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Synthesis, characterization and computational study of CuI nanoparticles immobilized on modified poly (styrene-co-maleic anhydride) as a green, efficient and recyclable heterogeneous catalyst in the synthesis of 1,4-disubstituted 1,2,3-triazoles via click reaction

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Funding information Iran National Science Foundation (INSF) Poly (styrene-co-maleic anhydride) (SMA) was modified by reactionwith4-amino-2-methyl-10H-thiene [2,3-b][1,5]-benzodiazepine (ATD) hydrochloride, providing an imide with the appropriate sites for the coordination of Cu(I)ions. This modified SMA was reacted with CuI to obtain immobilized Cu(I) NPs. This Cu(I) NPs (CuI/ SMI-TD) was fully characterized by conventional techniques such as FT-IR, NMR, SEM, TEM, EDAX and ICP-AES analysis. The SEM and TEM images clearly showed CuI NPs as spherical shapes and the size of particles is 30-60 nm. Moreover, a quantitative description for experimental features of CuI/SMI-TD was presented via computational assessment for the interactions between copper metal ions and coordination sites of SMI-TD ligand. The catalytic activity of this new catalyst was examined in the regioselective synthesis of 1,4-disubstituted-1,2,3 triazoles in a classical copper-catalyzed reaction a so-called click reaction. The catalyst showed highly efficient catalytic activity, excellent reusability, high yield and more importantly excellent, regioselectivity. The catalyst was recoverable through simple filtration and can be reused at least five times without significant loss of catalytic activity. The heterogeneous nature of the catalyst was confirmed based on the hot filtration test and ICP-AES analysis.

KEYWORDS

1,2,3-Triazoles, click reaction, density functional theory, heterogeneous copper nanocatalyst, poly(styreneco-maleic anhydride) (SMA), quantum theory of atoms in molecules

1 | INTRODUCTION

Catalysts can be divided into three main types, heterogeneous, homogeneous and biocatalysts. The recovery of homogeneous catalysts is difficult. Thus, the process is not cost-effective. Moreover, although their selectivity is good to excellent but their thermal stability is poor. Due to their selectivity, in some cases the homogeneous catalysis is more desirable. However, the heterogeneous catalysis in general is much more in demands. Nowadays, heterogeneous catalysts have stirred up the interest of synthetic organic chemists due to their potential advantage such as facile recovery and reusability. Thus, heterogeneous catalysis in chemical industries has become an important field of research in their R&D sections as well as attracted much attention in academia.^[1]

In addition to solid supports, multifunctional polymers are frequently used for altering the homogeneous catalysts

to their heterogeneous counterparts. These polymers are potentially advantageous due to their special features, which are chiefly depended on their very large size and unique properties. Polymer-supported reagents provide the striking and practical strategies for efficient and clean reactions of novel chemical archives with extensive applications in the chemical, pharmaceutical or agrochemical industries.^[2]

In spite of importance and usefulness of polymeric supports^[3] the applications of polymeric materials as supports has largely been overlooked. A literature survey shows relatively few example of the utilization of polymers or modified co-polymers in the area of heterogeneous organocatalyzed reactions. In general, most polymers have lower thermal stability in comparison with mesoporous materials. In addition, the polymers and co-polymers have low mechanical stability. The use of organic–inorganic polymer composite instead of polymers and co-polymers has circumvented these problems. Nowadays the applications of hybrid organic–inorganic polymers have attracted much attention.^[4]

The unique structural features and outstanding properties of polymeric materials have overcome the drawbacks associated with such materials and make them useful for being used as suitable supports for converting the homogeneous catalysts to their heterogeneous counterpart. Significantly, these hybrid organic–inorganic materials gain some merits of polymeric materials such as their flexibility resulting in easy processing with standard techniques. Due to their elasticity, organic functionalities, transparency, stability, hardness and chemical and thermal stability, the polymers, co-polymers and their modified structures are considered as ideal supports. Therefore, the design and preparation of organic–inorganic hybrid polymers with new and versatile scaffolds as heterogeneous catalysts are in much demand.^[5–11]

1,2,3-Triazoles are important and useful heterocycles. They have several applications as agrochemical agents, dyes, corrosion inhibitors, photo stabilizers, and photographic materials. Several 1,2,3-triazole derivatives show interesting biological activities.^[7–11]

One of the most general method for the syntheses of 1,2,3-triazole derivatives, is the well-known Cu(I) catalyzed-1,3-dipolar Huisgen cycloaddition reaction involving azides with alkynes.^[12]

