



ORIGINAL ARTICLE

Construction of a new 2D coral-like covalent organic framework as CuI nanoparticles carrier for the preparation of diverse triazoles



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KEYWORDS

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Heterogeneous catalyst

Abstract In this work, a novel two-dimensional coral-like covalent organic framework (COF) with hydrazone linkages containing pyridine dicarbohydrazone moieties namely PDC-COF was designed and developed through a condensation reaction between the tri(4-formyl phenoxy) cyanurate (TFPC) and 2,6-dimethylpyridine-3,5-dicarbohydrazone (DMPDC) without applying inert atmosphere and using of any acidic catalyst. PDC-COF applied as carrier for CuI nanoparticles for construction of a robust heterogeneous catalyst (PDC-COF/CuI). This catalyst shows high thermal stability (up to 500 °C), good porosity ($\approx 50 \text{ m}^2 \text{ g}^{-1}$), acceptable crystalline structure with coral-like morphology. Accordingly, the obtained data revealed that the synthesized PDC-COF/CuI is highly active heterogeneous catalyst for the preparation of diverse triazoles by using different starting materials under green and mild reaction conditions. In addition, in comparison with the reported data in the literature, all of the prepared compounds have good yields (71–93%) and relatively short reaction times (45 min–15 h). Moreover, PDC-COF/CuI shows excellent stability and reusability (up to 6 times) without any significant decreases in its catalytic performance.

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1. Introduction

In few last years, covalent organic frameworks (COFs) as versatile, reticular and irreplaceable class of porous organic polymers with inherent porosity and excellent adjustable functionality have attracted considerable attention (Geng et al., 2020; Lee and Cooper, 2020; Dey et al., 2021; Cusin et al., 2021). Advanced features such as high specific surface area, tunability, sustainability, low density, high thermal and chemical stability and possibility of post-synthetic modification have led to a promising outlook towards these compounds (Pachfule

et al., 2018; Altaf et al., 2021; Li et al., 2020). Unique and tremendous utilities have been devoted to these pre-designable polymers which include catalytic applications, gas storage and separation, energy storage, mass transport, sensor, drug delivery and etc. (Yang et al., 2016; Schneemann et al., 2021; Yang et al., 2020; Xu et al., 2021; Babu et al., 2019; Scicluna and Vella-Zarb, 2020; Liu et al., 2019; Gao et al., 2018; Lyu et al., 2019). In general, different features of COFs such as the chemical stability, catalytic activity and adsorption behavior are in turn affected by essence of linkages. Hydrazone linkages due to their irreversible tautomerization of enol to keto and intramolecular hydrogen bonding interactions between N–H and C=O groups can be enhanced the stability and crystallinity of polymer geometry (Li et al., 2019; Uribe-Romo et al., 2011; Mitra et al., 2017; Qian et al., 2020). In addition, hydrazone linkages are privileged active sites for

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confining metals and this is a developing trend in relevant areas (Zhuang et al., 2021; Li et al., 2015; Yang et al., 2016). These architectures have well-defined durable skeletons and coherent pores which their morphology can be predicted already and also, they can be active catalytic precursors for many organic transformations (Liu et al., 2020; Krishnaraj et al., 2021; Cheng and Wang, 2021; Puthiaraj et al., 2016). Catalytic utilities of COFs are well known in the domain of photocatalysis, metal-based catalysis, asymmetric catalysis and electrocatalysis (Liu et al., 2019; Xu et al., 2020; Rogge et al., 2017; Zhang et al., 2021; Li et al., 2020). Hereupon, there are intensifying efforts for post-synthetic metalation of these versatile systems which leads to a revolutionary prospect in heterogeneous catalysis (Dong et al., 2021; Ma et al., 2020).

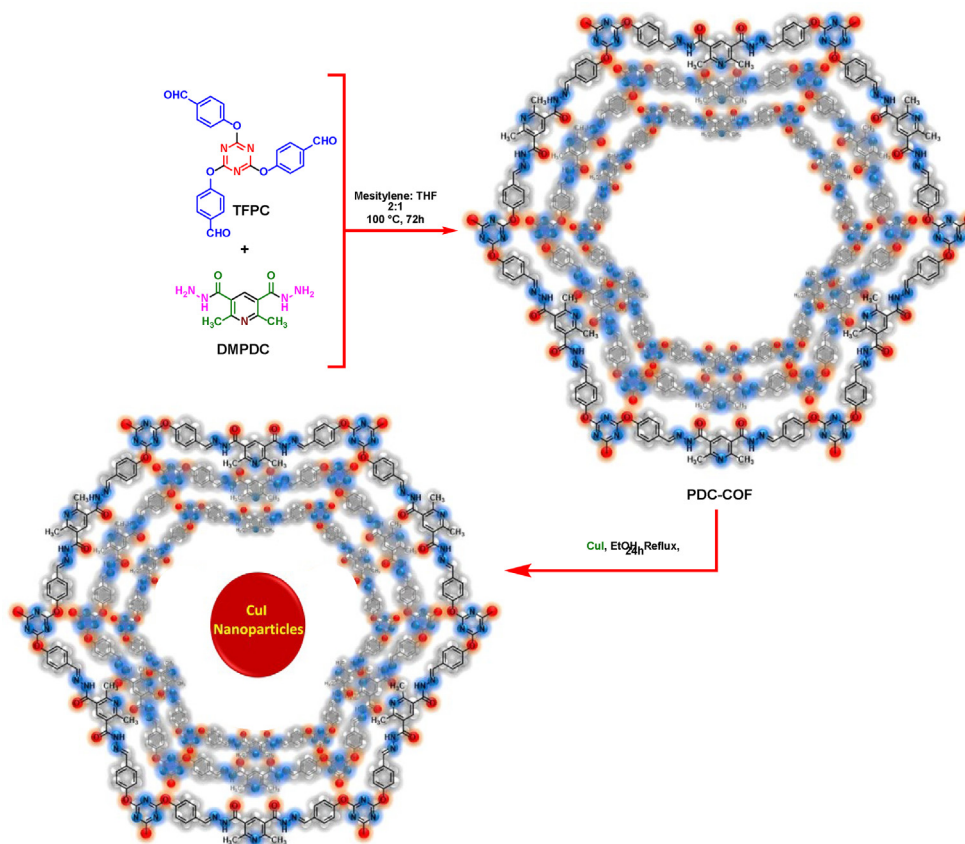
The catalytic applications of CuI nanoparticles due to their high natural abundance, selectivity, high activity and low cost have achieved a great deal of interest such as electrocatalysis, organometallic catalysis, photocatalysis, and gas-phase catalysis (Kolb et al., 2001; Rostovtsev et al., 2002; Wu et al., 2014; Gawande et al., 2016). In this regard, CuI nanoparticles as catalyst represent a paradigm example of click chemistry and is regarded as one of the most critical synthetic trends for the preparation of triazoles (Qin et al., 2010). However, the CuI-based catalyst alone has limitations and was applied only once and coordination of copper residues with the constructed triazole ring prevents its easy separation. However, CuI supported porous polymers such as CuI supported COFs as a heterogeneous catalyst can easily separate and reuse several times (Qin et al., 2007; Chen et al., 2022).

