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1. Introduction

In the recent past, the use of magnetic nanoparticles (MNPs) in various applications has attracted extensive attention from the scientific community. They have found applications in the fields of technology, catalysis, medical science, environmental remediation *etc.*^{1,2} In particular, MNP supported catalysts have been widely employed as catalysts for various organic reactions.^{3–5} The ease of recovery of the catalysts by simple magnetic separation is the major advantage of these MNPs. This can solve the problems associated with isolation and reusability that are faced in many catalyst promoted transformations.^{1,3–5} Another important feature of the MNP-supported catalysts is their high catalytic activity due to their high surface-to-volume ratio and high degree of stability in both aqueous and organic media.⁶

The amide bond is the basic structural framework of many natural polymers, bioactive molecules, proteins, fine chemicals and drugs.^{7,8} *N*-Heteroaryl amides in general and *N*-(pyridin-2-yl) benzamide in particular are important building blocks for many bioactive molecules.^{9–11} They have wide application in

Cul incorporated cobalt ferrite nanoparticles as a magnetically separable catalyst for oxidative amidation reaction[†]

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A Cu-incorporated magnetic nanocatalyst (CoFe₂O₄@SiO₂-SH-Cul) has been developed by immobilizing Cul on the modified surface of CoFe₂O₄ magnetic nanoparticles. The surface of the silica coated cobalt ferrite magnetic core was first treated with 3-mercaptopropyl triethoxysilane to produce the thiol functionalized nanoparticle CoFe₂O₄@SiO₂-SH. Further treatment of the nanoparticle with Cul produced the desired magnetic nanocatalyst. The versatility of the catalyst has been demonstrated for the synthesis of *N*-(pyridin-2-yl) benzamide *via* oxidative amidation of aryl aldehydes with 2-amino pyridine in the presence of an oxidant. The reaction was carried out in DMSO at 80 °C using TBHP (70% aqueous) in the presence of 20 wt% of the catalyst. Notably, the catalyst could be separated from the reaction mixture in the presence of an external magnetic field. During the study, a new compound *N*-(pyridin-2-yl)anthracene-2-carboxamide has been synthesized and its turn on fluorescence sensing properties towards various metal ions have been studied. Fluorescence experiments and theoretical studies indicated that the newly synthesized carboxamide molecule can be used for fluorescence sensing of the Hg²⁺ ion in aqueous solution.

the treatment of osteoporosis^{12,13} and possess antiulcer^{14,15} and tumor growth inhibition properties.¹⁶ Development of new methods for obtaining this particular functionality has received extensive attention recently because of its wide-scale application in various fields.^{17,18}

Traditional methods for the synthesis of *N*-heteroaryl amides involve the reaction of activated carboxylic acid with amine derivatives.¹⁹ There are several limitations associated with these methods. To overcome those limitations alternative synthetic pathways have been developed which include classical named reactions such as Staudinger,^{20–22} Ritter,²³ and Beckmann^{24,25} and hydrative coupling reactions of alkynes and azides.^{26,27} A few other synthetic pathways using aldehydes, alcohols, alkynes and amines have also been found in the literature for the synthesis of amides.²⁸ Among them, organic chemists have focused more on the oxidative amidation of aldehydes and amines in the presence of transition metal catalysts. Cu, Rh, Ru, La, Pd, Ni, Au, Fe *etc.* are a few transition metals the complexes of which along with an extra oxidant have been utilized for this amidation reaction.²⁹

Maheswari *et al.* reported a metal free approach for oxidative amidation of aldehydes and alcohols for the synthesis of *N*-(pyridin-2-yl)benzamide.³⁰ Li and co-workers initially reported the reaction of aldehydes and aliphatic aminehydrochlorides using CuI as the catalyst and *tert*-butyl hydroperoxide (70% aqueous) as the oxidant in the presence of AgIO₃ and CaCO₃.³¹ Later, a modified version of Li's work was

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reported by Chen for the synthesis of primary, secondary and tertiary amides from aldehydes and amine hydrochloride salts using copper sulfate and copper oxide as catalysts.³² Thereafter, various other catalytic systems have been reported for this particular transformation, which include the use of heteropolyanion-based ionic liquids under microwave-promoted conditions,³³ CuI/TBHP,³⁴ CuI/air,²⁹ Rh(m)/Ag₂CO₃,³⁵ and Cu(OTf)₂/I₂-SDS.³⁶ Some of these protocols have some limitations such as use of toxic and expensive metal reagents and oxidants and narrow substrate scope and are usually non-recyclable. Therefore, there is a necessity for easy and efficient catalytic processes for the synthesis of amides.