Cu(I)-catalyzed-1,3-cycloaddition reaction of (CuAAC) an azide and terminal alkyne is a widely utilized, reliable, and straightforward way for construction of covalent connections between scaffolds containing different functional groups. CuAAC catalyzed Huisegn reaction has emerged as the leading example of click chemistry to designate a set of conventional bond-forming reaction in a 'near-perfect' fashion for the rapid construction of the desired molecules. A click reaction is easy to conduct, afforded the desired product in high to excellent yields with the generation little or no by-products. It works perfectly under many conditions and is unpretentious by the nature of the groups present in the starting materials.^[13,14]

Recently, the application of heterogeneous copper catalysts based on solid supports, including various polymers has been attracted much attentions. By immobilization of Cu(I) species, two goals are achieved, a) stabilization of Cu(I) ions, b) preparation an easily separable Cu(I) heterogeneous catalyst which can be used in the regioselective synthesis of 1,4-disubstituted 1,2,3-triazoles via click reaction under green conditions. The synthetic organic chemists frequently try to design copper catalysts for developing click reaction.^[15]

The copper(I) salts are immobilized as NPs on high surface area supports such as aluminum oxyhydroxide nanofiber,^[16] activated carbon^[17] and different polymeric and magnetic materials^[18–20] for higher stability and better dispersion of nanoparticles. Moreover, the easy separation and recycling properties of the heterogeneous catalyst are well known and established. These advantages make them superior over naked Cu(I) counterparts.^[16–20] Metal NPs have been proven and established to have very large surface area, showing high catalytic potency under the green conditions and promoting the reaction being completed in relatively short time.

Among these polymeric supports, immobilization of CuI nanoparticles (NPs) on poly (styrene-co-maleic anhydride) (SMA) has found effective applications in click reactions. SMA is a commercially available co-polymer bearing reactive anhydride moiety. Thus, this co-polymer can easily be modified using nucleophilic compounds to have such structure which after reaction, offering basic nitrogen atom (atoms) suitable for being coordinated with an appropriate metal in NPs form. Furthermore, SMA polymer chains are flexible and may contain a variety of functional groups that are able to immobilize nanoparticles and their precursors efficiently by dispersive or van der Waals, electrostatic, hydrogen bonding or covalent bonds. Thus, the modification of SMA support was investigated and applied as several efficient heterogeneous catalysts.^[21–26]

We are interested in catalyzed synthesis of various heterocyclic systems, via multicomponent reactions under green conditions, using heterogeneous catalysts^[27–34] We have recently investigated the synthesis and characterization of copper-aminated KIT-5 and silica-bonded propyl-N-sulfamic acid nanocatalysts and their applications in various organic transformations^[28–30] We have also assessed the reaction of SMA modified with 2-aminopyridine, 3-aminopyridine, 4aminopyridine and 2-aminothiazole reacted them with CuI and PdCl₂NPs to prepare nanocatalysts and applied them in the synthesis of 1,4-disubstitued-1,2,3-triazoles via click reaction as well as, Hantzsch 1,4-dihydropyridine synthesis and Sonogashira coupling reactions.^[31] Armed with these experiences, herein, we investigated the modification of SMA with 4-amino-2-methyl-10H-thiene [2,3-b][1,5]-benzodiazepine (ATD)as an amino nitrogen heterocycle with several coordinating sites. Then we immobilized CuI NPs on modified SMI-TD polymeric support and assessed its catalytic application in the regioselective synthesis of 1,2,3triazoles via click reaction. Furthermore, in continuation of our recent overgrowing studies on computational assessment of metal NPs complexation process in the synthesis of polymeric and silica heterogeneous catalysts and also regioselective behavior of Cu and Pd-catalyzed organic transformations,^[28-34] in this work we have concentrated on several possible coordinating modes of copper metal ions on modified SMI-TD ligand model, via density functional theory (DFT)^[35] and quantum theory of atoms in molecules (QTAIM)^[36,37] approaches. Strictly speaking, we presented the theoretical interpretations for immobilization behavior of CuI NPs on SMI-TD support based on various QTAIM reliable indicators and compare our calculated results with the experimental results.

2 | EXPERIMENTAL

2.1 | Materials

SMA polymer was obtained from KARABOND Company (general formula is $[(C_8H_8)_{0.6}(C_4H_2O_3)_{0.4}]_n$ with Mw = 182,000, Mn (g/mol) = 86,666, and Mw/Mn = 2.1). Triethylamine (TEA) and N,N-dimethylformamide (DMF) were distilled before use. Other reagents were purchased from Aldrich and Merck with high-grade quality and used as received.