Recently, catalytic performance of copper decorated COFs as heterogeneous catalytic platforms have been drawn great attentions, in several reactions such as Henry, carbon-carbon coupling, carbon-nitrogen (Chan-Lam) coupling, Huisgen reactions and photocatalysis processes (Romero-Muñiz et al., 2021; Han et al., 2018; Han et al., 2018; Chen et al., 2022). Due to their high atom economy, efficiency, regioselectivity, and functionality tolerance, Cu (I)-coordinated COFs

are integral parts of click chemistry domain. Formation of triazole families through COF/Cu(I)-catalyzed cycloaddition reactions are indisputable synthetic routes which represents several benefits such as mild reaction conditions, simple recovering and reusing method of catalyst and easy workup procedure (Romero-Muñiz et al., 2021; Haque et al., 2020; Bu et al., 2021; Jin et al., 2019). Surveying of literatures of recent years, reveals several reports for applying copper decorated COFs in Huisgen reaction (Muller and Bräse, 2011; Vilé et al., 2022).

Over the last few decades, five-membered *N*-heterocycle compounds exhibit comprehensive versatility and utility. Synthesis of 1,2,3-triazoles as a major family of five-membered *N*-heterocycles, have been emerged as a prominent academic and industrial research field (Song and Deng, 2018; Feng et al., 2020; Deng et al., 2019). These special fragments are associated with a wide range of biological and chemical compounds (Zeng et al., 2020; Schulze and Schubert, 2014; Xu et al., 2020). Also, 1,2,3-triazole moiety is necessary for the construction of many energetic materials, pharmacological compounds, luminescent systems, dyes and chemo-sensors and have been flourished by their extensive biological activities such as anti-bacterial, anti-cancer, anti-microbial, anti-malarial, c-Met kinase and xanthine oxidase inhibitors (Barve et al., 2017; Grob et al., 2021; Tasca et al., 2015; Sajja et al., 2017). Copper(I)-catalyzed transformation is the most useful tool for the synthesis of 1,3,5-triazoles and this is a paradigm of click chemistry (Castillo et al., 2020; Liang and Astruc, 2011).

In this investigation, a new 2D covalent organic framework with hydrazone linkages as CuI nanoparticles carrier was synthesized *via* a straightforward procedure through a condensation reaction between the tri(4-formyl phenoxy) cyanurate (TFPC) and 2,6-dimethylpyridine-3,5-dicarbohydrazide (DMPDC) without applying inert atmosphere and using of any acidic catalyst and its catalytic application was investigated for the preparation of diverse triazoles by using different starting materials (Schemes 1 and 2).



Scheme 1 Representation of experimental procedure for the synthesis of PDC-COF/CuI.

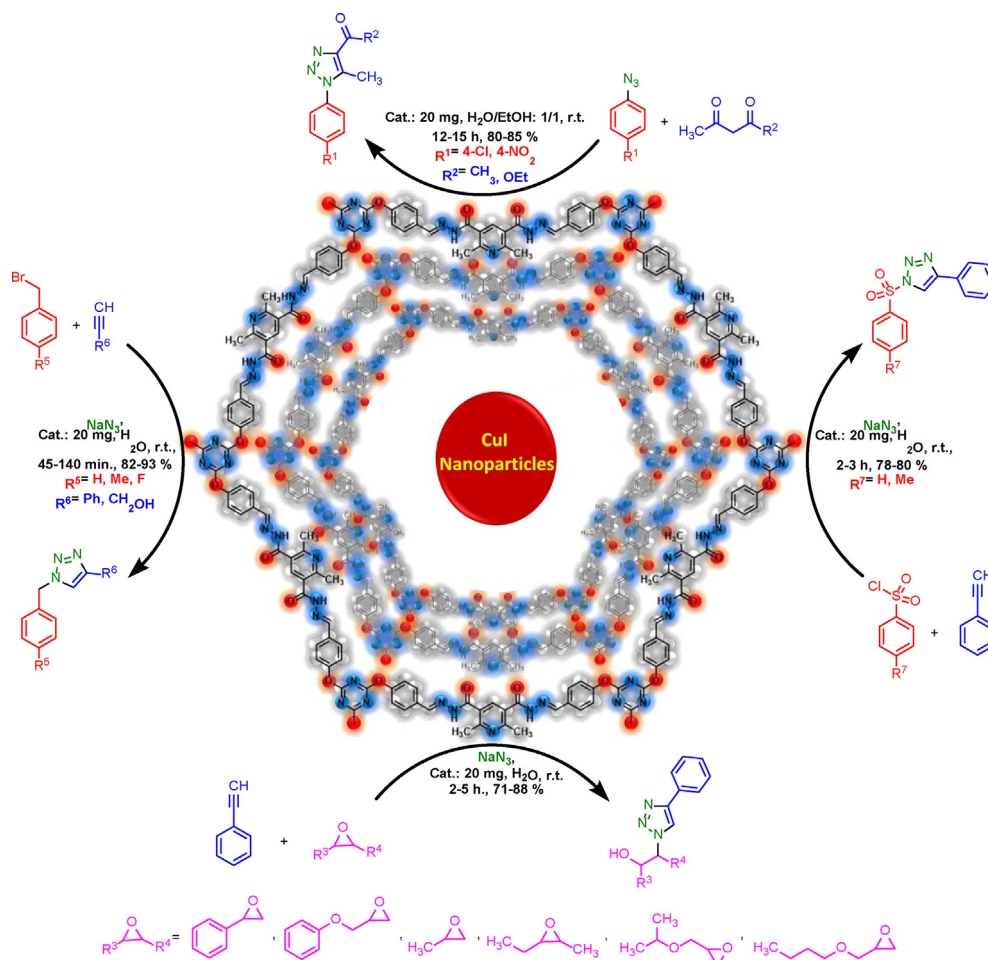
2. Results and discussion

2.1. Spectroscopic characterization of PDC-COF and PDC-COF/CuI

The formation of PDC-COF/CuI was confirmed by several techniques. Different parameters such as chemical composi-

tion, morphology, porous structure, specific surface area and thermal stability of the PDC-COF/CuI were investigated with more details in below.

