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Fabrication of polypyrrole/Cu(II) nanocomposite through liquid/liquid interfacial polymerization: A novel catalyst for synthesis of NH-1,2,3-triazoles in PEG-400

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Abstract

In the present paper, we have reported the synthesis and application of polypyrrole (PPy)/Cu(II) nanocomposite as an efficient heterogeneous catalyst for synthesis of 4-aryl-NH-1,2,3-triazoles. The nanocomposite was prepared via liquid/liquid interfacial polymerization where copper and initiator (FeCl₃) were dispersed in the aqueous phase and the monomer was dissolved in the organic phase. The synthesized sample was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), transmission electron microscopy (TEM) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Spectroscopic analyses showed successful incorporation of Cu in the polymer matrix and the decoration of copper nanoparticles within the PPy matrix was observed from the morphological analysis. Herein, we have developed a simple one-pot, multi component system using PPy/Cu catalyst for synthesis of NH-triazoles. Keeping in view the principles of green chemistry, the reactions were performed in low-cost and environment friendly solvent polyethylene glycol 400 (PEG 400). A very low loading of copper (0.01 mol %) catalyzed the reaction very efficiently with excellent yield of the desired product. Furthermore, the catalytic system can be recovered and recycled up to 5th consequent cycles maintaining its catalytic activity with excellent yields of triazoles. To the best of our knowledge no previous work has been reported for synthesis of 4-aryl-NH-1,2,3-triazoles using this efficient novel catalyst.

Keywords: 4-aryl-NH-1,2,3-triazoles; heterogeneous catalysis; interfacial polymerization; nanocomposite; polypyrrole
INTRODUCTION

Pi-conjugated polymer nanocomposite has become an attractive area in nanoscience due to their diverse applications in various fields such as super capacitors [1], battery electrodes [2], sensors [3], catalyst [4] and many other fields [5]. Addition of small quantity of nanofiller can dramatically improve various properties of the polymer nanocomposite due to which they have attracted a lot in the recent research fields [6]. Out of many conducting polymers, polypyrrole (PPy) is one of the most important conducting polymers due to its good redox behavior, electrical conductivity, ease of preparation and good environmental stability [7]. The exceptional physical properties and electrochemical behavior of PPy with pronounced stability towards air make it more interesting in the field of research [8]. The presence of pi-conjugated polymer within the catalyst system not only acts as binder but also improves the activity of the catalyst. PPy possesses high conductivity due to the positive charge created on its backbone. During polymerization, polypyrrole matrix balances its electrical neutrality by incorporating anions from solution. In our work, FeCl₃ is used as the oxidizing agent and it provides Cl⁻ ion as counter ion. PPy is very unique because it can switch its state from conducting (oxidized form) to insulating state (reduced or neutral form) (Scheme 1).

Scheme 1: Conducting and insulating form of Polypyrrole

1,2,3-triazoles are a very fundamental class of N-heterocycles that are indispensable motifs in many biologically essential compounds such as anti-cancer, anti-HIV, anti-bacterial, anti-microbial and anti-allergic drug molecules [9–13]. Due to their unique properties such as high chemical stability, strong dipole moment, aromatic character etc. this class of heterocyclic moiety
is extensively used in drug discovery, material chemistry, bio-pharmaceutical and medicinal chemistry [14,15]. Moreover, 1,2,3-triazoles are of significant importance as photo-stabilizers, dyes, agrochemicals and corrosion inhibitors [16,17]. Among 1,2,3-triazole compounds, 4-aryl-NH-1,2,3-triazoles have gained tremendous interest in the field of pharmaceutical industry [18–21]. Research reveals that many medicinally relevant scaffolds are composed of amide bonds. Interestingly, the close similarity of NH-triazoles to amide bonds has been successfully utilized in synthesis of a large number of privileged drug molecules (Figure 1) [22]. Literature reveals that NH-triazole molecules act as unique template for the inhibition of human methionine amino peptidase (hMetAP2) inhibitors and indoleamine 2,3-dioxygenase (IDO) [23,24]. NH-triazoles also serve as important precursors for arylation of 1,2,3-triazoles [25] as well as key intermediates for a series of fundamental organic transformations [26]. Due to the versatile and significant importance of 4-aryl-NH-1,2,3-triazoles, it is of utmost importance to develop efficient and suitable methodologies to access this structural motif.