2.2 | Equipment

The FT-IR spectra of the samples were recorded in the range of 500–4,000 cm⁻¹ using KBr pellet technique on FT-IR Bruker Tensor 27 instrument. Band intensities are assigned as strong (s), medium (m) and weak (w). ¹H NMR spectra were recorded using a Bruker AQS Advance spectrometer, with CDCl₃ or DMSO-d₆ as solvent. Scanning electron microscope (SEM) Lecia Cambridge S 360 was used to observe the morphology of modified and unmodified polymer matrix.

Transmission electron microscope (TEM) recorded using a Philips CM30 300kv.Energy dispersive X-ray spectroscopy (EDAX) Genesis, with an SUTW detector equipped with SEM equipment was used to carry out the EDAX analysis in order to confirm immobilization of CuI NPs on modified polymeric support. Copper content was measured by ICP-AES on a Varian Vista pro analyzer. All yields refer to isolated products.

2.3 | Preparation of SMI-TD [poly (styreneco-maleic imide)]-ATD (4 -amino-2-methyl-10H-thiene [2,3-b][1,5]-benzodiazepine (ATD)

ATD hydrochloride (1.00 gr) was dissolved in water (1 ml) and then NaOH (5%) (1 ml) was added to adjust the solution to pH 8. The solid was filtered and dried under vacuum at 50-60 °C. In a 100 ml glass reactor, SMA (a) (1.00 g), ATD (b) (3.00 g, 11.28 mmol) in dry DMF (8 ml) were placed under N₂ atmosphere. The reaction mixture was heated in oil bath at 35 °C for 3.5 h. To this mixture triethylamine (0.3 ml, 2 mmol), acetic anhydride (0.6 ml, 6 mmol) and sodium acetate (0.33 g, 4 mmol) were added respectively by syringe (Scheme 1). The temperature of the reaction was increased to 75 °C for further 3.5 h. Then reaction mixture was cooled to room temperature. The precipitated product was [SMI-TD (c)] filtered and washed with methanol and dried under reduced pressure at 70 °C to constant weight. Back titration using NaOH (0.2 N) was performed for determination of amine content of SMI-TD^[38,39] For this purpose, 0.05 g of the SMI-TD was stirred in 10 ml of HCl (0.2 N) for 30 min. The SMI-TD was removed and washed successively with deionized water. The excess of HCl was then titrated with NaOH (0.2 N) in the presence of phenolphthalein as an indicator. Amine site content of the synthesized SMI-TD was found to be 8.86 mmol g^{-1} .

2.4 | Immobilization of CuI NPs onto SMI-TD (synthesis of CuI/SMI-TD nanoparticles)

CuI (0.355 mg, 0.00187 mmol) was dissolved in acetonitrile (2 ml) under ultrasonic irradiation to produce a pale yellow solution. In order to provide CuI NPs, to this mixture DMF (20 ml) was added at room temperature.^[40] To this mixture,



dry modified polymer SMI-TD(c) (1.00 g) was added. This reaction mixture was then stirred at for 5 h under nitrogen atmosphere at reflux temperature. Finally, the CuI/SMI-TD (d) was filtered and washed with acetonitrile (3 times with 20 ml) and dried under vacuum at 60 °C overnight (Scheme 2). The copper content was determined by ICP-AES analysis and found being 4.75% w/w.

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2.5 | Determination of copper content in nanocatalyst

The Cu content was determined by inductively coupled plasma (ICP-AES) analysis. For this purpose concentrated hydrochloric/nitric acids (HCl: HNO₃ (1:1) ν/ν)was used to digest the copper species. Then, Cu content was measured by ICP-AES. The ICP data for fresh Cu nanocatalyst was determined around 4.75% and after five runs only 15%, decrease in copper content was observed. The efficiency of this nanocatalyst was tested in the regioselective synthesis of 1,2,3-trizoles via click reaction. This investigation was performed for the fresh and reused catalyst. The test was successful for the when the freshly prepared catalyst was used. The recovered catalyst was also reused for five consecutive runs successfully in which no appreciable loss in its activity was observed.