Although several homogeneous Cu-based catalysts have been reported, the use of recyclable catalysts for oxidative amidation has received scant attention, with a few methods outlined.³⁷ There are only a few reports available in the literature on the use of heterogeneous catalyst for oxidative amidation of aldehydes using 2-aminopyridine. For example, the use of Cu₂O/MWCNTs and CuI/MWCNTs as heterogeneous catalysts has been reported by Kathyayini.37a Rostamnia and co-workers reported the use of graphene oxide supported Pd-nanoparticles for oxidative amidation of aldehydes in the presence of H₂O₂ as the oxidant.^{37b} Heteropolyanion-based ionic liquids have been found to be active catalysts under microwave irradiation for oxidative amidation reaction in the presence of TBHP as the oxidant.³³ Literature search revealed that there is no report on the use of magnetic nanoparticle derived catalysts for such transformations. Hence, magnetic nanoparticles functionalized with different spacer groups and loaded with metals may be an important substitute.^{1,38} In continuation of our work on functionalized magnetic nanoparticles,39-46 we wish to report a new magnetically recoverable copper iodide catalyst supported over thiol functionalized cobalt ferrite nanoparticles for oxidative amidation of aldehydes and 2-amino pyridines. During the course of our investigation, we synthesized a new compound N-(pyridin-2-yl) anthracene-9-carboxamide which is useful for turn on selective fluorescence sensing of the Hg²⁺ ion in solution.

2. Materials and methods

2.1. Preparation of the $CoFe_2O_4$ (a) SiO₂-3-mercaptopropyl-siloxane CuI composite

The CoFe₂O₄@SiO₂-3-mercaptopropylsiloxane CuI composite catalyst was synthesized following a four-step sequential procedure. Initially the co-precipitation method was followed for the synthesis of cobalt ferrite under constant ultrasonic irradiation conditions.^{39,40}

Bare cobalt ferrite MNPs are very unstable and often get agglomerated. To prevent cobalt ferrite MNPs from agglomeration, a coating of silica using tetraethyl orthosilicate (TEOS) was applied over the nanoparticles to form a stable $CoFe_2O_4$ @SiO₂ nanocomposite.⁴¹ For silica coating, 200 mg of cobalt ferrite MNPs was dispersed in water under ultrasound irradiation (53 kHz) for 1 h using an ultrasonicator bath. To this dispersion, 8 mL of aqueous ammonia solution (25 wt%) and 100 mL of ethanol were added sequentially and sonicated for another 1 h (during ultrasound irradiation, the temperature of the bath gradually increases from room temperature to 60 °C). Thereafter, 1.0 mL of tetraethyl orthosilicate (TEOS) was added dropwise to this mixture under continuous ultrasonication. Ultrasonication was continued with the reaction mixture for 5 h, followed by vigorous stirring (using a magnetic stirrer) at room temperature for 24 h. The resulting reaction mixture was centrifuged and washed several times with water and ethanol. Finally, it was dried in an oven at 50 °C for 6 h to yield the desired CoFe₂O₄@SiO₂ nanocomposite (yield: 1.035 g).

In the next step, we modified the surface of the $CoFe_2O_4(@SiO_2 nanocomposite by incorporating a linker with a thiol end functionality. Thus, the thiol-functionalized cobalt ferrite silica composite was prepared by refluxing 250 mg of the <math>CoFe_2O_4(@SiO_2 nanocomposite with 2 mmol 3-mercapto-propyl triethoxysilane (MPTES) (M. Wt: 238.42 g mol⁻¹, density: 0.987 g mL⁻¹) in the ethanol–water mixture in a ratio of 1:1 for 5 h. The products were separated by centrifugation, washed 3 times with 20 mL of water, and dried overnight in the oven at 60 °C to obtain 410 mg of the thiol functionalized cobalt ferrite silica nanocomposite (CoFe_2O_4@SiO_2-SH).⁴⁷$

The last step of catalyst synthesis involves the binding of the active metal species with the thiol end-group. To accomplish this, a solution of CuI (95 mg, 0.5 mmol) in acetone (20 mL) was prepared by ultrasonic irradiation (30 min), 200 mg of the $CoFe_2O_4$ @SiO₂-SH nanocomposite was added under continuous ultrasonication and finally the mixture was kept under ultrasonic irradiation for 30 min. The mixture was stirred at room temperature for 6 h. The final product (the $CoFe_2O_4$ @SiO₂-SH-CuI nanocomposite) was separated by centrifugation, washed with water followed by acetone and dried overnight in the oven at 60 °C (yield: 235 mg).