At first, by applying FT-IR, analysis the main functional groups and chemical structure of PDC-COF/CuI, PDC-COF, DMPDC and TFPC were investigated *via* a comparative



Scheme 2 General experimental route for preparation of triazoles by using PDC-COF/CuI as catalyst.

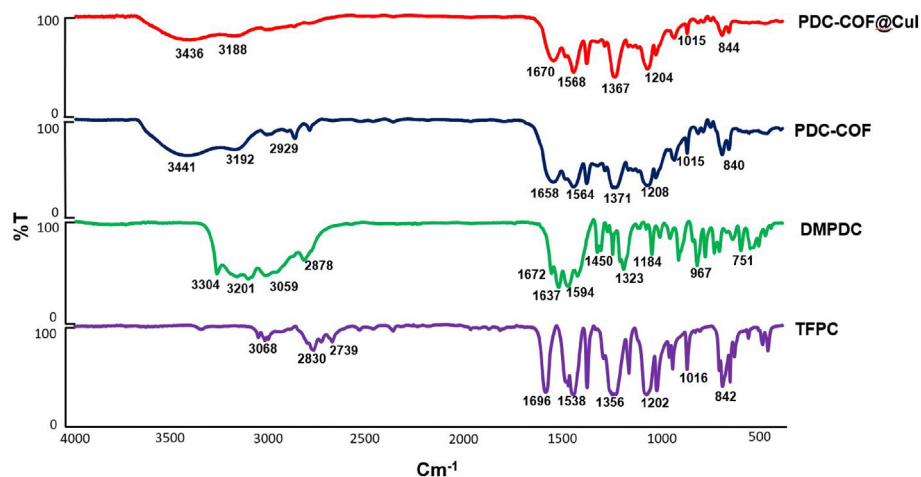


Fig. 1 Comparison of FT-IR spectra of PDC-COF/CuI, PDC-COF and DMPDC and TFPC as two key monomers.

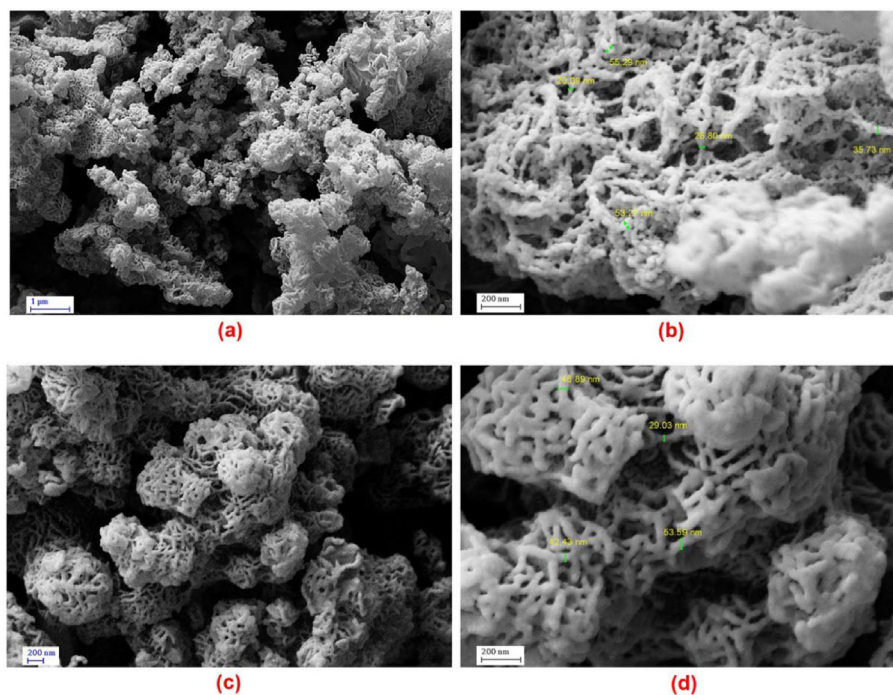


Fig. 2 FESEM images of PDC-COF (a–b) and PDC-COF/CuI (c–d).

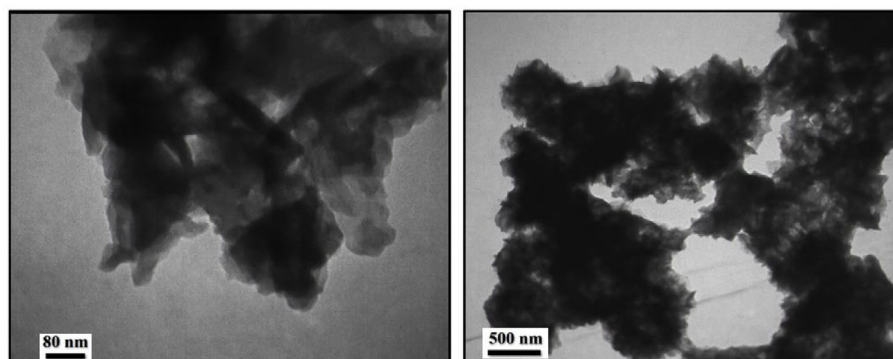


Fig. 3 TEM images of PDC-COF.

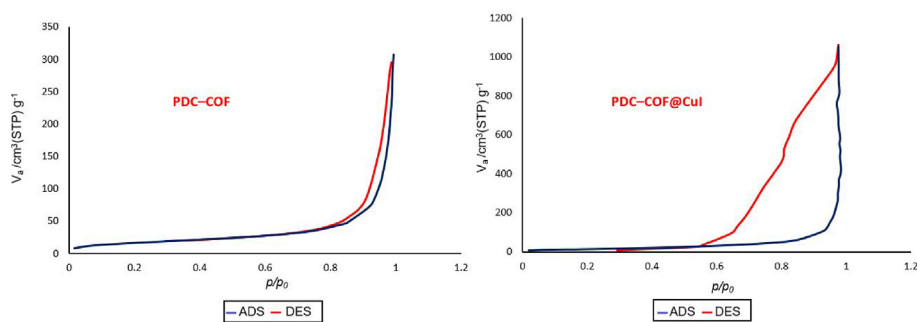


Fig. 4 Nitrogen adsorption/desorption isotherms of PDC-COF and PDC-COF/CuI.

manner. According to FT-IR spectrum of TFPC monomer, the clear bands of C=C, C=O and CHO appeared at 1538, 1696 and 2830 cm^{-1} . Also, in FT-IR spectrum of DMPDC monomer, the typical vibrational modes of N–H, NH_2 , amide

type C=O and C=N groups are shown respectively at 3304, 3201, 1672 and 1637 cm^{-1} . In FT-IR spectrum of PDC-COF, the appearance of a new peak in 1658 cm^{-1} is a definitive sign for the formation of imine linkages. Furthermore, deletion