2.6 | Synthesis of 1,4-disubstitued 1,2,3-triazoles: General procedure

According to Scheme 3, in a 25 ml round-bottom flask, alkyne (1) (1 mmol), sodium azide (2) (1.1 mmol), appropriate α -

haloketones or alkyl halide (5a-g) (1 mmol) and water (10 ml) were placed. Then, the CuI/SMI-TD (4) (0.03 g) was added. The reaction mixture was stirred under reflux for the indicated time (Table 1). The copper content in the catalyst was 4.75% (w/w) (Each gram of heterogeneous catalyst includes 0.25 mmol of copper). For 1 mmol of reactants, 0.01 mmol of catalyst is required, which is equal to 0.019 g. The progress of the reaction monitored by TLC (using n-hexane: ethyl acetate; 7:3 as eluent). Upon completion of the reaction, the hot mixture was filtered off and the resin (CuI/ SMI-TD) was washed with 25 ml hot ethanol and dried at 70 °C for 3 h under reduced pressure for further use. The crude was recrystallized from EtOH/ H₂O (3:1 v/v) to give the corresponding pure crystalline product (5a-g) (Table 1). All compounds were known and their physical and spectroscopic data wear compared with those of authentic compounds and found being identical.^[17,41–44] The spectral (IR, ¹H NMR, ¹³CNMR) data for new compound of this work (5b in Table 1) is as follows.

2.7 | 1-(2-Bromophenyl)-2-(4-phenyl-1H-1,2,3triazol-1-yl) ethanone(5b)

Mp, 180–185 °C,**IR** (**KBr**): 1,733, 1,253 (s) cm⁻¹.¹**H** NMR (250 MHz, DMSO): d = 8.51 (s, 1H, CH), 8.03–7.81 (m, 4H, Ar-H), 7.48–7.30 (m, 5H, Ar-H), 6.24 (s, 2H, CH₂) ppm.¹³CNMR (31 MHz, DMSO): δ = 192.01, 146.78, 133.56, 132.53, 131.13, 130.63,129.39, 128.91,128.34, 125.60, 123.42, 56.39, 38.93 ppm.

The suggested mechanism is illustrated in Scheme 4. As shown, the modified polymeric support plays an important



TABLE 1 Click reaction catalyzed by CuI/SMI-TD (in situ) nanocatalyst via optimized reaction conditions for the synthesis of 1,4-disubstituted-1H-1,2,3-triazoles

	(1) (2	$aN_3 + or Cl H_2 (3)$	1A-ATD Cat. (4) D, reflux PI	$ \begin{array}{ccc} N = N \\ or \\ N = N \\ D \\ Sa-g) \end{array} $	
Entry (5a–g)	R	Product	Time (min)	Yield (%) ^a	Mp (°C) (Lit.)
Α	C ₆ H ₅ -	N=N N	20	78	170–173 (169–170)[16, 40]
В	<i>о</i> -Вг-С ₆ Н ₅ -	Br O N=N	40	82	180–185 [This Work]
С	p-OMe-C ₆ H ₅ -	MeO N=N	45	87	142–147 (140–142) [42]
D	p-Cl-C ₆ H ₅ -	CI N=N	25	75	100–104 (106–109) [43]
Ε	<i>p</i> -Me-C ₆ H ₅ -	Me N=N	30	85	155–157 (158–160) [43]
F	<i>p</i> -Br-C ₆ H ₅ -	Br N=N	25	84	117–121 (115–118) [43]
G	C ₆ H ₅ CH ₂ Cl	N=N N N	25	80	126–129 (128–130) [45]

^arefer to pure and isolated products

role, preventing the conversion of required Cu(I) into Cu(II) cation. Initially, a terminal alkyne is converted to the corresponding copper acetylide (step A). In the next step, the σ -bond copper acetylide bearing a π -bond copper coordinates to the azide (**B**₁) in which the six-membered copper metallacycle is formed (**B**₂). Then, six-membered copper metallacycleis subjected to ring contraction to generate a triazolyl-copper derivative (**B**₃) that is followed by protonolysis, thus delivers the triazole product and terminates the catalytic cycle (**C**).

The new catalyst was applied to a model click reaction involving the click reaction to give 5a (Table 1). For optimization of the reaction conditions initially, different

solvents were examined (Table 2). As it can be realized water as the greenest and inexpensive solvent can be used as solvent of choice. The optimum amount this new catalyst was tested in the model reaction (Figure 1). Figure1 shows that among various amount of catalyst (0.005 g– 0.05 g), the best amount is (0.03 g). We also demonstrated that by increasing in the catalyst amount from 0.03 g to 0.04 g and 0.05 g, the time and yield of reaction does not change considerably and so we can claim that the optimum value of catalyst is 0.03 g.