2.2. Characterization

The synthesized CoFe2O4@SiO2-SH-CuI nanocomposite was characterized using various analytical techniques. The FT-IR spectra (using Affinity-1 SHIMADZU) of CoFe2O4@SiO2-SH-CuI samples were recorded in the form of KBr pellets in the mid IR-region of 4000–500 cm^{-1} with a resolution of 4 cm^{-1} . Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku X-ray diffractometer with Cu-Ka radiation at a wavelength of 1.5418 Å operated at a voltage of 40 kV and a current of 30 mA. FESEM and EDX analyses were performed using a ZEISS Sigma 300 scanning electron microscope equipped with an energy dispersive X-ray spectrometer (EDX). For FESEM analysis, the nanoparticles were affixed uniformly over the aluminium stub and then mounted in the instrument. TEM analyses were performed using a JEOL JEM-2100 electron microscope. For TEM analysis, the sample was first dispersed in ethanol and a drop of dilute ethanolic dispersion of the particles was added on the copper grid and then dried in an oven. The thermogravimetric analysis (TGA) of copper incorporated magnetic samples was performed on a Mettler Toledo TGA/

DSC 1, STAR system analyzer in the temperature range of 300 K–1023 K at a heating rate of 10 K min⁻¹ in a nitrogen gas atmosphere. The magnetic properties of the functionalized $CoFe_2O_4$ *i.e.* $CoFe_2O_4$ @SiO₂-SH-CuI nanoparticles were determined using a vibrating sample magnetometer (Lakeshore 7410). The samples were analysed at room temperature by fixing 35 mg of the solid sample to the tip of the vibrating rod.

The PXRD pattern confirmed the coating of silica over cobalt ferrite. The surface functionalization over cobalt ferrite with propyl and thiol moieties was confirmed using IR spectroscopy. FESEM and energy dispersive X-ray (EDX) analyses were performed to determine the morphology and the composition of various elements present in the nanocomposite. TEM analysis was carried out to determine the particle size of the composite. In addition to the use of these characterization techniques, the thermal stability and magnetic properties of the nanocomposite were determined using thermogravimetric analysis (TGA) and vibrating sample magnetometer (VSM) analysis.

The products obtained from amidation reaction were characterized using ¹H and ¹³C-NMR spectroscopy (using a Bruker 300 MHz instrument). For fluorescence sensing experiments, UV-Vis spectroscopy and fluorescence spectroscopy were carried out on a Shimadzu UV 1800 spectrophotometer and a Hitachi F-7000 fluorescence spectrophotometer.

Single crystal X-ray diffraction data were collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromator and a Mo K α fine-focus sealed tube ($\lambda = 0.71073$ Å). The crystallographic cif file of the new compound was deposited with the CCDC 1941942.†

2.3. General procedure for the amidation reaction

In a typical reaction, aldehyde (1.2 mmol), 2-amino pyridine (1 mmol), catalyst (20 wt%), and TBHP (70% aqueous, 2 mmol) were mixed in DMSO (2 mL) in a 10 mL Schlenk tube. The reaction mixture was tightly capped and subjected to continuous stirring at 80 °C for 12 h. After completion of the reaction (monitored by TLC), the catalyst was separated using an external magnet and the reaction mixture was taken in ethyl acetate. The organic layer was washed using brine solution and dried over sodium sulfate. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography using 230–400 silica mesh with 15% ethyl acetate and petroleum ether as the eluent to obtain the desired product.

Experimental data for the new compound. *N*-(Pyridin-2-yl) anthracene-9-carboxamide (3l): Light yellow crystals, m.p. 117–119 °C; ¹H NMR (300 MHz, CDCl₃) δ : 9.88 (s, 1H), 8.54 (d, 2H, 6 Hz), 8.13 (d, 2H, 8.1 Hz), 8.03 (d, 8.1 Hz, 2H), 7.71–7.65 (m, 1H), 7.57–7.47 (m, 4H), 7.21 (d, 4.2 Hz, 1H), 6.78–6.74 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ : 168.4, 151.4, 147.2, 138.4, 130.9, 128.7, 128.5, 127.9, 127.2, 126.9, 125.6, 124.7, 119.8, 114.3; HRMS (ES) *m/z* calculated for C₂₀H₁₅N₂O [M + H] 299.1184; found: 299.1188.