![Figure 1: Biologically active NH-1,2,3-triazoles](image)

Over the past few decades, there has been significant awareness pertaining to the strict legislation on maintenance of “principles of green chemistry” in all synthetic applications and
pathways [27,28]. Hence, in order to eliminate the use of hazardous organic solvents from chemical industries, an important goal of current research is to introduce non-toxic, cost-effective and non-volatile “green solvents” [29–32]. In recent years, PEGs have served as a suitable alternative to conventional organic solvents due to their attractive physico-chemical properties such as thermal stability, chemical inertness, non-toxic and mostly non immunogenic. PEGs are stable even at high temperature i.e. up to 150-200 °C and show good solubility both in water and many organic solvents. In organic syntheses some of the eminent applications of this class of green solvent include Williamson ether synthesis, oxidation and reduction reactions, coupling reactions etc. [33,34]. These superior properties offer PEG the new gold standard as green alternative solvent in current scientific and research arena. The current researches in synthetic chemistry have observed the renaissance of multicomponent reactions (MCRs) as powerful tool for synthesis of complex organic molecules via operational simplicity and easy purification of product. MCRs allow the formation of multiple bonds in single step and hence render several advantages such as convergence, facile automation, extraction and purification process etc. In addition, MCRs minimize the reaction time thereby increasing the overall yield of product formation. In 1838, Laurent and Gerhardt first reported the multicomponent reactions [35]. Since then, many research groups have incorporated MCR in synthetic reactions such as Ugi [36], Biginelli [37], Hantzsch [38], Strecker [39] including efficient synthesis of 1,2,3-triazoles [40].

While designing a new catalyst, the key points are its easy separation from the products and the possibility of recycling. In this aspect, nanosized metallic catalysts in solid supports create a perspective type of catalytic materials. The formation of nano-catalysts in redox-polymerization of heterocyclic precursor oxidized by metal ions is one of the promising approaches for catalytic application [41]. When Cu is encapsulated in the PPy, the polymer matrix provides a large surface area for easy dispersion of the Cu metal. Additionally, the redox behaviour of polypyrrole seems to be a convenient support for the active phase of oxidative-reductive catalyst. This synergistic effect and redox properties of polypyrrole with Cu particles are believed to enhance the catalytic activity of catalyst towards efficient synthesis of NH-1,2,3-triazoles.

Based on the above findings and observations, we are hereby reporting for the first time the use of copper (II) filled polypyrrole nanocomposite as heterogeneous catalyst for synthesis of 4-aryl-NH-1, 2,3-triazoles. To the best of our knowledge, no study has been conducted on the combination of PPy and Copper (II) nanocomposite for triazole preparation.
EXPERIMENTAL

Materials

Pyrrole monomer was purchased from Spectrochem Pvt. Limited, Mumbai, India. Ferric chloride (anhydrous) was obtained from Alpha Chemica. Copper (II) sulphate pentahydrate was procured from Merck. Carbon tetrachloride was obtained from Paskem Fine Chemical. PEG-400 (Merck), Nitromethane (CH\textsubscript{3}NO\textsubscript{2}, 98%, TCI), Nitroethane (C\textsubscript{2}H\textsubscript{5}NO\textsubscript{2}, 98%, Spectrochem), Sodium Azide (NaN\textsubscript{3}, 99%, Spectrochem) and all aldehydes (Spectrochem with 98% purity) were purchased and used without any further purification. The products obtained were purified by column chromatography over silica gel (120-200 mesh). Thin-layer chromatography was carried out using silica gel 60F\textsubscript{254} plates and visualized under UV light.

Preparation of Polypyrrole/Cu(II) nanocomposite

Liquid/liquid interfacial polymerization method was used to prepare polypyrrole/copper nanocomposite (Scheme 2). Initially, 3 mL of pyrrole monomer was dissolved in 17 mL of carbon tetrachloride in a beaker to get the organic phase. 10 mL of 0.01 M aq. copper sulphate solution and 10 mL of 0.05 M aq. ferric chloride solution (acts as an initiator) was mixed together to form the aqueous phase. Subsequently, the aqueous phase was added to the organic phase drop wise. The beaker was then kept undisturbed for the next 24 hours. Throughout this time, it was observed that a thin black film developed slowly between the interface of organic and aqueous phase. The product thus obtained was filtered and washed several times with deionised water and ethanol to remove impurities, unused FeCl\textsubscript{3} and any other soluble organic byproducts. Eventually the product was air dried and used as catalyst for NH-1,2,3-triazole synthesis (Scheme 3).
Scheme 2: Pictorial representation of interfacial polymerization
Scheme 3: Schematic representation for preparation of Polypyrrole/Copper nanocomposite