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Thus, catalyst **4** was successfully catalyzed the model reaction to give the corresponding 1,4-disubstituted 1,2,3,3-triazoles, regioselectively.







 $R^1 = Ph$

 $R^2 = CH_2COPh$

Entry	Solvent	Condition	Time (min)	Yield (%)
1	Ethanol	Reflux	25	72
2	Water	Reflux	20	78
3	Ethanol/ Water	Reflux	20	80
4	CH_2Cl_2	Reflux	55	62
5	CH ₃ CN	Reflux	60	70



FIGURE 1 The optimum amount of the CuI/SMI-TD nanocatalyst in the synthesis of 5a in water

2.8 | Reusability of nanocatalyst

In the preparation of new heterogeneous catalyst, the important factor is reusability. The recovered novel catalyst **4** was reused in model reaction under optimized conditions for five consecutive runs to afford **5a** with reasonable yields (Table 1). After each usage, the catalyst was washed with acetone, filtered and dried at 70 °C and then reused again. It clearly showed that the catalyst worked effectively for at least 5 times without any appreciable loss of activity (Figure 2).



FIGURE 2 The reusability of CuI/SMI-TD nanocatalyst

Furthermore, we examined whether copper was being leached out from the solid support to the solution. For this purpose, the model reaction was conducted using wellcharacterized immobilized CuI NPs (CuI/SMI-TD complex). A typical hot filtration test^[45] was performed in the model reaction to investigate whether the reaction proceeded in a heterogeneous or a homogeneous fashion. For the rigorous proof of heterogeneity, a test was conducted by filtering of the catalyst from the reaction mixture at 100 °C after 1.5 h. Then, the filtrate was further allowed to react to the completion (3 h). In this case, no change in conversion was observed. This observation suggests that the catalyst is heterogeneous in nature. No evidence for leaching of copper or decomposition of the complex catalyst was observed during the catalytic reaction. It was noticed that after filtration of the catalyst from the reactor at the reaction temperature, our model click reaction did not proceed further. Thus, the results of the hot filtration test suggested that Cu was not being leached out from the solid catalyst during the click reactions. Therefore, the present catalyst can be considered heterogeneous in nature and can be contemplated as a good candidate for commercial applications.

3 | RESULTS AND DISCUSSION

3.1 | Preparation and characterization of the catalyst

Due to the high reactivity of cyclic anhydride moiety in the SMA, it was considered as an ideal and attractive polymeric support in organic synthesis.^[21-26] In continuation of our previous work using modified SMA polymer for the immobilization of metal nanoparticles and their applications in multicomponent reactions.^[31] Initially, SMA was reacted with 4-amino-2-methyl-10H-thiene [2,3-b][1,5]-benzodiazepine (ATD) hydrochloride as a cyclic imidization to obtain the corresponding modified polymer SMI-TD. Successful cyclic imidization of SMA (a) with ATD (b) under optimized reaction conditions were confirmed by FT-IR spectroscopy. FT-IR spectrum clearly showed that maleic anhydride moiety in SMA was converted into the corresponding maleimide ring by nucleophilic attack of NH₂ group of ATD to SMA. In Figure 3, the spectra of pure SMA (a), ATD (b) and SMI-TD product (c) were illustrated. As shown in IR spectrum of pure SMA in Figure 3(a), a typical doublet of anhydride units can be observed at 1848 and 1772 cm⁻¹. The FT-IR data for pure amine (Figure 3b) shows two peaks clearly at 3299 and 3114 cm⁻¹ attributed to primary N-H stretching. After the reaction of SMA with amine a new imide band at 1716-1783 cm⁻¹ appeared in the prepared SMI-TD and no band at 3300-3500 cm⁻¹ for amino groups was observed. These results indicated the completion of imidization of SMA by ATD to afford the desired product SMI-TD.

NMR data was found very useful for the characterization of the modified polymer. The 1 H NMR data for SMA and



FIGURE 3 FT-IR spectra of a) SMA, b) ATD, c) SMI-TD

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ATD were reported previously,^[38,46] as follows; SMA: [1.10 (m, 2H), 1.90 (s, 1H), 2.20 (s, 3H), 2.60 (s, 1H), 2.80 (m, 1H), 6.30–7.7 (9H, Ar-H), 7.9 (s, 1H), 9.3 (s, 1H). ATD: 2.25 [s, 3H, CH₃ attached to thiophenemoiety], 6.82 (s, 1H, CH), 6.87–6.99 (m, 4H, (Ar-H), 2.5 (s, 2H, NH₂). In the ¹H NMR spectrum of prepared SMI-TD (Figure 4), a symmetric pseudo quartet peak assigned to the N–H protons of the seven membered rings is observed at around 9.3 ppm. The absence of NH₂ protons of ATD at 2.5 is consistent with the fruitful attachment of ATD to SMA resulting in the preparation of desired polymeric support.