2.4. General procedure for UV and fluorescence measurements

Various metal salts used in fluorescence titrations were in the form of sulphates (Cu, Cd, and Mg), chlorides (Fe, Ni, Hg, Al, and Ca) and nitrates (Ag and Pb). All the metal solutions $(Ag^+, Al^{3+}, Ca^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Cd^{2+}, Ni^{2+} and Pb^{2+})$ and compound **3** were prepared in acetonitrile and water (1 : 1 v/v). The stock solutions were prepared with 1×10^{-3} M concentration. All the experiments were performed at room temperature. UV-vis spectra were recorded in the wavelength range of 200–500 nm and fluorescence was recorded at a fluorescence excitation wavelength of 320 nm. For fluorescence titration a solution of the compound in CH₃CN-H₂O (v/v, 1:1) (200 µL) was taken in a quartz cell and 2 µL of metal solution was added for each measurement into the quartz cell $(0-9.9 \times 10^{-3} \text{ M})$ by using a micropipette.

2.5. DFT calculations

The structure of the compound *N*-(pyridin-2-yl) anthracene-9carboxamide was optimized using density functional calculations with the Gaussian 09 series of programs.⁴⁸ The B3LYP formulation^{49,50} of density functional theory (DFT) was applied using the LANL2DZ basis set.

Results and discussion

3.1. Synthesis of the catalyst and characterization

The synthetic steps for the preparation of the $CoFe_2O_4$ ($@SiO_2$ -SH-CuI magnetic nanocatalyst are shown in Scheme 1. Cobalt ferrite NPs used as the magnetic core were synthesized by following a reported procedure, *via* the co-precipitation method.^{39,40} To impart stability and prevent agglomeration, the cobalt ferrite magnetic core was coated with TEOS and subsequently surface functionalized with MPTES. Finally, copper iodide was immobilized onto the thiol functionalized cobalt ferrite to yield the desired $CoFe_2O_4$ ($@SiO_2$ -SH-CuI nano-composite catalyst. The synthesized catalyst was characterized using various characterization techniques such as FT-IR, XRD, FE-SEM, EDX, TEM, TGA and VSM analysis.



Scheme 1 Synthesis of the CoFe₂O₄@SiO₂-SH-Cul nanocomposite.



Fig. 1 The IR spectra of the CoFe₂O₄@SiO₂-SH-Cul nanocatalyst.

Fig. 1 shows the FT-IR spectrum of the $CoFe_2O_4$ ($@SiO_2$ -SH-CuI nanocomposite. The IR spectrum exhibits a strong peak at 594 cm⁻¹ and a broad band at around 3300–3500 cm⁻¹ which are due to the stretching vibration of the Fe–O bond and the O–H bond, respectively. Other peaks at about 1095 cm⁻¹, 1550 cm⁻¹, 2426 cm⁻¹ and 2980 cm⁻¹ correspond to Si–O–Si stretching, O–H stretching of adsorbed water, and the S–H and C–H bond stretching of the mercapto and propyl groups of MPTES respectively.^{51–53} These data indicate the presence of the mercapto propyl group on the surface of cobalt ferrite nanoparticles.

Fig. 2 displays the XRD pattern of the $CoFe_2O_4$ ($3SiO_2$ -SH-CuI nanocomposite, which indicates the crystalline nature of the synthesized composite. Peaks at 2-theta 25.6°, 50.1°, 52.5°,67.5°, 69.5° and 77.3° represent the characteristic peaks of cubic CuI and other peaks at 2 theta 29.6°, 35.75°, 42.3° and 61.3° resemble the characteristics peaks of cobalt ferrite nanoparticles. This indicates the successful incorporation of CuI over cobalt ferrite.⁵⁴ The average particle size of CoFe₂O₄ ($3SiO_2$ -SH-CuI was found to be 49.10 nm, based on the Debye–Scherrer formula.

The structure and morphology of the synthesized nanocomposite were studied by SEM analysis. The SEM image of the sample is presented in Fig. 3. The SEM image reveals that the particles are of uniform size with spherical morphology. Fig. 4 shows the EDX (Energy Dispersive X-ray) spectrum of the



Fig. 2 The XRD pattern of CoFe₂O₄@SiO₂-SH-Cul MNPs.

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Fig. 3 The SEM image of CoFe₂O₄@SiO₂-SH-Cul MNPs.



Fig. 4 The EDX image of CoFe₂O₄@SiO₂-SH-Cul MNPs.

Table 1 Elemental composition

Element	Weight%	Atomic%
СК	25.13	43.17
O K	28.31	36.50
Si K	15.47	11.36
S K	1.65	1.06
IL	12.75	2.07
Fe K	7.13	2.63
Co K	3.64	1.28
Cu K	5.93	1.92

 $CoFe_2O_4$ (BSiO₂-SH-CuI nanocomposite. Table 1 shows the distribution of various elements obtained from EDX analysis of the synthesized product. From the table, the iron/cobalt ratio in the nanoparticles determined by EDX was found to be 2.05% which is very close to the atomic ratio in the formula $CoFe_2O_4$ with 1.92 atomic% of copper incorporation.