10 mL CuSO$_4$.5H$_2$O + 10 ml FeCl$_3$ Solution

Solution B

Pyrrole solution in CCl$_4$
Solution A

Solution B is added dropwise on solution A
Kept undisturbed for 24 h (Room temperature)

Filtered, washed and dried

Polypyrrole/Cu nanocomposite

Polypyrrole

Cu particle
General procedure for the synthesis of NH triazoles

A mixture of aromatic aldehyde (1 mmol), nitroalkane (2 mmol), sodium azide (3 mmol) and polypyrrole/copper (PPy-Cu) catalyst (5 mg) were stirred at 100°C in 2 mL PEG-400 solvent under aerobic condition. The reaction progress was monitored by TLC. After completion, the reaction mixture was allowed to cool at room temperature and extracted by ethyl acetate (3×10 mL). The organic layer was then dried over anhydrous sodium sulphate followed by concentrating the filtrate under reduced pressure. The final product obtained was then purified by column chromatography over silica gel by using a mixture of ethyl acetate/hexane. The purified products were characterized by $^1$H and $^{13}$C NMR spectroscopy (Supporting Information).

RESULTS AND DISCUSSION

Characterization of the as-synthesized catalyst

The morphology of the newly synthesized catalyst was characterized by transmission electron microscopy (TEM) as shown in Figure 2. The images demonstrate that the PPy/Cu(II) nanocomposite has a spherical morphology and the composite exhibits discrete spheres with an average diameter in the range of ~20 nm to ~80 nm. This may be due to the active surface entrapment of the polymer and stabilization of the Cu by immobilizing and preventing their aggregation into larger particles.

Figure 2: TEM images of the catalyst (a) low magnification and (b) high magnification
The SEM micrographs of the PPy and the PPy/Cu catalyst are depicted in Figure 3(a) and 3(b) respectively. The SEM image of pristine polymer indicates the hemispherical nature of polymer. Interestingly, the SEM image of the as-synthesized catalyst was found to be quite similar but the particles are bigger in size as compared to the pristine polymer which may be due to the well distribution of copper metal in the polymer backbone. This uniform distribution of the copper over polymer surface escalated their catalytic activity resulting in satisfactory yields of the desired product.

Figure 3: SEM images of (a) pure PPy and (b) PPy/Cu nanocomposite

The compositional analysis of the synthesized catalyst was further analyzed by Energy Dispersive X-Ray Dispersion (EDX) study (Figure 4). The EDX spectrum of PPy/Cu(II) catalyst shows various peaks of copper, carbon and nitrogen which confirmed the presence of these elements in the composite structure. The copper peak was mainly due to the copper source; carbon and nitrogen peaks came from the polymer unit. The peak for oxygen can be attributed to the open air reaction condition employed during preparation of catalyst. The peak around 2.6 in the EDX spectrum corresponds to Cl- ion, present in the nanocomposite. When FeCl₃ attacks the monomers, the monomers get converted into positively charged species by donating electrons to Fe³⁺ and the Cl⁻ ion binds with these positive charges to maintain electrical neutrality of the polymer. The Cl- ions which are not utilized as counter ions are being washed off with water. Due to the Cl- ions present in the nanocomposite which act as counter ions, a peak arises at around 2.6 in the EDX spectrum of the nanocomposite.
The X-Ray diffraction pattern (XRD) depicts the successful incorporation of the copper metal in the matrix of the polymer. The XRD pattern of pure PPy and PPy/Cu composite are represented in Figure 5 (a) and (b) respectively. The intense diffraction peak at 2θ value of 26.65° was characteristic peak of the crystalline PPy. In the PPy/Cu composite three sharp peaks are observed. The characteristic peaks at 2θ = 25.3° represents PPy. The diffraction peaks at 2θ = 10.42° and 42.4° can be attributed to the standard cubic phases of copper.
The FTIR spectra of PPy and PPy/Cu composite were recorded in the range of 4000 cm\(^{-1}\) to 400 cm\(^{-1}\). In the FT-IR spectrum of PPy (Figure 6), the strong bands at 3433 cm\(^{-1}\), 2926 cm\(^{-1}\) and 1578 cm\(^{-1}\) correspond to the absorption of N–H stretching, C–H stretching and C=C ring stretching of pyrrole respectively. The bands at 1380 cm\(^{-1}\), 1187 cm\(^{-1}\) and 1042 cm\(^{-1}\) are due to C–H vibration, C–C stretching and in-plane deformation of C–H bond of pyrrole ring respectively.

