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ARTICLE

Fabrication of magnetic amino-functionalized nanoparticles for *S*-arylation of heterocyclic thiols†

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A series of uniformed mono-disperse magnetic nanoligands (MNLs) ($CoFe_2O_4$-NH_2 (MNL **A**), $Fe_3O_4@Si(CH_2)_3NH_2$ (MNL **B**), $Fe_3O_4@Si(CH_2)_3NHC(O)(CH_2)_2PEI$ (MNL **C**) and $Fe_3O_4@Si(CH_2)_3NHC(O)PEI$ (MNL **D**)) were obtained by loading two ligands, an aminosilane coupling agent and PEI-600, onto magnetic nanoparticles prepared using a solvothermal method. The catalytic applications of the synthesized MNLs were explored for the cross-coupling reaction of heterocyclic thiols with aromatic iodides. The reactions were carried out in the presence of CuI (5 mol%), MNL (10 mol% N) and K_2CO_3 (1.3 eq.) in DMF at 120°C. A variety of heterocyclic sulfides were afforded in good to excellent yields (up to 98%) when MNL **B** was used. The magnetic, crystal, organic matter structure and morphology of MNL **B** exhibited no obvious changes after five consecutive cycles. XPS Characterization of MNL **B** revealed the combination of a small amount of Cu^0 nanoparticles, but this had no significant effect on catalytic performance.

Introduction

Methods for the formation of C–S bonds are important tools in synthetic chemistry, but are comparatively less well understood than C–N or C–O bond formation.[1] Couplings can be achieved under harsh reaction conditions, such as high reaction temperature combined with the use of toxic and high boiling polar solvents like quinoline or HMPA. Alternatively, sulfides can be prepared by reducing aryl sulfones or aryl sulfoxides using strong reducing agents such as $LiAlH_4$ and DIBAL-H.[2] To overcome these difficulties, considerable attention has been focused on the development of catalytic systems for C–S cross-coupling.[3] Organosulfur chemistry has also benefitted significantly from progress associated with catalysis mediated by transition metals, including Pd,[4] Ni,[5] Cu,[6,7] Co,[8] Fe,[9] In,[10] La,[11] Au[12] and Bi.[13] The strong coordination properties of organosulfur compounds are responsible for deactivation of metal catalysts.

Nanoscale catalysts offer several advantages over traditional methodologies, including an increase in exposed active surface area for selective binding of substrates, which makes this a more effective process.[14] Recently, nanocatalysts have been used to form C–S bonds between aryl halides and thiols. The use of CuO nanoparticles for the catalysis of C–S cross-coupling was first reported in 2007.[15] These reactions are effective at 80°C in DMSO in the presence of KOH under a nitrogen atmosphere without ligands, and CuO is found to be inferior to CuO nanoparticles as catalysts of the C–S coupling reaction. Additionally, Ricardo[16] et al. reported excellent product yields under ligand-free conditions by combining nanotechnology and ionic liquids to facilitate C–S cross-coupling using CuO nanopowder as a catalyst in $[bmmim]^+BF_4^-$.

Although these results are promising, the small size of nanoparticles often makes their separation and recycling difficult. In order to circumvent such problems, super-paramagnetic nanocatalysts with high surface area,[17] whose flocculation and dispersion can be controlled reversibly by application of a magnetic field, have been employed as a heterogeneous catalyst for C–S cross-coupling reactions. $CuFe_2O_4$ nanopowder has been used to catalyze aryl-sulfur bond formation between aryl halides and thiols/disulfides.[18] Also, a magnetically recoverable heterogeneous Cu catalyst (nano-FeDOPACu) has been used to synthesize diarylsulfides via a one-pot multicomponent reaction under microwave irradiation.[19] Hence, the development of an alternative, inexpensive, air-resistant, and recyclable ligand, for the formation of the C–S bond, is highly desirable. In previous studies, the small molecular ligand 1,10-phenanthroline, had proven to be efficient in a copper(I)-catalyzed C–S cross-coupling reaction.[20] Similarly, we report in this study the cross-coupling of heterocyclic thiols with aromatic iodides, catalyzed by CuI and magnetic nanoligands (MNLs) modified by the addition of an aminosilane coupling agent aminopropyl-triethoxysilane (APTES) and polyethylene imine-600 (PEI-600) (Fig.S1†). Additionally, we report a detailed characterization (i.e., magnetic properties, crystal structure, organic structure and morphology) of the nanocomposite, before and after use.