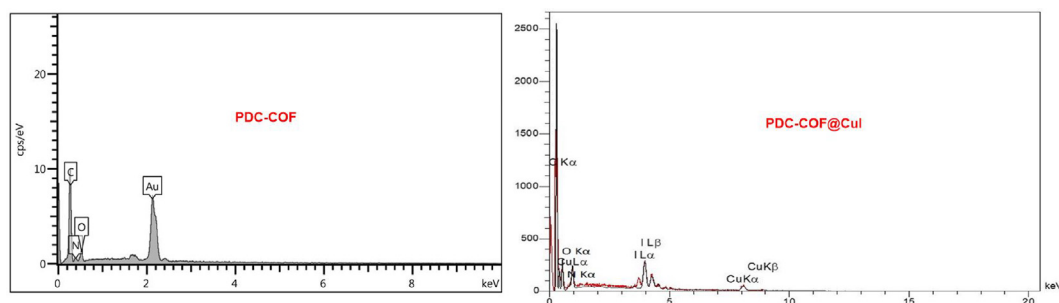


Fig. 5 EDX analysis of PDC-COF and PDC-COF/CuI.

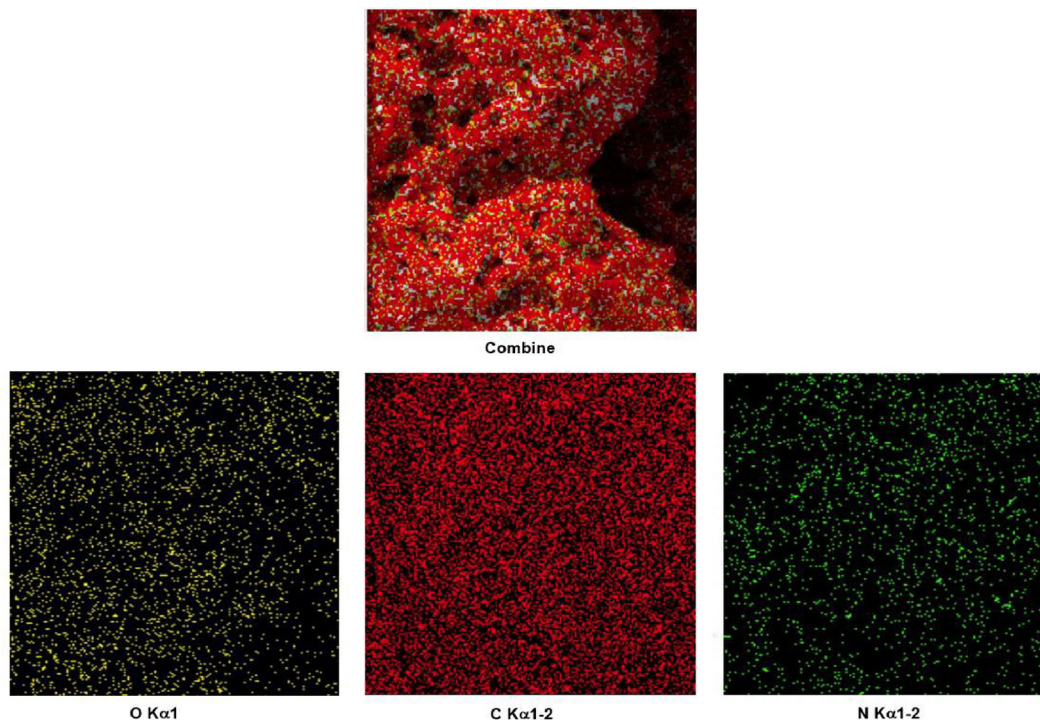


Fig. 6 Elemental mapping analysis of PDC-COF.

of stretch vibration band of NH_2 (in DMPDC monomer) and manifestation of a broad peak at about $3200\text{--}3600\text{ cm}^{-1}$ verified the successful construction of PDC-COF. In addition, there are a little difference between PDC-COF and PDC-COF/CuI. This is a good indication that CuI is confined in the PDC-COF networks and yet no change in its structure has taken place (Fig. 1). Also, the chemical structure of DMPDC and TFPC and was verified by ^1H NMR and ^{13}C NMR analysis (see ESI).

2.2. Investigation of morphology of PDC-COF and PDC-COF/CuI

The morphologies of PDC-COF and PDC-COF/CuI were investigated by FESEM and TEM analysis (Figs. 2 and 3). Interestingly, FESEM images showed that PDC-COF possessed a steady filamentous and coral-like morphology with an average size in the range of about 26–53 nm. Furthermore, the network-like structure and high porosity for both of the PDC-COF and PDC-COF/CuI are clearly recognizable in

achieved FESEM images. Also, this network structure does not contain small polymer fragments, which confirms the removal of unwanted small oligomeric fragments and starting materials. In addition, FESEM images of PDC-COF/CuI confirmed that the morphology remained almost unchanged after adding CuI. On the other, this ordered filamentous and coral-like morphology has become an ideal candidate for fixing of CuI nanoparticles on its surface and/or cavities. Also, the flake and layered morphology of PDC-COF verified by TEM images. Furthermore, the aggregation observed in TEM images can be attributed to the hydrogen bonding and $\pi\text{--}\pi$ stacking interactions between layers.

2.3. Porosity of PDC-COF and PDC-COF/CuI

Nitrogen adsorption/desorption isotherms of PDC-COF and PDC-COF/CuI at 77 K were shown in Fig. 4 which the presence of hysteresis loops confirms their mesoporous structure. As expected, after adding CuI to PDC-COF, a decrease in the BET surface area of PDC-COF/CuI ($50.3\text{ m}^2\text{ g}^{-1}$) and its