![FTIR spectrum of pure PPy](image)

**Figure 6: FTIR of pure PPy**

The characteristic absorptions of PPy in the PPy/Cu composite can be observed in Figure 7. The peaks at 3097 cm\(^{-1}\) and 2930 cm\(^{-1}\) correspond to N–H and C–H stretching and the strong bands at 1558 cm\(^{-1}\) and 1200 cm\(^{-1}\) represent C-C and aromatic C-H stretching vibration in the pyrrole ring respectively. The band of C-H in plane deformation vibration is situated at 1048 cm\(^{-1}\) and the peak at 921 cm\(^{-1}\) is due to out of plane ring deformation. The peak at 777 cm\(^{-1}\) corresponds to the C–H wagging vibrations. The FTIR spectral wavelength and intensity of peaks of PPy/Cu (II) nanocomposite showed the peak shift compared to the pristine PPy as reported elsewhere which indicates the incorporation of Cu (II) nanoparticles to the PPy ring.
Catalytic Study

At the very outset, we investigated the catalytic performance of the as-synthesized PPy-Cu catalyst towards NH-triazole synthesis by taking 4-bromo-benzaldehyde, nitromethane and sodium azide as the model substrates under various reaction parameters. Initially, the effect of the catalytic amount of PPy-Cu catalyst that is required for the effective synthesis of NH-triazole products was explored (Table 1, entries 1-7). It can be seen from Table 1, 20 mg of the catalyst produced 96% of the desired product within just an hour (Table 1, entry 1). Decreasing the amount of catalyst to 15 mg and 10 mg, also afforded the requisite product with satisfactory yield (Table 1, entries 2, 3). The catalytic significance of the synthesized catalyst was then investigated by decreasing the catalyst loading to 5 mg affording 96 % yield in 1 hour duration (Table 1, entry 4). However, further decrease in catalyst loading resulted in slight decrease in the yield of the product along with longer consumption of time (Table 1, entry 5). The necessity of the catalyst in the reaction was confirmed by a controlled experiment carried out in absence of the catalyst. The reaction in absence of the catalyst produced NH-triazoles in poor yield (Table 1, entry 6).
Table 1: Optimization of catalyst quantity in the synthesis of 4-aryl-NH-1,2,3-triazoles.

![Reaction scheme](image)

\[ \text{CHO} + \text{CH}_3\text{NO}_2 + \text{NaN}_3 \xrightarrow{\text{catalyst, 100°C}} \text{PEG 400} \rightarrow \text{N=N} \]

\( ^a \text{Reaction conditions: } 4\text{-bromobenzaldehyde (1 mmol), nitromethane (2 mmol), NaN}_3 \)

| Entry | Catalyst (mg) | Time (h) | Yield\(^b\) (%) |
|-------|---------------|----------|-----------------|
| 1     | 20            | 1        | 96 %            |
| 2     | 15            | 1        | 96 %            |
| 3     | 10            | 1        | 96 %            |
| 4     | 5             | 1        | 96 %            |
| 5     | 2             | 2        | 84 %            |
| 6     | -             | 2        | 25 %            |
| 7     | 5             | 0.5      | 85 %            |
|       |               | 0.25     | 68 %            |

(3 mmol), catalyst, solvent (PEG-400) (2 mL), in air.

\( ^b \) Isolated yield

Encouraged by the significant performance of the catalyst towards NH-triazoles synthesis, we then extended our study to develop suitable solvent and temperature for efficient synthesis of NH-triazoles (Table 2, entries 1-12). Initially, the reaction was performed under neat condition taking 4-bromo-benzaldehyde, nitromethane and sodium azide as the model substrates at 100°C under aerobic condition. Notably, poor yield of the requisite product was obtained (Table 2, entry 1). Being the universal solvent, water was used as solvent but not much improvement in reaction kinetics was observed affording poor yield (Table 2, entry 2). As a result, a wide variety of organic solvents were investigated and moderate yields were obtained (Table 2, entries 3-9) in each case. Keeping in view the principles of green chemistry, the efficiency of the solvent PEG 400 was explored and interestingly best results were obtained in this case (Table 2, entry 10). Additionally, optimization of the reaction temperature was also performed by lowering the temperature to 70°C but poor yield of the product was observed (Table 2, entry 11). As a controlled experiment the reaction was investigated at room temperature condition as well but only trace amount of the product was found (Table 2, entry 12). Moreover, the reaction was performed using CuSO\(_4\) (0.1
mol %) as catalyst. It was found that, very less amount of product could be isolated in this case. Hence, after investigating a wide array of optimal parameters, 5 mg of PPy-Cu catalyst (0.01 mol % Cu, from ICP-AES analysis) in PEG 400 as green solvent at 100°C was found to be the optimized condition in our present study.

