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# One-pot synthesis of 1- and 5-substituted 1*H*tetrazoles using 1,4-dihydroxyanthraquinone– copper(II) supported on superparamagnetic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> magnetic porous nanospheres as a recyclable catalyst

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An effective one-pot, convenient process for the synthesis of 1- and 5-substituted 1*H*-tetrazoles from nitriles and amines is described using 1,4-dihydroxyanthraquinone–copper(II) supported on  $Fe_3O_4@SiO_2$  magnetic porous nanospheres as a novel recyclable catalyst. The application of this catalyst allows the synthesis of a variety of tetrazoles in good to excellent yields. The preparation of the magnetic nanocatalyst with core–shell structure is presented by using nano- $Fe_3O_4$  as the core, tetraethoxysilane as the silica source and poly(vinyl alcohol) as the surfactant, and then  $Fe_3O_4@SiO_2$  was coated with 1,4-dihydroxyanthraquinone–copper(II) nanoparticles. The new catalyst was characterized using Fourier transform infrared spectroscopy, X-ray diffraction, transmission electron microscopy, field emission scanning electron microscopy, dynamic light scattering, thermogravimetric analysis, vibration sample magnetometry, X-ray photoelectron spectroscopy, nitrogen adsorption–desorption isotherm analysis and inductively coupled plasma analysis. This new procedure offers several advantages such as short reaction times, excellent yields, operational simplicity, practicability and applicability to various substrates and absence of any tedious workup or purification. In addition, the excellent catalytic performance, thermal stability and separation of the catalyst make it a good heterogeneous system and a useful alternative to other heterogeneous catalysts. Also, the catalyst could be magnetically separated and reused six times without significant loss of catalytic activity. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: core-shell; magnetic nanocatalyst; magnetic separation; one-pot reactions; 1- and 5-substituted 1H-tetrazoles

## Introduction

Tetrazoles are an increasingly popular functionality with a wide range of applications such as in pharmaceuticals as lipophilic spacers and metabolically stable surrogates for carboxylic acids in medicinal chemistry, ligands in coordination chemistry, special explosives in materials science, in photography and information recording systems and valuable precursors to a variety of nitrogen-containing heterocycles in organic synthesis.<sup>[11]</sup> They have been found to be potential TNF alpha inhibitors, P2X7-antagonists<sup>[2]</sup> and inhibitors of anandamide cellular uptake.<sup>[3]</sup> Furthermore, tetrazoles are screened for various biological activities such as anticonvulsant, antiulcer, anti-inflammatory, antifungal, antiviral, antibacterial, antiulcer and antitubercular activities.<sup>[4–6]</sup>

Tetrazole rings can be prepared in several ways. The routes to 1-substituted tetrazoles include acid-catalysed cycloaddition between hydrazoic acid and isocyanides,<sup>[7]</sup> acetic acid- or trifluoroacetic acid-catalysed cyclization between primary amines, or their salts, with an orthocarboxylic acid ester and sodium azide,<sup>[8]</sup> acid-catalysed cycloaddition between isocyanides and trimethyl azide<sup>[9]</sup> and cyclizations from an amine, triethyl orthoformate and so-dium azide using PCl<sub>5</sub>,<sup>[10]</sup> Yb(OTf)<sub>3</sub>,<sup>[11]</sup> In(OTf)<sub>3</sub>,<sup>[12]</sup> Pd(OAc)<sub>2</sub>/ZnBr,<sup>[13]</sup> natrolite zeolite<sup>[14]</sup> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ligand/Cu(II)<sup>[15]</sup> as catalysts.

Many methods for the synthesis of 5-substituted tetrazoles have been proposed based on [3 + 2] cycloaddition of azide ion to corresponding organic nitriles. The reactions were carried out using numerous homogeneous catalysts such as  $Zn(OTf)_2$ ,<sup>[16]</sup>  $Cu_2(OTf)_2$ ,<sup>[17]</sup>  $Fe(OAc)_2$ ,<sup>[18]</sup>  $BF_3$ – $OEt_2$ ,<sup>[19]</sup>  $AlCl_3$ <sup>[20]</sup> and  $AgNO_3$ ,<sup>[21]</sup> and using some heterogeneous catalysts such as Zn/Al hydrotalcite,<sup>[22]</sup> COY zeolites,<sup>[23]</sup>  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>,<sup>[24]</sup> nano-ZnO/Co<sub>3</sub>O<sub>4</sub>,<sup>[25]</sup> nano-CuFe<sub>2</sub>O<sub>4</sub>,<sup>[26]</sup> AlPO-5 microporous molecular sieves<sup>[27]</sup> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/Salen of Cu(II).<sup>[28]</sup>