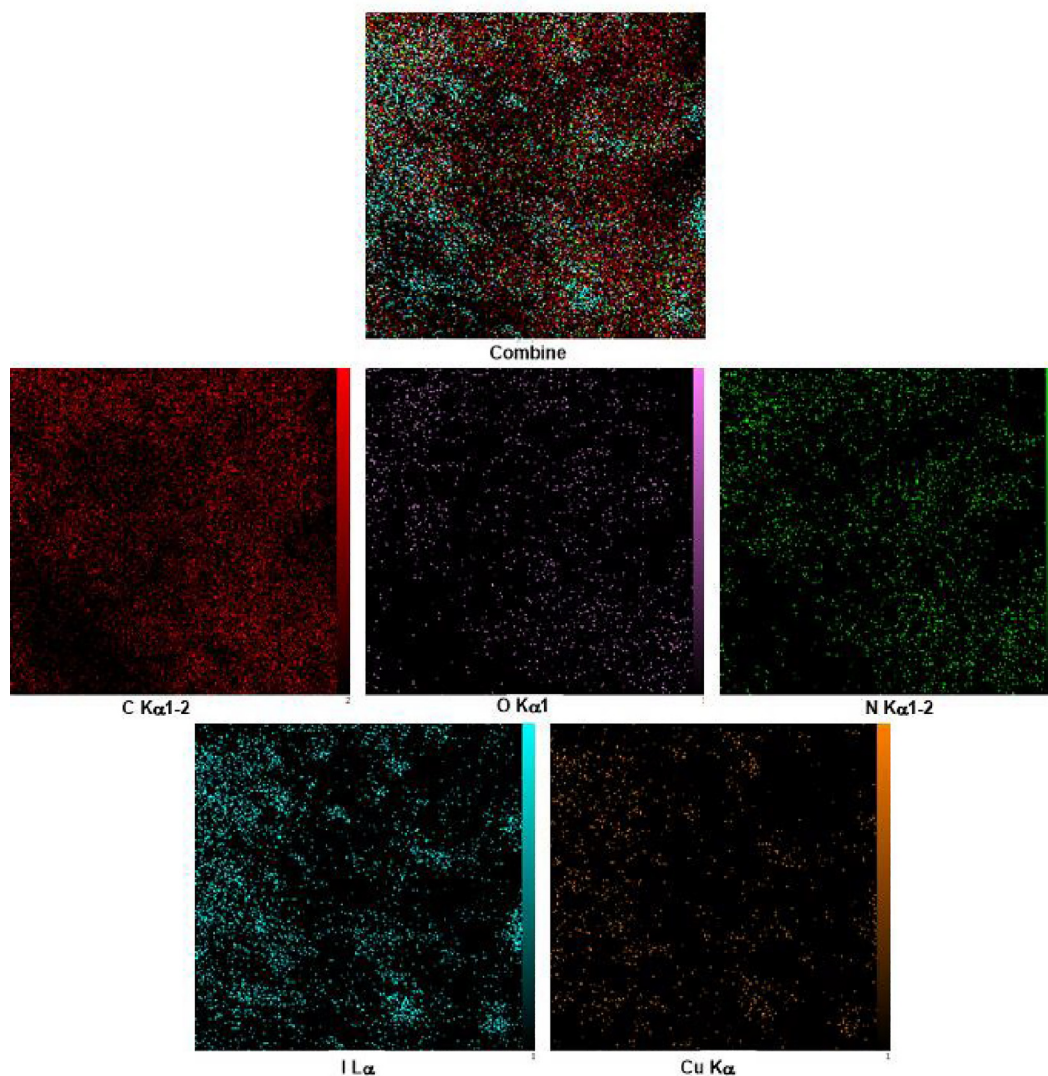


Fig. 7 Elemental mapping analysis of PDC-COF/CuI.

total pore volume is $1.63 \text{ cm}^3 \cdot \text{g}^{-1}$ compared to the pristine PDC-COF ($60.7 \text{ m}^2 \cdot \text{g}^{-1}$) and its total pore volume is $0.44 \text{ cm}^3 \cdot \text{g}^{-1}$ are observed. These results are in agreement with confinement of a significant amount of CuI nanoparticles on surface and/or cavities. In addition, the general reduction in specific surface area is due to the presence of flexible hydrazone linkages (Li et al., 2019).

2.4. Confirmation of presence of desired elements

The EDX analysis of PDC-COF and PDC-COF/CuI are shown in Fig. 5 which confirms that C, N and O elements are present in both structures. Also, in addition to mentioned elements, the EDX analysis of PDC-COF/CuI clearly reveals the presence of Cu and I elements within the structure (Fig. 4). Moreover, the obtained results of elemental mapping analysis from PDC-COF and PDC-COF/CuI confirm the above points and also, illustrate uniform distribution of predicted elements (Figs. 6 and 7).

2.5. Crystalline structure

XRD as a robust technique can provide a useful information for exploring crystallographic structures of COFs. According to the previously relevant reports, there are varied XRD patterns from COFs and other porous organic polymers that have amorphous phases, while metal decorated COFs have distinctive and sharp peaks (Sebati and Ray, 2018; Luykx et al., 2008). Also, the XRD pattern depends on the amount of trapped metal (Mondal et al., 2016). As depicted in Fig. 8, the XRD pattern of PDC-COF represents the presence of amorphous phases (Fig. 8a), while CuI adding changes the XRD pattern and leads to appearance of sharp peaks which verified the presence of crystalline CuI nanoparticles within the structure of PDC-COF/CuI (Fig. 8a-b). Interestingly, in this case when 1 g of PDC-COF and 0.3 g of CuI were used, its associated XRD pattern is almost identical to the XRD pattern of CuI (Fig. 8b, see: ICDD Card # 01-0581). But, when 1 g of PDC-COF and 0.1 g of CuI were used, the PDC-COF XRD pattern is poorly observed (Fig. 8 c).

2.6. Thermal stability

The thermal stability is one of the most important parameters of practical applications of COFs. The TGA/DTG analysis was performed for PDC-COF and PDC-COF/CuI and fortunately the results show excellent thermal stability with thermal decomposition temperature about 500 °C for both PDC-COF and PDC-COF/CuI. It goes without saying that there is very little weight loss before 500 °C that is related to trapped solvents (Fig. 9).

2.7. Catalytic performance studies

According to revealed results from precise characterization of PDC-COF/CuI, it is a suitable candidate as a heterogeneous catalyst for organic transformations. So, we conducted the triazole synthesis reactions by using PDC-COF/CuI as an efficient catalyst. At first, benzyl bromide, phenyl acetylene and sodium azide were selected as model substrates for determination of optimal reaction conditions. Gratifyingly, all of reactions were performed at room temperature that is in accordance with the green chemistry principles. The parameters of solvent and amount of catalyst loading were investi-