Table 2: Optimization of reaction conditions

![Reaction diagram](image)

| Entry | Solvent | Temperature | Time (h) | Yield\(^b\) (%) |
|-------|---------|-------------|----------|-----------------|
| 1     | -       | 100°C       | 1        | 30 %            |
| 2     | H\(_2\)O| 100°C       | 1        | 55 %            |
| 3     | DMSO    | 100°C       | 1        | 72 %            |
| 4     | DMF     | 100°C       | 1        | 71 %            |
| 5     | DCM     | 100°C       | 1        | 78 %            |
| 6     | Toluene | 100°C       | 1        | 49 %            |
| 7     | EG      | 100°C       | 1        | 81 %            |
| 8     | EG:H\(_2\)O | 100°C | 1 | 78 % |
| 9     | DMSO:H\(_2\)O | 100°C | 1 | 75 % |
| 10    | PEG-400 | 100°C       | 1        | 98 %            |
| 11    | PEG-400 | 70°C        | 1        | 72 %            |
| 12    | PEG-400 | RT          | 24       | Trace           |
| 13\(^c\) | PEG-400 | 100°C       | 1        | 35 %            |
| 14\(^d\) | PEG-400 | 100°C       | 1        | 30 %            |

\(^a\)Reaction conditions: 4-bromobenzaldehyde (1 mmol), nitromethane (2 mmol), NaN\(_3\) (3 mmol) and catalyst (5 mg), solvent (2 mL), in air, \(^b\)Isolated yield, \(^c\)controlled reaction using CuSO\(_4\) (0.1 mol %), \(^d\)controlled reaction using PPy (0.1 mol %)
With the optimized reactions conditions in hand, the scope of the PPy-Cu catalyst was then explored towards a wide range of electronically diverse aldehydes (Scheme 4, entries a-n). As exemplified in Scheme 4, all reactions proceeded very smoothly affording the requisite product in excellent yield with high purity. All substrates, having ortho-, meta- and para- substitution showed satisfactory reactivity towards formation of NH-triazole product. Aromatic aldehydes bearing halogen atoms such as Br, Cl and F afforded the requisite NH-triazole in excellent yields. Salicylaldehyde and 2,4-dichlorobenzaldehyde also proceeded very smoothly with the as-synthesized catalyst affording the desired product in satisfactory yields (Scheme 4, entries f,g). Furthermore, heterocyclic moieties thiophen-2-aldehyde and furan-2-aldehyde also reacted efficiently resulting in excellent yield of NH-triazole product (Scheme 4, entries i,j). In order to extend the scope of the synthesized catalyst, the reactivity of another nitroalkane i.e. nitroethane was investigated under optimized reaction condition. Pleasantly, it was found that in presence of nitroethane also, the reaction proceeded quite smoothly affording the requisite triazole in excellent yields (Scheme 4, entries k-n).
In this work, PPy is used as a catalyst support to enhance the catalytic activity of composite. PPy can exist in several oxidation states in neutral, oxidized or reduced forms \cite{45,46}. It can undergo protonation/ deprotonation in the polymer chain as well as can interact with dopant \cite{47,48}. In situ polymerization of pyrrole monomer leads to the formation of polypyrrole matrix which stabilizes the Cu particles on its surface and prevents it from aggregation. As a result, there is no need of adding surface stabilizers. PPy itself has no catalytic activity but the polypyrrole matrix provides a large surface area, thereby improving the dispersion of copper in the composite material. This synergistic effect of polypyrrole with Cu particles is believed to enhance the catalytic activity of catalyst towards efficient synthesis of NH-1,2,3-triazoles.

Scheme 4: PPy/Cu (II) nanocomposite catalyzed NH triazole synthesis

[16]
On the basis of literature reports [22,49], here we have proposed a plausible mechanism for this reaction (Scheme 5). Initially, aromatic aldehyde reacts with nitromethane in presence of sodium azide to form nitroolefin (A). The catalytic reaction proceeds via coordination of nitroolefin in the surface of PPy/Cu catalyst (B) followed by nucleophilic addition of sodium azide leading to the formation of intermediate C. Subsequently, the intermediate C undergoes cyclization followed by elimination of HNO₂. In the final step, the desired 4-aryl-NH-1,2,3-triazole product is formed by utilizing proton from the solvent (D).