## Results and discussion

Characterization of magnetic nanoligands

Fe_3O_4 MNPs were chosen as catalyst supports based on their high magnetic susceptibility and their capacity for surface functionalization. The preparation of MNLs is presented in
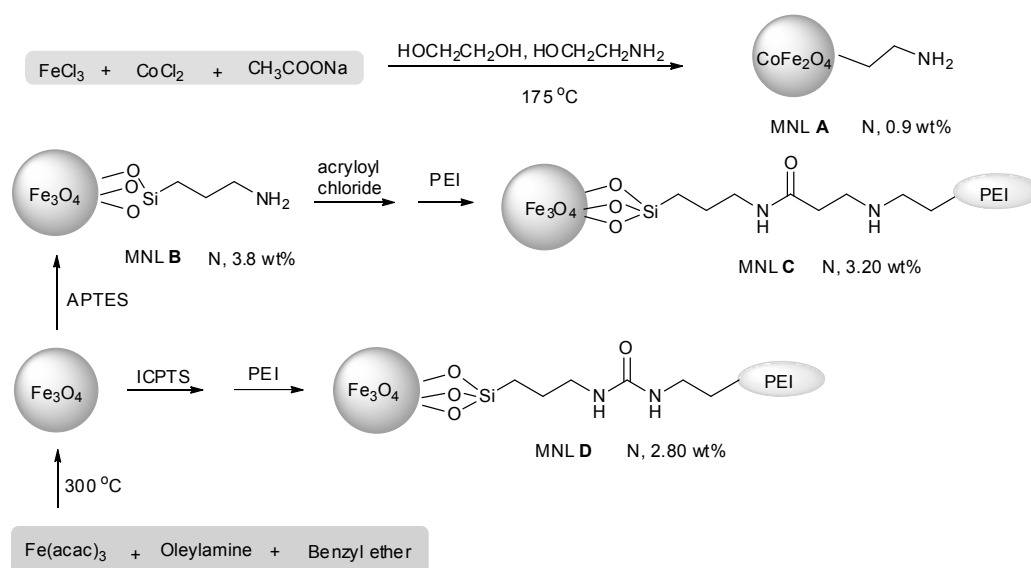
Scheme 1 Synthesis of MNLs A, B, C and D.

Scheme 1. The nitrogen content values for MNLs **A**, **B**, **C** and **D** were 0.64, 2.71, 2.28, 2.0 mmol•g^{-1}, respectively. The smaller size of the Fe$_3$O$_4$ NPs (8 nm) resulted in a larger surface area with higher activity, and the nitrogen content of MNL **B** may reach as much as 3.8 wt%, which is higher than the previously reported value of 0.61%.[21]

Transmission electron microscope (TEM) was used to characterize the morphology and crystal structure. CoFe$_2$O$_4$ particles are spherical, nearly monodisperse, and have average diameters of approximately 23±3 nm (Fig.1a and 1b). TEM images of Fe$_3$O$_4$ MNPs prepared via the thermal decomposition of Fe(acac)$_3$ in benzyl ether and oleylamine, clearly indicate that the 8 nm iron oxide MNPs are rounded and monodisperse (Fig.1c and 1d). Additionally, we observed no significant changes in the crystalline structure, size, or morphology of the Fe$_3$O$_4$ MNPs after modification (Fig. 1e and Fig. 1f).
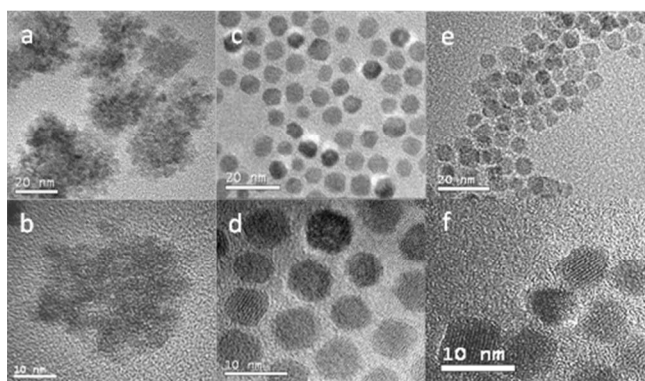

Fig. 1 TEM of MNL **A** (a, b), Fe$_3$O$_4$ NP (c, d) and MNL **B** (e, f).