The presence of various elements in the nanocomposite determined by FESEM-EDX was further confirmed using EDX elemental mapping. Fig. 5 shows the elemental mapping and the results confirm the presence of C, O, Si, S, Fe, Co, Cu and I in the CoFe₂O₄(@SiO₂-SH-CuI nanocomposite.

Fig. 6 displays the TEM images of the synthesized $CoFe_2O_4$ and $CoFe_2O_4$ @SiO₂-SH-CuI nanocomposite. TEM images reveal the uniform coating of silica and the spacer group (thiol) over the cobalt ferrite MNPs. Thus, uniform coating of the thiol group is accountable for the effective binding of copper iodide nanoparticles. The images indicate that the par-

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Fig. 5 Energy dispersive X-Ray (EDX) mapping analysis of CoFe $_2O_4@SiO_2\mbox{-SH-Cul MNPs}.$

ticles were nearly spherical in shape and most of the particles are in the range of 15–20 nm. Fig. 6(c) shows the HRTEM image of $CoFe_2O_4$ @SiO₂-SH-CuI MNPs. From the HRTEM image, the interplanar distance was found to be 0.31 nm which corresponds to the spinel phase of the polycrystalline nanoparticles. Various concentric rings in the SAED pattern indicate the crystalline nature of the synthesized composite.

The target $CoFe_2O_4$ (a) SiO₂-SH-CuI nanocomposite was synthesized in four consecutive steps and in each step, the nanocomposite was isolated before proceeding to the next step.

Patterns resulting from thermogravimetric analysis (TGA) of each intermediate nanocomposite *i.e.*, CoFe₂O₄, CoFe₂O₄@SiO₂ and CoFe₂O₄@SiO₂-SH along with the CuI incorporated composite catalyst are presented in Fig. 7. The TGA pattern shows that nanoparticles undergo an initial weight loss within 100 °C in all the four steps, which corresponds to the loss of moisture and volatile components in the sample. With the subsequent modification of the surface of cobalt ferrite, the weight loss percentage increases due to the decomposition of the various organic functional groups of TEOS and MPTES that were functionalized over the surface of



Fig. 6 TEM images of (a) cobalt ferrite and (b) CoFe₂O₄@SiO₂-SH-Cul MNPs. (c) The HRTEM image of CoFe₂O₄@SiO₂-SH-Cul MNPs. (d) The SAED pattern of CoFe₂O₄@SiO₂-SH-Cul MNPs.



Fig. 7 TGA plots of (a) $CoFe_2O_4$; (b) $CoFe_2O_4$ @SiO₂; (c) $CoFe_2O_4$ @SiO₂-SH; and (d) $CoFe_2O_4$ @SiO₂-SH-Cul MNPs.

cobalt ferrite. A further weight loss of 25.13% was observed in the last step above 450 °C for the $CoFe_2O_4$ @SiO₂-SH-CuI nanocomposite which is attributed to the crystallization process.^{51,52}

Fig. 8 shows the DTA curve of the synthesized $CoFe_2O_4(@SiO_2-SH-CuI nanocomposite.$ From the DTA curve three distinct exothermic and one endothermic peaks are observed. The endothermic peak at around 250 °C can be ascribed to the loss of water. The exothermic peaks at 340 °C, 400 °C and 450 °C may be due to the rearrangement of the crystal structure or the degradation of $CoFe_2O_4(@SiO_2-SH-CuI MNPs.$ Thus, the nanocomposite is thermally stable below 340 °C.⁵⁵



Fig. 8 The DTA curve of CoFe₂O₄@SiO₂-SH-Cul MNPs.



Fig. 9 The M-H loop in the VSM measurement of CoFe₂O₄@SiO₂-SH-Cul MNPs.

Table 2 Optimization of reaction condition
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Magnetic property measurements of the synthesized $CoFe_2O_4$ @SiO₂-SH-CuI nanocomposite were performed using the VSM measurement at room temperature in the range of ±1.5 T. Fig. 9 shows the *M*-*H* loop obtained at the maximum applied field. The magnetization curve of the $CoFe_2O_4$ @SiO₂-SH-CuI nanocomposite ascertains the ferromagnetic behaviour with coercivity (*H*_C) and saturation magnetization (*M*_S) values of 222 Oe and 1.9324 emu g⁻¹ respectively. Magnetization retention (*M*_r) of the nanomaterial was found to be 0.24875 emu g⁻¹.

Thus, the above analysis of the data clearly demonstrates that CuI species has been successfully loaded over the surface of thiol functionalized cobalt ferrite. These results explain that the synthesized material is magnetic and crystalline in nature with the size in the range 15–20 nm and the particles are thermally stable up to 300 $^{\circ}$ C.