In spite of relative insolubility of nanocatalyst in most organic solvents, TEM, SEM, EDAX, Map image and ICP-AES analysis were recorded. The scanning electron micrographs of the CuI/SMI-TD catalyst (Figure 5a) clearly show that the CuI NPs were homogeneously immobilized on the SMI-TD surface. Furthermore, the TEM image (Figure 6a) clearly showed CuI NPs as spherical shape and the size of particles is around 30-60 nm. That proved that CuI particles in our catalyst are actually nanosized. These results are supported by SEM data. The area distribution image (Figure 6b) showed that the copper NPs were homogeneously immobilized on the surface of the polymer.

As shown, the CuI NPs practically were immobilized onto SMI-TD surface uniformly, providing an ideal and effective nanocatalyst with high area for being applied in catalyzed organic reactions.

Energy dispersive spectroscopy analysis of X-rays (EDAX) data for the CuI/SMI-TD nanocatalyst was illustrated in Figure 7. The EDAXs confirms that polymer matrix is containing CuI NPs onto surface. This data along with other results such as SEM and FT-IR approve the attachment of CuI NPs onto SMI-TD.

It should be noticed that we used commercial CuI in this process and finally produced CuI NPs as spherical shape with the size of particles around 30–60 nm that were characterized by SEM, TEM and FT-IR analysis. This synthetic feature confirmed the experimental preference of in situ preparation methods to the conventional procedures.

Based on our obtained experimental results, we can claim that CuI/SMI-TD nanocatalyst can be synthesized via in situ preparation method and can be used as a heterogeneous catalyst with high catalytic activity in the regioselective synthesis of 1,4-disubstituted 1,2,3-triazoles under green and mild conditions. Furthermore, we demonstrated that low amount of catalyst is required (about 0.03 gr) and it is recoverable through simple filtration process and can be reused for five runs with no considerable loss of catalytic activity.

3.2 | Computational section

In this section, we have assessed computationally the immobilization behavior of copper metal ions on SMA modified by



FIGURE 4 The NMR Spectrum of SMI-TD pre-catalyst



FIGURE 5 The SEM images of the CuI/SMI-TD nanocatalyst

ATD as an amino agent with several coordinating sites, using DFT^[35] and QTAIM^[36,37] computations. Strictly speaking, we investigated the metal–ligand interactions on the different active coordinating sites of CuI/SMI-TD complex via topological analysis of electron density functions.

In this respect, initially we designed an effective model for modified SMA ligand and three effective models for CuI/SMI-TD complex with different active coordinating sites hereafter denoted as Cu-N complex, Cu-NH complex and Cu-S complex (as were illustrated in Scheme 5). It should be noted that these models have a reliable compromise between accuracy and time saving efficiency of computational procedure.

In the first step, we have determined the optimized structure of ligand and complexes at M06/6-31G* level of theory. It should be mentioned that M06 functional^[47] has been introduced as a hybrid meta-GGA (generalized gradient approximation) exchange-correlation functional that was recommended for use in organometallic and inorganometallic thermochemistry, kinetic studies and noncovalent interactions. In the case of iodine, the effective core potential (ECP), LANL2TZ (f), was used together with the accompanying basis set to describe the valence electron density.^[48] All stationary points were determined as minima after verifying the presence of all real frequencies. The GAMESS suite of programs^[49] has been applied in DFT calculations.

In Figure 8, we have presented the theoretical optimized structures of SMI-TD ligand, Cu-N complex, Cu-NH complex and Cu-S complex obtained at M06/6-31G* level of theory.