In the XRD pattern of MNLs **A**, B, **C** and D (Fig. S2†), the half-peak widths of the ligands remained unchanged, and the NP sizes were consistent with the sizes observed before surface modification. The field dependent magnetization curves of the ligands at room temperature (Fig. S3†) illustrate the importance of the dispersion state of the magnetic nanoparticles. The saturation magnetization (Ms) value for Fe$_3$O$_4$ nanoparticles was 48.9 emu•g^{-1}, and Ms value for MNLs **A**, **B**, **C** and **D** were found to be 70.6 emu•g^{-1}, 33.5 emu•g^{-1}, 16.3 emu•g^{-1}, and 45.3 emu•g^{-1}, respectively. The decreasing Ms values were found to correspond with the addition of surface functionalization, although these species could still be separated magnetically. In the IR spectra (Fig. S4†) of the nanoparticles, the appearance of characteristic bands confirmed the existence of the magnetic core and provided evidence of surface amine-functionalization. Also, the C=O peaks for MNLs **C** and **D** were observed at 1711 cm^{-1} and 1558 cm^{-1}, respectively. It may be that the amino group makes the electron cloud of the C=O double bond move to the oxygen atom, resulting in a decrease in the bond force constant.

Table 1 C–S coupling of 5-methyl-1,3,4-thiadiazol-2-thiol with iodobenzene: screening of catalysts.
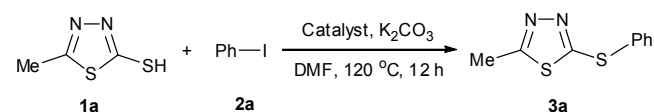
| Entry	Catalyst	Yield^a (%)
1	CuI (5 mol%)	41
2	MNL**A** (10 mol%)	5
3	CuI (5 mol%) + MNL**A** (10 mol%)	83

^{a}Isolated yield

Catalytic studies

Experiments were performed to identify the appropriate conditions for the coupling reaction of 5-methyl-1,3,4-thiadiazol-2-thiol (**1a**) with iodobenzene (**2a**) (1.2 equiv.) using K$_2$CO$_3$ (1.3 equiv.) as a base and DMF as a solvent at 120°C.

The desired product **3a** was obtained at 41% yield when 5 mol% CuI was used (Table 1, entry 1), and 5% yield in the presence of 10 mol% MNL **A** (Table 1, entry 2). The reaction gave 83% yield catalyzed by 5 mol% CuI and 10 mol% MNL **A** (Table 1, entry 3).

Of the four ligands, MNL **B** was the most effective, due to its ability to form a more active catalytic centre with CuI (Table 2, entries 1–4). MNL **A**, obtained though one-step synthesis, exhibited the lowest nitrogen content. In comparison to the aliphatic amine of MNL **B**, the nitrogen content of MNLs **C** and **D** included amides, and these ligands showed weak coordination with CuI. So, the catalytic activity of MNLs **C** and **D** was relatively low. After investigating the reaction in different solvents (Table 2, entries 5–7), we found that the reaction catalyzed by MNL **B** failed to yield the desired product in THF or toluene. However, a moderate yield was obtained for MNL **B** in DMSO. In addition, for various bases (e.g., Cs_2CO_3, NaOAc, KOH and Na_3PO_4), the product **3a** was obtained in 75–92% yield (Table 2, entries 8–11). Thus, the optimized reaction conditions included CuI (5 mol%), K_2CO_3 (1.3 equiv.) and MNL **B** (10 mol%) in DMF at 120°C for 12 h.