3.2. Catalytic activity studies

The catalytic activity of the $CoFe_2O_4$ ($@SiO_2$ -SH-CuI magnetic nanoparticles was tested for the oxidative amidation reaction of benzaldehyde and 2-amino pyridine in the presence of an oxidant. In order to find the optimum conditions, the initial study was carried out by taking benzaldehyde and 2-amino pyridine as model substrates. The results are summarized in Table 2. The initial experiment using an equimolar amount of substrates (1 mmol each) in DMSO (2 mL) in the presence of 20 wt% of the catalyst did not yield any positive result after carrying out the reaction for 12 h at 100 °C (entry 1). However, the addition of 1 mmol *tert*-butyl hydroperoxide (TBHP, 70% aqueous) to the previous reaction mixture resulted in the formation of the desired *N*-(pyridin-2-yl)benzamide in 47% yield.

The column chromatographic technique was used for the isolation of the desired product. In order to improve the yield,

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Entry	Solvent	Catalyst (wt%)	Aldehyde (mmol)	Oxidant (mmol)	Time (h)	Temp. (°C)	Yield (%)
1	DMSO	20	1	No oxidant	12	100	NR
2	DMSO	20	1	TBHP (1)	12	100	47
3	DMSO	20	1	TBHP (2)	12	100	69
4	DMSO	20	1.2	TBHP (2)	12	100	89
5	DMF	20	1.2	TBHP (2)	12	100	63
7	Dioxane	20	1.2	TBHP (2)	12	100	54
9	MeCN	20	1.2	TBHP (2)	12	85	68
10	EtOAc	20	1.2	TBHP (2)	12	80	17
11	Toluene	20	1.2	TBHP (2)	12	80	28
12	Hexane	20	1.2	TBHP (2)	12	70	Trace
13	DMSO	20	1.2	$H_2O_2(2)$	12	100	72
14	DMSO	20	1.2	TBHP (2)	6	100	63
15	DMSO	20	1.2	TBHP (2)	12	80	87
16	DMSO	10	1.2	TBHP (2)	12	80	58
17	DMSO	No catalyst	1.2	TBHP (2)	24	100	NR
18	DMSO	$CoFe_2O_4(20)$	1.2	TBHP (2)	24	100	NR

Reaction conditions: 2-Amino pyridine (1 mmol), solvent (2 mL), oxidant, isolated yield.

a series of experiments were performed by changing the reaction conditions. Further reaction with the increase in the concentration of TBHP to 2 mmol could improve the reaction yield to 69%. The reaction performed with an equimolar amount of reactants yielded the desired product in a comparatively lower amount as the aldehyde source was totally consumed and the unreacted amine was left behind in the reaction. So the amount of aldehyde was increased to 1.2 mmol, which could improve the yield of the reaction to 89%. Thereafter, the reaction was examined using different solvents such as DMF, dioxane, acetonitrile, ethyl acetate, toluene and *n*-hexane. However, results were not found to be encouraging.

Hydrogen peroxide was found to be inferior to TBHP for this particular reaction (Table 2, entry 11). Lowering the temperature or the catalyst amount produced diminishing results. Moreover, a blank reaction under the optimized conditions without the catalyst was found to be ineffective. In order to examine the effect of CuI on the catalytic activity of the $CoFe_2O_4@SiO_2$ -SH-CuI MNPs, the reaction was performed using cobalt ferrite $CoFe_2O_4$ as the catalyst (Table 2, entry 15). The reaction did not proceed at all even after continuing the reaction for 24 h.

With the optimized reaction conditions in hand, the scope and generality of this oxidative amidation were explored using various aryl aldehydes. The results are described in Table 3. From the table it can be seen that aryl aldehydes bearing functional groups such as -Me, -Br, -Cl, -NO2 and -OMe on the aromatic ring could be transformed into the corresponding N-(pyridin-2-yl) benzamide in moderate to high yield. Substrates with electron donating groups show higher reactivity compared to those with electron withdrawing groups. Moreover, the presence of a substituent at the para-position produces higher yields. For example, the reaction produces higher yield in the case of 4-bromo benzaldehyde (Table 3, entry 3f) than that resulting from 2-bromo benzaldehyde (Table 3, entry 3g). This may be due to steric hindrance caused by the bromo-substituent at the orthoposition. Other aldehydes such as anthracene carboxaldehyde and furfural produced the product in moderate yield.