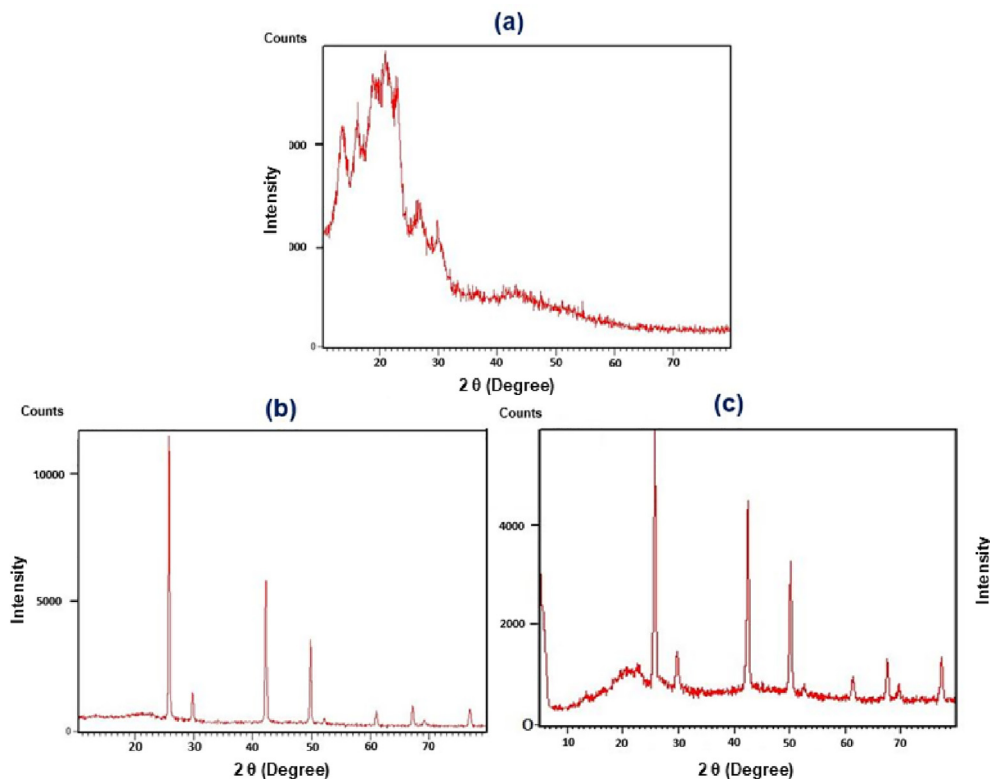


Fig. 8 XRD patterns of PDC-COF (a), PDC-COF/CuI when 1 g of PDC-COF and 0.3 g of CuI were used (b) and PDC-COF/CuI when 1 g of PDC-COF and 0.1 g of CuI were used.

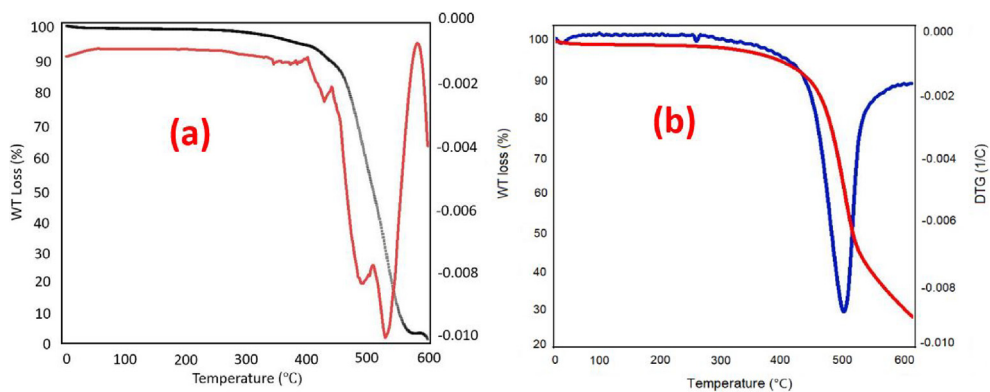
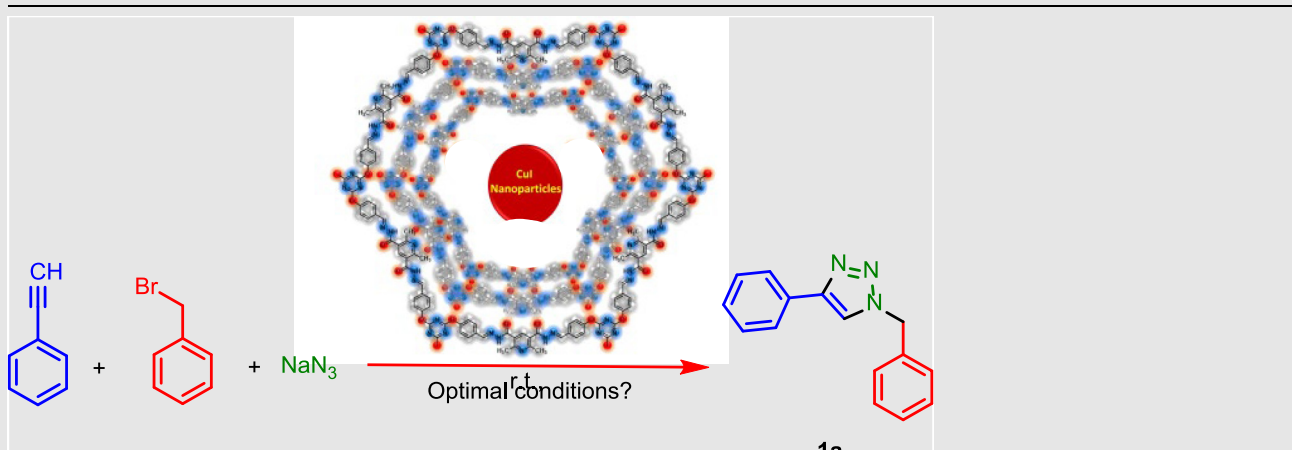


Fig. 9 TGA/DTG curves of PDC-COF (a) and PDC-COF/CuI (b).

Table 1 Optimizing of the reaction conditions for the synthesis of **1a**.^a


Entry	Solvent	Catalyst loading (mg)	Time (min.)	Yield (%) ^b
1	–	20	45	70
2 ^c	H ₂ O	20	45	93
3	EtOH	20	45	90
4	EtOH–H ₂ O (1:1)	20	45	92
5	EtOAc	20	90	55
6	CH ₃ CN	20	90	78
7	CH ₂ Cl ₂	20	45	85
8	THF	20	60	82
9	H ₂ O	30	45	93
11	H ₂ O	10	45	76
12	H ₂ O	–	120	–

^a Reaction conditions: Benzyl bromide (1 mmol, 0.171 g), phenyl acetylene (1 mmol, 0.102 g) and sodium azide (1.2 mmol, 0.078 g).
^b Related to isolated yields.
^c Optimal reaction conditions.

gated and the model reaction was tested in different protic, aprotic and equal mixture of H₂O–EtOH that the model reaction has a good yield in most of solvents. However, because of its compatibility with the environment and the principles of green chemistry, water was selected as the best solvent. After that, different amount of catalyst including 30, 20, 10 mg were used which the obtained data revealed that the 20 mg of catalyst is the best amount. Moreover, it is worthy to mention that in the absence of the catalyst no product was produced (Table 1).