Scheme 5: Plausible mechanism for PPy/Cu nanocomposite catalysed NH-triazole synthesis

Furthermore, we have tested the catalytic efficiency of our catalyst for synthesis of two IDO1 inhibitors, namely, 4-Phenyl-1H-1,2,3-triazole and 4-(2-chlorophenyl)-1H-1,2,3-triazole (Scheme 6, entries i,ii). It is noteworthy to mention that both the reactions proceeded smoothly resulting in satisfactory yield of the desired IDO1 inhibitors (Scheme 6).
(i) \[ \text{CHO} + \text{CH}_3\text{NO}_2 + \text{NaN}_3 \xrightarrow{\text{PPy/Cu catalyst, PEG 400, 100°C}} \text{IDO1 inhibitor} \]

3 h, 88%

(ii) \[ \text{CHO} + \text{CH}_3\text{NO}_2 + \text{NaN}_3 \xrightarrow{\text{PPy/Cu catalyst, PEG 400, 100°C}} \text{IDO1 inhibitor} \]

3 h, 84%

Reaction conditions: Aromatic aldehyde (1 mmol), nitromethane (2 mmol), NaN₃ (3 mmol) and catalyst (5 mg), solvent (2 mL), in air.

Scheme 6: Synthesis of two pharmaceutically important NH-1,2,3-triazoles

Re recyclability of the catalytic system

In order to emphasize the synthetic utility of the catalytic system, the recyclability of the catalyst as well the solvent was investigated (Scheme 7). A consecutive one-pot, three component reaction was carried out using 4-bromobenzaldehyde, nitromethane and sodium azide with the PPy/Cu catalyst in PEG 400 as solvent. After successful completion of the first cycle, the reaction mixture was extracted with diethyl ether (3×10 mL). The organic layer was then separated leaving behind the catalyst dispersed in PEG 400 solvent. Subsequent 2nd cycle of the reaction was carried out with the catalyst along with PEG 400 solvent with the same substrates but without addition of extra solvent and catalyst. Interestingly, quite consistent result was obtained in the 2nd cycle as well. The results of the consecutive cycles confirmed that our catalytic medium including both the catalyst as well the solvent can be effectively reused up to 5th cycle without notable loss in its catalytic activity. It was observed that the catalytic activity of the PPy/Cu nanocomposite slightly decreased in the 5th cycle (89 %) because of which we did not proceed to further cycles. The slight decrease in yield of the product may be due to a gradual physical loss during the process of separation, filtration and washings performed after each consecutive runs.
A few literature reports are depicted in Table 3 to compare the efficiency of our synthesized catalyst with other catalytic methods. To our delight, the catalytic efficiency of the newly synthesized catalyst was found to be quite satisfactory resulting in excellent yield of desired products.

**Table 3**: Comparison of catalytic efficiency of our PPy/Cu nanocatalyst with reported catalytic systems for synthesis of 4-aryl-NH-1,2,3-triazoles

| Entry | Catalyst                      | Solvent     | Temperature | Yield | Reference |
|-------|-------------------------------|-------------|-------------|-------|-----------|
| 1     | PPy/Cu nanocomposite          | PEG 400     | 100°C       | 98 %  | Our work  |
| 2     | Fe₃O₄@Folic acid              | Choline azide | 80°C       | 85 %  | [50]      |
CONCLUSION

We have designed a significant polypyrrole/copper (II) nanocomposite via liquid-liquid interfacial polymerization. The morphology along with structural analysis of the catalyst was investigated by several characterization techniques such as TEM, SEM, EDX, XRD, IR and ICP-AES analysis. The as-synthesized catalyst acted as an efficient catalyst for synthesis of a wide variety of 4-aryl-NH-triazoles with extremely low copper loading (0.01 mol %). Moreover, the catalyst along with the solvent PEG 400 can be recovered easily and reused up to 4th consecutive cycle maintaining the consistency of the catalytic activity. According to the literature analysis, this catalytic system represents one of the novel approaches towards synthesis of 4-aryl-NH-1,2,3-triazoles with several advantages such as high reactivity, operational simplicity and easy recyclability.

CONFLICT OF INTEREST

The authors declare no competing financial interest.

Electronic supplementary information (ESI) available: Analytical data of the synthesized compounds including copies of $^1$H and $^{13}$C NMR spectra are included in the supporting information.

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RUNNING HEAD

NH-1,2,3-triazoles synthesis in green solvent
DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supporting information of this article.

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