3.3. Catalyst recycling test

The recyclability of the CoFe₂O₄(a)SiO₂-SH-CuI magnetic nanocatalyst was also investigated by carrying out repeated runs of the used material. The reusability test was performed for the reaction of benzaldehyde with 2-aminopyridine under the optimized conditions. Upon completion of the reaction, the catalyst was separated from the reaction mixture via magnetic decantation and washed with excess of ethyl acetate to remove the traces of the previous reaction mixture. It was then dried in an oven at 60 °C for 6 h and kept in a vacuum desiccator for further use. A comparative analysis of SEM images and EDX spectra of both fresh and reused catalysts was performed. Fig. 10 shows the SEM image and EDX analysis of the reused catalyst. The SEM image of the reused catalyst indicates no significant deformation of the catalyst after reuse. However, a slight decrease in Cu concentration was observed in the case of the reused catalyst (Table 4).

Table 3 Substrate scope for oxidative amidation reaction



Reaction conditions: 2-Amino pyridine (1 mmol), aldehyde (1.2 mmol), catalyst 20 wt%, DMSO (2 mL), 70% aq. TBHP (2 mmol).

These experiments revealed that the catalytic activity of the nanocomposite significantly decreases after the first cycle of reuse (Fig. 11), which is due to decrease of Cu-content in the reused catalyst. Hence the catalyst is not suitable for repetitive reuse as the third run provides significantly lower yields.

4. Fluorescence sensing properties

After having success in synthesizing a variety of *N*-(pyridin-2-yl) aryl-amides, we also examined the optical properties of a newly synthesized compound (Table 3, entry 3l), namely *N*-(pyridin-2-yl) anthracene-9-carboxamide (L). The crystal structure of compound L (CCDC 1941942†) is shown in Fig. 12. The single crystals were grown using the pure product from aqueous acetonitrile. The collected X-ray data were refined in the $P2_1/c$ monoclinic space group and the ORTEP diagram indicated that the asymmetric unit contains four molecules. Compound L shows strong absorption in the UV region. Upon excitation at 320 nm, the compounds showed fluorescence in



Fig. 10 The EDX spectra and the SEM image of the reused ${\rm CoFe_2O_4@SiO_2-SH-Cul}$ catalyst.

Table 4 Elemental composition of the reused catalyst

Element	Weight%	Atomic%
СК	18.37	30.73
O K	34.70	43.58
Si K	22.85	16.35
S K	4.66	2.92
ΙL	1.36	0.21
Fe K	9.09	3.27
Co K	4.17	1.42
Cu K	4.80	1.52

the range of 350–450 nm. Compound L (Table 3, entry 31) exhibited selective fluorescence turn on response to a wide variety of competing metal ions.

Fig. 13 shows the UV-vis spectra of compound L and HgCl₂ solution and the effect of the ligand on different Hg²⁺ metal ion concentrations. The spectra were recorded in the CH₃CN:H₂O mixture (1:1). Ligand L shows absorption at 380 nm, 361 nm, 345 nm, 275 nm and 244 nm respectively. The Hg salt shows absorption maxima at 230 nm. Upon gradual addition of Hg^{2+} to L, the intense peak at 244 nm shifted to 238 nm and the shoulder peak at 275 nm disappeared. In addition to this, the intensity of peaks at 380 nm, 361 nm and 345 nm diminished. Thus, the interaction of L and Hg²⁺ was confirmed by UV-vis spectroscopy (Fig. 13). The spectra show an isosbestic point at 310 nm and upon excitation at 320 nm in a fluorescence spectrophotometer the ligand shows weak fluorescence emission in the range of 345 nm to 485 nm with maximum emission at 375 nm.⁵⁶ Literature search reveals various turn on fluorescent probes developed for sensing and detection of the Hg²⁺ ion.⁵⁷⁻⁵⁹ It







Fig. 12 The ORTEP diagram of *N*-(pyridin-2-yl) anthracene-9-carboxamide (L) with 50% probability ellipsoids.



Fig. 13 UV spectra of the ligand at different amounts of Hg^{2+} ion $(0-9.9 \times 10^{-3} \text{ M})$ in the CH_3CN-H_2O mixture (1:1).

has been observed that upon addition of the Hg^{2+} ion, the fluorescence intensity of the solution increases significantly.