After optimization of the reaction conditions, the substrate scope of PDC-COF/CuI catalyzed click reactions for the preparation of triazoles by applying different starting materials were explored. In the first path, phenyl acetylene or prop-2-yn-1-ol, sodium azide and different benzyl bromide derivatives or sulfonyl chloride derivatives were applied for the preparation of triazoles. Then, after preparation of 1-azido-4-chlorobenzene and 1-azido-4-nitrobenzene, triazole systems were synthesized by the reaction of these aryl azides and acetyl acetone or ethyl acetoacetate. In the third series, different epoxide derivatives, sodium azide and phenyl acetylene were used that leads to formation of another series of triazoles (Table 2). All the products were obtained with good to high yields.

In another investigation, recycling and reusing capability of PDC-COF/CuI as a significant parameter was evaluated by its

reusing up to six times. For this purpose, the model reaction (synthesis of triazole **1a**) was performed under optimal reaction conditions. After completing of each of reactions, the reaction mixture was dissolved in EtOH for separating of insoluble catalyst via centrifuging method. However, slight reduction has occurred in the reaction yield of product (Scheme 3).

In separate study, to confirm the S_N2 type reaction for ring opening of epoxides, **1m** as model compound was oxidized by Jones reagent (Scheme 4). According to revealed result, oxidation of hydroxy functional group in **1m** yielded ketone that shown S_N2 type reaction for ring opening of epoxides and synthesis of desired triazoles (Zarei et al., 2019).

In another study, we investigated the facility and efficiency of PDC-COF/CuI with some of the previously reported works for the preparation of **1a** molecule. Accordingly, the presented catalyst shows a good catalytic performance with a shorter reaction time and a high yield of product (Table 3).

3. Experimental section

3.1. Experimental procedure for the synthesis of PDC-COF

Initially, DMPDC and TFPC were synthesized according to the previous reports (Torabi et al., 2021; Dinari and Hatami, 2019). Then, a mixture of TFPC (0.456 mmol, 0.2 g), DMPDC

Table 2 Preparation of varied triazoles in the presence of PDC-COF/CuI as catalyst (Bi et al., 2021; Bonyasi et al., 2018; Kafle and Handy, 2017; Khoshnevis and Eshghi, 2021; Khoshnoud and Pourali, 2021; Reddy et al., 2019; Singh et al., 2013; Tarabi, 2021; Torabi et al., 2022; Whiting and Fokin, 2006; Yarie 2021).

1a , 45 min., 93 % 124-127 °C [128-130] ⁶⁷	1b , 55 min., 82 % 102-103 °C [103-105] ⁶⁸	1c , 45 min., 90 % 123-124 °C [129-131] ⁶⁹	1d , 3 h., 78 % 101-104 °C [105-107] ⁷⁰	1e , 2 h., 80 % 99-101 °C [105-106] ⁷¹	
1f , 140 min., 91 % 106-109 °C [109-110] ⁷²	1g , 12 h., 82 % 139-141 °C [132-134] ⁷³	1h , 15 h., 80 % 114-116 °C [116-118] ⁷⁴	1i , 15 h., 85 % 122-124 °C [124-125] ⁷⁵	1j , 15 h., 82 % 95-97 °C [90-92] ⁷⁶	
1k , 2 h., 83 % 111-114 °C [114-116] ⁶⁷	1l , 2 h., 78 % 102-104 °C [new]	1m , 2 h., 88 % 104-107 °C [105-107] ⁷⁵	1n , 3 h., 75 % 114-117 °C [124-126] ⁶⁷	1o , 4 h., 76 % 75-76 °C [62-64] ⁶⁷	1p , 5 h., 71 % 69-71 °C [64-66] ⁶⁷

(0.676 mmol, 0.15 g) and mixture of mesitylene/THF (6 mL, 2:1) was added into a 10 mL test tube and sonicated at room temperature for 15 min. In the next step, the mixture of reaction was sealed in a 25 mL Teflon lined stainless steel vessel and heated at 100 °C for 72 h. After completing the reaction, the obtained yellow precipitate was washed several times with MeOH and CHCl₃. Finally, the remained solid was dried in a vacuum oven for 12 h at 70 °C.

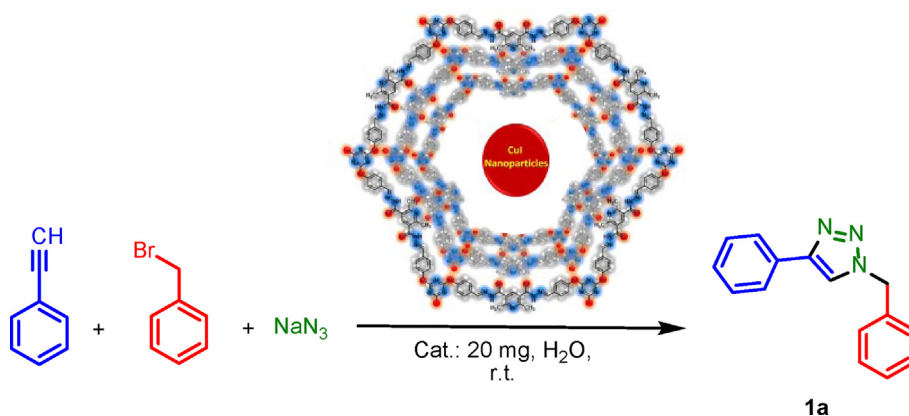
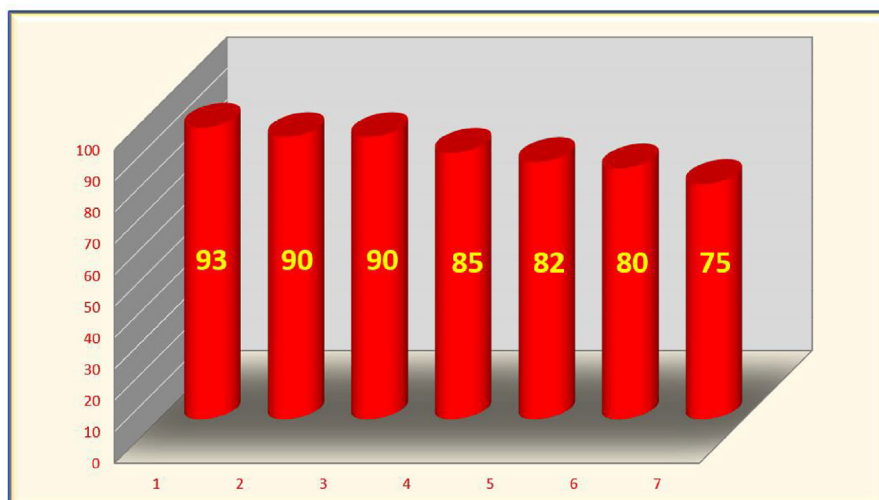
3.2. Synthesis of PDC-COF/CuI

1 g of the synthesized PDC-COF, 0.1 g of CuI and 40 mL dry EtOH were added into a 10 mL round-bottomed flask and stirred at room temperature for 12 h, following which the solid

was washed with dry EtOH and then was activated by vacuum at 70 °C.