Table 2 Optimization of reaction conditions.[a]
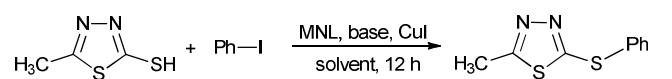
Entry	MNL	Base	Solvent	Temp. (°C)	Yield [b](%)
1	A	K_2CO_3	DMF	120	83
2	B	K_2CO_3	DMF	120	94
3	C	K_2CO_3	DMF	120	87
4	D	K_2CO_3	DMF	120	79
5	B	K_2CO_3	Toluene	110	NR
6	B	K_2CO_3	THF	66	NR
7	B	K_2CO_3	DMSO	120	77
8	B	Cs_2CO_3	DMF	120	75
9	B	NaOAc	DMF	120	92
10	B	KOH	DMF	120	89
11	B	Na_3PO_4	DMF	120	84

[a]Reaction conditions: MNL/CuI/base/5-methyl-1,3,4-thiadiazol-2-thiol/iodobenzene = 0.1: 0.05: 1.3: 1: 1.2 (mmol); reaction time: 12 h. [b] Isolated yield.

Using the optimized reaction conditions, we extended the scope of this catalytic protocol to the cross-coupling reactions of aryl iodides with heterocyclic thiols (Table 3). The coupling of 5-methyl-1,3,4-thiadiazol-2-thiol with aryl iodides having electron-donating groups resulted in a slightly low yields (Table 3, entries 2–3), however, high yields were obtained in the presence of electron-withdrawing groups (Table 3, entries 4–5). For 5-aryl-1,3,4-thia-diazol-2-thiol, both electron-donating and electron-withdrawing groups led to high yields (Table 3, entries 6–12). When 4,5-diphenyl-4*H*-1,2,4-triazol-3-thiol, 4,6-di-methylpyrimidine-2-thiol and 5-(*o*-tolyl)-1,3,4-oxadiazol-2-thiol were treated with iodobenzene, the desired products were afforded at 94, 91 and 88% yield, respectively (Table 3, entries

13–15). Furthermore, thiophenols were investigated for this reaction. As expected, the coupling reactions of thiophenols with 5-methyl-1,3,4-thiadiazol-2-thiol proceeded in good yields (Table 3, entries 16–18). The results demonstrated that the catalytic activity of magnetic nano-ligands was slightly lower than that resulting from the 1,10-phenanthroline catalyst,[20] although these novel catalysts exhibited good reusability.

Table 3 C–S cross-coupling of thiols with aryl iodides catalyzed by MNL**B**.[a]

| Entry	Thiol	Aryl iodide	Time (h)	Yield [b] (%)
1			12	94
2			18	91
3			18	88
4			14	98
5			14	94
6			14	88
7			18	94
8			18	91
9			18	88
10			18	98
11			18	94
12			14	88
13			12	94
14			12	91
15			20	88
16			12	81
17			12	82
18			12	79

[a] Reaction condition: MNL **B**/CuI/K_2CO_3/thiol/aryl iodide = 0.1:

0.05: 1.3: 1: 1.2 (mmol). [b] Isolated yield.

Recovery and reusability of MNL B

The reusability of MNL **B** was also examined (Table 4). MNL **B** was magnetically separated from the mixture after completion of the reaction, washed with deionized (DI) water, ethanol, ethyl acetate by sonication, and dried at 40°C in vacuum for direct use in additional catalytic reactions. The results showed that MNL **B** could be reused at least five times without major loss of activity.

Table 4 Recycling experiments of MNL**B** in the C–S bond coupling reaction.[a]
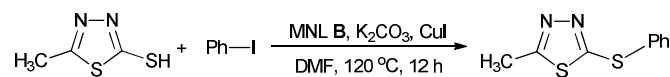
Run	1	2	3	4	5
Yield [b] (%)	94	94	90	90	89

[a]Reaction conditions: MNL **B**/CuI/K_2CO_3/5-methyl-1,3,4-thiadiazol-2-thiol/iodobenzene = 0.1:0.05:1.3:1:1.2 (mmol). [b]Isolated yield.