FIGURE 6 The TEM images of the copper nanoparticle (6a–TEM image) and distribution image of cu NPs on polymer support (6b–distribution area spot)



FIGURE 7 EDAXs data of CuI/SMI-TD nanocatalyst



SCHEME 5 Schematic representation of three coordinating modes in polymer-supported copper catalyst

We have also evaluated comparatively the bond order of some selected key bonds in modified SMA ligand with its corresponding CuI/SMI-TD complexes to characterize the variation of bond orders via complexation. In Table 3, we have listed M06/6-31G* calculated bond orders of some selected chemical bonds in the coordination sphere of Cu-N complex, Cu-NH complex and Cu-S complex, respectively. The reported results of Table 3 show that the bond order of C-N and C-S in



FIGURE 8 Atomic numbering and energy-minimized structures obtained at M06/6-31G*level of theory for SMI-TD ligand, cu-N complex, cu-NH complex and cu-S complex

TABLE 3 The calculated values of some selected bond orders in SMI-TD ligand, cu-N complex, cu-NH complex and cu-S complex obtained at M06/6-31G* level of theory. Note that the numbering of atoms for ligand and complex is in accordance with Figure 7

	free ligand	Complex
bonded atoms		
Cu-N complex		
C1-O	1.838	1.338
N1-C2	1.736	1.377
N1-C3	0.988	0.856
Cu-NH complex		
N2-C4	0.858	0.744
N2-C5	1.007	0.856
N2-H1	0.819	0.760
Cu-S complex		
S-C5	1.077	0.902
S-C6	1.039	0.899

4-amino-2-methyl-10 h-thiene^{[2,3-b][1,5]} benzodiazepine moiety (ATD) and carbonyl group of SMA shifted toward lower values due to the donation of shared electrons from these chemical bond to copper through the complexation which is in confirmation with our FT-IR spectroscopic observations.

In order to obtain more accurate information about the nature of bonding and interactions, in the next step, we concentrated on topological study of electron density via QTAIM approach^[35,36] and interpret the nature of metal–ligand interactions in CuI/SMI-TD complexes. In this respect, the calculated wave functions of electron density have been employed to investigate the variation of some electronic features of key bonds along complexation reaction by performing AIM2000 program package.^[50]

In Tables 4–6, we have listed M06/6-311G** calculated values of electron density, ρ_b , its Laplacian, $\nabla^2 \rho_b$, electronic kinetic energy density, V_b , electronic potential energy density, G_b , total electronic energy density, H_b and $|V_b|/G_b$ ratio in Cu-N complex, Cu-NH complex and Cu-S complex, respectively, at some selected bond critical points (BCPs) that have an important role in the coordination sphere.

It should be stated that the electron density at BCPs could be attributed to the strength of bond between two atoms. The large positive values of ρ_b with the negative values of $\nabla^2 \rho_b$ are indicative of covalent interaction while for an electrostatic interaction, ρ_b has the small values with the positive values of $\nabla^2 \rho_b$. Furthermore, a reliable indicator for description of interatomic interactions is the total electronic energy density, that is defined as V_b + $G_b = H_b$ at BCPs. In the closed-shell interactions, H_b has the positive value and for shared interactions, it is negative.^[51–53] In Figure 8, we have displayed QTAIM molecular graphs of SMI-TD ligand, Cu-N complex, Cu-NH complex and Cu-S complex, including all bond and ring critical points and their associated bond paths.

TABLE 4 Mathematical properties of some selected BCPs in cu-N

 complex. The properties have been obtained via QTAIM analysis on the

 M06/6-311G** calculated wave function of electron density. Note that

 numbering of atoms is in accordance with Figure 8

	$ ho_b$	$\nabla^2 \rho_b$	G _b	$\mathbf{V}_{\mathbf{b}}$	$\mathbf{H}_{\mathbf{b}}$	$ \mathbf{V}_b /\mathbf{G}_b$
Cu-I BCP	0.059	0.091	0.042	-0.061	-0.019	1.452
Cu-C1 BCP	0.143	0.043	0.121	-0.231	-0.110	1.909
Cu-H2 BCP	0.020	0.092	0.020	-0.018	0.002	0.900
Cu-N1 BCP	0.137	0.518	0.202	-0.276	-0.074	1.366
C3-N1 BCP	0.285	-0.855	0.159	-0.532	-0.373	3.345
C2-N1 BCP	0.356	-1.102	0.303	-0.882	-0.579	2.910

TABLE 5 The same as Table 4, for Cu-NH complex

	$ ho_b$	$\nabla^2 \rho_b$	G _b	$\mathbf{V}_{\mathbf{b}}$	$\mathbf{H}_{\mathbf{b}}$	$ V_b /G_b$
Cu-I BCP	0.078	0.058	0.050	-0.087	-0.037	1.740
Cu-H4 BCP	0.023	0.099	0.022	-0.020	0.002	0.909
Cu-N2 BCP	0.116	0.457	0.169	-0.224	-0.055	1.325
C4-N2 BCP	0.256	-0.693	0.120	-0.415	-0.295	3.458
C5-N2 BCP	0.276	-0.805	0.131	-0.464	-0.333	3.541
H1-N2 BCP	0.319	-1.566	0.146	-0.483	-0.437	3.308

