-mL roundbottomed quartz cell was used for the reaction. The UV-light source was a Philips UV-C (TUV T8; germicidal) lamp. The optical intensity value of 40 mW cm⁻² adjacent to the quartz reaction chamber was measured by a hand-held optical power meter (Newport) during the course of the reaction.
- b. Daylight + Et_3N : a 50-mL round-bottomed glass flask was used for the reaction. A Philips LED bulb (8718291753032), 6.5 W, was considered as equivalent to the daylight source. The optical intensity adjacent to the glass reaction chamber was 3.5 mW cm⁻².
- c. Dark + Et_3N : the reaction was performed in a dark room. All other reaction conditions remained identical as mentioned in condition (b).
- d. Daylight in the absence of Et₃N: all reaction conditions remained identical as mentioned in (b) in the absence of Et₃N.
- e. Dark (in the absence of Et_3N): all reaction conditions remained identical as mentioned in (c) in the absence of Et_3N .

The reaction was monitored using the thin-layer chromatography technique and stirred for 3 hr. The reaction mixture was then filtered, and the filtrate was dried. The solid material was diluted with distilled water and extracted with ethyl acetate. The combined organic layer was collected and further purified by recrystallization or by the column chromatography technique.

The 1 H and 13 C NMR spectra of all compounds are included in the supporting information.

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CONFLICT OF INTEREST

There are no conflicts to declare.

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Additional supporting information may be found online in the Supporting Information section at the end of the article.

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