3.3. General procedure for the preparation of triazole derivatives (1a-1f) by using PDC-COF/CuI as catalyst

Benzyl bromide derivatives (1 mmol) or sulfonyl chloride derivatives (1 mmol), phenyl acetylene (1 mmol, 0.102 g) or prop-2-yn-1-ol (1 mmol, 0.056 g), sodium azide (1 mmol, 0.065 g) and PDC-COF/CuI (0.02 g) were added to the 20 mL of H₂O and stirred at 25 °C for appropriate time. After completing each of reaction which were confirmed by TLC techniques (*n*-hexane/ethyl acetate, 7/3), the remained solid was extracted with ethyl acetate and H₂O. Then, organic phase



Scheme 3 Recycling test of PDC-COF/CuI in the preparation of **1a**.

was separated and its solvent was evaporated to give pure product.

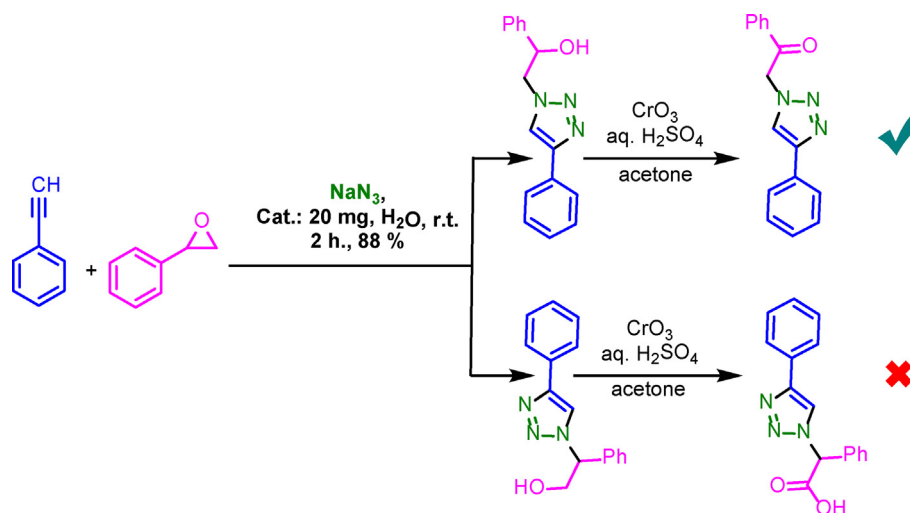
3.4. Preparation of triazole derivatives (1 g-1j) in the presence of PDC-COF/CuI

1-Azido-4-nitrobenzene (1 mmol, 0.164 g) or 1-azido-4-chlorobenzene (1 mmol, 0.153 g) and acetyl acetone (1.1 mmol, 0.11 g) or ethyl acetoacetate (1.1 mmol, 0.143 g) and PDC-COF/CuI (0.2 g) were added to the mixture of 20 mL H₂O/EtOH (1:1) and vigorously stirred at room temperature. The progress of reaction was tested by TLC (*n*-hexane/ethyl acetate, 7/3). After completing of each reaction, the desired product was extracted with ethyl acetate and H₂O. Then, organic phase was separated and its solvent was evaporated.

Finally, the remained solid was washed with H₂O to give pure solid.

3.5. Preparation of triazole derivatives (1 k-1p) in the presence of PDC-COF/CuI

Epoxide derivatives (1 mmol), phenyl acetylene (1 mmol, 0.102 g), sodium azide (1 mmol, 0.065 g), PDC-COF/CuI (0.2 g) and 20 mL of H₂O as solvent were added into a 50 mL round-bottomed flask and stirred at room temperature. The progress of reaction was tested by TLC (*n*-hexane/ethyl acetate, 7/3). After completing each of reactions, 100 mL ethyl acetate was added to the mixture of reaction and extracted. Then, organic phase was separated and purified by TLC plate techniques with *n*-hexane/ethyl acetate as eluent.



Scheme 4 General procedure for oxidation of hydroxy functional group of **1m** to confirm the S_N2 type reaction.

Table 3 Comparative investigation of catalytic activity of PDC-COF/CuI and some of those other previously reported papers upon the preparation of **1a**.^a

Entry	Catalyst	Time	Yield (%)
1	PDC-COF/CuI (20 mg), H₂O, r.t.	45 min.	93
2	D-sorbitol/urea/NH ₄ Cl/CuI (5 mol%), 85 °C (Ilgen and König, 2009)	5 h	91
3	2-(2'-hydroxyphenyl)-2-oxazoline-Cu(OAc) ₂ , (1 mol%), H ₂ O, 70 °C (Bagherzadeh et al., 2017)	12 h	87
4	CuAl ₂ O ₄ (5 mg), H ₂ O, 80 °C (Khalili et al., 2019)	45 min.	97
5	[Cu(CPA)(BDC)] _n , (10 mol%), H ₂ O/MeOH, 70 °C (Naskar et al., 2021)	60 min.	93
6	RuH ₂ CO(PPh ₃) ₃ , (2 mol%), H ₂ O, 80 °C (Siyang et al., 2015)	2 h	89
7	Si-1,5,7-triazabicyclo[4.4.0]dec-5-ene /Cu, 3 mol%, DMF, 40 °C (Coelho et al., 2010)	3 h	83
8	SBA-15-Tz-Ru(II) TPP (15 mg), H ₂ O, 90 °C (Du et al., 2018)	12 h	88
9	NHC-copper complexe, (5 mol%), MeOH, r.t. (Szadkowska et al., 2017)	24 h	73

4. Conclusion

In summary, a novel two-dimensional coral-like covalent organic framework (COF) with hydrazone linkages containing pyridine dicarbohydrazone moieties CuI nanoparticles carrier namely PDC-COF/CuI was designed and synthesized *via* a green and simple route and in a precise study was fully characterized. Furthermore, the network-like structure and good porosity for both of the PDC-COF and PDC-COF/CuI well verified by FESEM images and BET data. According to TGA/DTG analysis, PDC-COF/CuI has excellent thermal stability up to 500 °C. Also, the prepared PDC-COF/CuI show high activity as a heterogeneous and recoverable catalyst for the preparation of diverse triazoles by using different starting materials under green and mild reaction conditions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Appendix A. Supplementary material

Supplementary material to this article can be found online at <https://doi.org/10.1016/j.arabjc.2023.105090>.

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