The fluorescence sensing properties of compound L towards different metal ions were investigated in a mixture of MeCN and H_2O in a 1:1 (v/v) ratio (200 µL). The study was carried out by the addition of different metal ions such as Ag^+ ,

Al³⁺, Hg²⁺, Mg²⁺, Fe²⁺, Ca²⁺, Cu²⁺, Ni²⁺, Cd²⁺ and Pb²⁺ to the solution of L. The initial study was performed by adding AgNO₃ solution to the solution of L, which induced an enhancement of the fluorescence intensity. The experiment was carried out by adding 2 µL of metal solution for each measurement into the quartz cell $(0-9.9 \times 10^{-3} \text{ M})$ by using a micropipette. Fluorescence emission showed an increasing trend with addition of metal salt solution and finally reached a saturation value. Thereafter, the spectra exhibit a decreasing trend till it reaches a steady value. This can be observed by plotting F/F_0 versus various metal ions (where F_{0} is the fluorescence of L in the absence of the metal ion and $F = F_{\rm m} - F_{\rm o}$ ($F_{\rm m}$ = fluorescence of L in the presence of the metal ion). The results are depicted in Fig. 14. It has been observed that the F/F_0 value of L in the presence of Hg²⁺ is 4.24, however other metal ions show a comparatively lower value under the present experimental conditions.

Thereafter, fluorescence emission of L was tested with different concentrations of the Hg^{2+} metal ion (Fig. 15). The fluorescence emission of the compound showed an increasing trend with stepwise addition of metal ions to L. The fluorescence intensity of L increased linearly up to 2:1 mole ratio and then the intensity remained constant. This indicated that the ligand and the metal ion form a 2:1 complex. The formation of a 2:1 complex between the ligand and Hg^{2+} was further established by using the Hill Plot (Fig. 16).

The plot of $\log\{(F_{\max} - F)/(F - F_{o})\}$ vs. $\log[\text{Hg}^{2+}]$ is shown in Fig. 16, where F_{o} , F and F_{\max} are fluorescence intensities of the compound at zero, at an intermediate stage and at the infinite



Fig. 14 F/F_0 response of L towards different metal ions in 1:1 (v/v) CH₃CN-H₂O.



Fig. 15 The fluorescence spectra of compound L at different amounts of Hg²⁺ ion (0–9.9 \times 10⁻³ M) in a mixed solution of CH₃CN-H₂O in a 1:1 ratio.



Fig. 16 A plot of complexation of compound L with Hg²⁺

concentration of Hg^{2+} ions, respectively. The plot gives a straight line with a slope of 1.51 and an intercept of 2.77 which indicates the binding of one Hg^{2+} ion per two ligands with log β = 2.77.

4.1. DFT calculations

The optimized structure of compound L (ligand) generated using the DFT method and the Gaussian 09 series of programs is presented in Fig. 17. Similarly, Fig. 18 presents the optimized structure of the complex with Hg^{2+} . For all cases, the B3LYP formulation^{49,50} of density functional theory was used employing the LANL2DZ basis set. The possibility of complex formation due to interaction of the ligand and Hg^{2+} was ascertained by calculating the vibrational frequency of the complex. Theoretical calculations reveal that two molecules of L take part in complex formation with one Hg^{2+} ion, through their amide nitrogen atoms (Fig. 18).

Fig. 19 shows the shapes of the HOMO and LUMO of L and the $Hg^{2+}L_2$ complex. From the DFT optimized HOMO-LUMO



Fig. 17 (a) The chemical structure of L and (b) the DFT optimized structure of *N*-(pyridin-2-yl)anthracene-9-carboxamide (right).



Fig. 18 The DFT optimized structure of the $Hg^{2+}L_2$ complex. N atoms (blue balls) and oxygen atoms (red balls).



orbitals it is clear that in the $Hg^{2+}L_2$ complex, the electron density of the metal atom participates in the formation of the LUMO of the complex.

From the DFT optimized HOMO–LUMO orbitals of the $Hg^{2+}L_2$ complex, the energy gap between these orbitals was found to be positive *i.e.* $\Delta E = E_{LUMO}-E_{HOMO} = 0.119$ eV. This value indicates the feasibility of complex formation between the ligand and Hg^{2+} .

5. Conclusion

In conclusion, a hybrid magnetic nanocatalyst ${\rm CoFe_2O_4} @SiO_2-$ SH-CuI has been prepared by incorporating CuI onto the

surface of a thiol functionalized magnetic nanoparticle. The newly developed catalyst has been utilized for the synthesis of *N*-(pyridin-2-yl) benzamide from an aromatic aldehyde and 2-aminopyridine in the presence of 70% aqueous TBHP as an oxidant. The coupling reaction could yield the desired product in moderate to excellent yields. Due to the magnetic properties of the nanocatalyst, it could be recovered with the aid of an external magnet. Furthermore, we have synthesized a new derivative *viz. N*-(Pyridin-2-yl)anthracene-9-carboxamide, which behaves as a fluorescent probe for the detection of the Hg²⁺ ion in aqueous solution.

Conflicts of interest

There are no conflicts to declare.

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