To further study the changes of MNL **B** activity, the morphology and structures of both the freshly synthesized MNL **B** and MNL **B** after the 5th run were evaluated. The typical hysteresis loops of the powder X-ray diffraction analysis at 300 K and the IR spectra (Fig. S5†) indicated that the material exhibited good stability under the described reaction conditions. The TEM analysis revealed degradation of both the morphology and the dispersity of the MNL **B** after the initial successful catalytic cycles (Fig.S6†). We could conclude that the small change resulting from coordination interaction between the ligand and copper during the reaction did not significantly alter catalytic performance.

The XPS technique had been employed to characterize the surface chemical composition of nanoligands. The XPS spectra of freshly synthesized MNL **B** and MNL **B** after the 5th run (Fig. S7†) indicated no obvious differences. The high-resolution spectra of Fe 2p, C 1s, N 1s, Si 2p, O 1s and Cu 2p were showed in Fig.S8†. The N 1s signal of freshly synthesized MNL **B** was observed at 398.3 eV which corresponding to the binding energy (Eb) of aliphatic amine (N–C, N–H) (Fig.S8c†). After the 5th run, this value increased approximately 1.3 eV due to the coordination interaction between copper and the nitrogen atom. The peaks for Cu 2p 1/2 (951.7 eV) and Cu 2p 3/2 (932.4 eV) (Fig. S8f†) were close to the standard data of Cu^0, which was produced by reduction of Cu(I). The existence of Cu 2p was consisted with an increase of N 1s binding energy, which was consisted with the formation of Cu^0 nanoparticles. This was slightly reduced the catalytic performance of the material as the nitrogen ligands, even though the Cu^0 nanoparticles could catalyze the C–S bond formation.[19]

Conclusions

Four uniformed monodisperse magnetic nano-ligands $CoFe_2O_4$-NH_2 (MNL **A**), $Fe_3O_4@Si(CH_2)_3NH_2$ (MNL **B**), $Fe_3O_4@Si$-$(CH_2)_3NHC(O)(CH_2)_2PEI$ (MNL **C**), $Fe_3O_4@Si(CH_2)_3NH$-$C(O)PEI$ (MNL **D**) were obtained through simple procedures and used as ligands with CuI for C–S bond coupling reactions. MNL **B** was found to be tolerant to the cross-coupling reaction

of heterocyclic thiols with aryl iodides having different functional groups, and a variety of heterocyclic sulfides were obtained in good to excellent yields (up to 99%). The magnetic nature of these ligands allowed for easy and rapid separation of the heterogeneous ligands from the reaction mixture. MNL **B** continued to exhibit good catalytic activity after five consecutive cycles.

Experimental section

General procedure for copper-catalyzed cross-coupling reaction of heterocyclic thiols 1 with aryl iodides 2

Aryl iodides **2** (0.24 mmol) were added to a solution of CuI (0.01 mmol, 1.9 mg), a magnetic nanoligand (0.02 mmol N, 9 mg), heterocyclic thiols**1** (0.2 mmol), and K_2CO_3 (0.26 mmol, 90 mg) in DMF (1.0 mL). The reaction mixture was heated at 120°C for 12 h under a nitrogen atmosphere. After cooling to room temperature, ethyl acetate (4 mL) and H_2O (4 mL) were added, and the organic phase was separated. The aqueous phase was extracted with ethyl acetate (3×4 mL). The combined organic phases were washed with saturated brine and dried over anhydrous Na_2SO_4. The organic solvent was then concentrated in vacuum to yield the crude products, which was purified by silica gel column chromatography using petroleum ether/ethyl acetate.

Recyclability experiments

Recycling reactions were performed using MNL **B**. After completion of the reaction, MNL **B** was recovered magnetically and the reaction solution was decanted. MNL **B** was washed with DI water (2×5 mL), ethanol (2×5 mL), ethyl acetate (2×5 mL), dried at 40°C under vacuum and reused for the next run. Recycle reactions were performed as described above.

Notes and references
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The aminosilane coupling agent and polyethylene imine-600 were loaded onto magnetic nanoparticles to obtain magnetic nanoligands (MNLs) **A**, **B**, **C** and **D**.