TABLE 6 The same as Table 4, for Cu-S complex

	$ ho_b$	$\nabla^2 \rho_b$	G _b	$\mathbf{V}_{\mathbf{b}}$	$\mathbf{H}_{\mathbf{b}}$	$ V_b /G_b$
n	0.079	0.061	0.052	-0.090	-0.038	1.730
Cu-S BCP	0.097	0.164	0.094	-0.148	-0.054	1.574
C5-S BCP	0.170	-0.232	0.050	-0.159	-0.109	3.180
C6-S BCP	0.172	-0.238	0.050	-0.161	-0.111	3.220



FIGURE 9 Complete molecular graphs (MGs) of SMI-TD ligand and cu-N complex, cu-NH complex and cu-S complex calculated by QTAIM analysis of M06/6-311G**electron density functions. Bond critical points: Green circles; ring critical points: Red circles; bond paths: Gray lines

The following facts can be extracted from the comparative survey of reported results in Tables 4-6, i) the large positive values of electron density in association with the negative values of $\nabla^2 \rho_b$ and H_b and also $|V_b|/G_b > 2$ values on C = O and C - N and C-S BCPs confirms the covalent character of these chemical bonds in SMI-TD ligand, Cu-N complex, Cu-NH complex and Cu-S complex. While at Cu-N, Cu-O and Cu-S BCPs, the small values of electron density with the positive values of $\nabla^2 \rho_b$ and small negative values of H_b and also $1 < |V_b|/G_b < 2$ calculated values demonstrate the semi covalent-electrostatic character for these interactions,^[52,53] ii) the calculated values of ρ_h at C = O and C - N and C-S BCPs (that have decrease through the complexation that proves the donation of shared electrons to the metal center and iii) comparison of the calculated electron density values of Cu-N and Cu-S BCPs in Cu-N complex, Cu-NH complex and Cu-S complex demonstrate that interaction of copper cation with nitrogen in Cu-N complex is stronger than interaction of Cu(I) ion with N and S in Cu-NH complex and Cu-S complex, respectively (0.137 for ρ_b calculated value on Cu-N BCP of Cu-N complex in comparison with 0.116 and 0.097 for ρ_b calculated values on Cu-N and Cu-S BCPs of Cu-NH complex and Cu-S complex, respectively.

Moreover, a more precise survey of QTAIM molecular graphs of Cu-N complex, Cu-NH complex and Cu-S complex in the coordination region demonstrate that there exist Cu-C, Cu-H and I-H BCPs in Cu-N complex. This electronic feature of Cu-N complex leads to the formation of three ring critical points and consequently stabilization of the complexation process (which were denoted as RCP1, RCP2 and RCP3, in Figure 9). It is worthwhile to notice that in topological analysis of the coordination sphere of Cu-NH complex and Cu-S complex, we can see only one ring critical point due to the existence of Cu-H and I-H BCPs in Cu-NH complex and Cu-S complex, respectively. In overall, on the basis of the bond order analysis and QTAIM calculated results we can predict that CuI NPs immobilize effectively on nitrogen site of polymer-supported catalyst.

4 | **CONCLUSION**

An organic–inorganic hybrid CuI/SMI-TD nanocatalyst was prepared in situ by an efficient, simple and inexpensive method. We studied the modification of SMA with ATD as a bigger base with more active sites than we had previously reported. Although ATD occupies more space in polymer chain, its more active sites resulted in multi- coordination with Cu(I) in comparison with common aromatics and heterocyclic amines.

We also investigated computationally the nature of interactions between copper metal ions with SMI-TD ligand in several CuI/SMI-TD complex models. In this line, we determined the mathematical properties of electron density functions via DFT and QTAIM approaches. Based on the stringent analysis of calculated values for QTAIM electronic indicators on BCPs and RCPs, we demonstrated that the interaction of copper cation with nitrogen atom in Cu-N complex is stronger than the interaction of Cu(I) ion with N and S atoms in Cu-NH complex and Cu-S complex, respectively, thus predicted that Cu NPs immobilize mainly on nitrogen site of polymer-supported catalysts. Furthermore, the analysis of our calculated bond orders and QTAIM results confirms reliably of IR spectroscopic data.

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