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Although most of these methods are worthwhile, many of them have one or more of the following drawbacks: long reaction time, elevated temperature conditions, low yields, expensive moisture-sensitive reaction conditions, tedious workup of the reaction mix-ture and difficulty in separation and recovery of the catalyst. In addition to this, some cases show formation of toxic hydrazoic acid and involvement of alkyltin-based reagents which warrant the safety of the procedure.<sup>[29]</sup> Thus, the choice of catalyst is one of the most crucial steps for achieving good results.

Magnetite nanoparticles are attracting increasing interest due to their unique magnetic responsivity, low toxicity, large surface-tovolume ratio, biocompatibility and potential applications in several fields.<sup>[30,31]</sup> Nanoscale magnetite (Fe<sub>3</sub>O<sub>4</sub>) has potential applications in magnetic resonance imaging contrast agents, magnetic bioseparations, treatment of cancer, drug delivery and catalysis.<sup>[32,33]</sup> However, magnetic nanoparticles easily aggregate because of anisotropic dipolar attraction and alter magnetic properties. Therefore, a protection layer is important to avoid such limitations.<sup>[34]</sup>

Recently, magnetic core–shell materials have gained much attention and undergone intensive investigation for their unique potential applications in medicinal, low cytotoxicity, chemically modifiable surface, magnetic responsivity, good stability, optical, biological, environmental and chemical areas.<sup>[35,36]</sup> Core–shell nanostructure magnetic catalysts can be easily separated conveniently and economically using an external magnetic field.<sup>[37,38]</sup>

Recently, surface-functionalized magnetic nanoparticles have been developed in a range of organic transformations, and studies of immobilization of organo-catalysts on core–shell nanoparticles have been reported.<sup>[39,40]</sup>

Therefore, in this paper, we report the preparation of 1,4dihydroxyanthraquinone-copper(II) immobilized on superparamagnetic  $Fe_3O_4@SiO_2$  nanoparticles as illustrated in Scheme 1 and its use as a recyclable catalyst for the synthesis of 1- and 5-substituted 1*H*-tetrazoles from amines and nitriles. In addition, using the methodology described, catalyst separation becomes easier and cost effective with an external magnetic field.

# Experimental

#### Materials and physical measurements

All the solvents were distilled, dried and purified using standard procedures. All the chemical reagents used in our experiments were purchased from Merck Chemical Company and were of high purity. Progress of reactions was monitored by TLC on silica gel polygram STL G/UV 254 plates. NMR spectra were recorded with a Bruker Avance DPX 250 MHz spectrometer in CDCl<sub>3</sub> and deuterated dimethylsulfoxide (DMSO- $d_6$ ) as solvents in the presence of tetramethylsilane as internal standard. A Shimadzu FT-IR 8300 spectrometer was used to record Fourier transform infrared (FT-IR) spectra using KBr pellets. Large-angle X-ray diffraction (XRD) patterns were recorded with a Bruker AXS D8-advance X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 1.5418). Transmission electron microscopy (TEM) observation was performed with a Philips EM208 microscope operated at a 100 kV accelerating voltage. Particle morphology was examined using field emission scanning electron microscopy (FE-SEM; Hitachi S-4160 instrument). Dynamic light scattering was performed with a HORIBA-LB550. Brunauer-Emmett-Teller (BET) surface area and porosity of nanoparticles were determined with a Micromeritics ASAP 2000 automatic analyser. Magnetic properties of the samples were measured using



**Scheme 1.** Preparation process of 1,4-dihydroxyanthraquinone–copper(II) supported on superparamagnetic  $Fe_3O_4@SiO_2$  nanoparticles.

a vibrating sample magnetometer (BHV-55). Thermogravimetric analysis (TGA) curves were recorded using a PerkinElmer device manufactured by Thermal Sciences. X-ray photoelectron spectroscopy (XPS) of the catalyst was performed with an XR3E2 (VG Microtech) twin anode X-ray source using Al K $\alpha$  radiation (1486.6 eV). The amount of Cu nanoparticles supported on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ was measured using inductively coupled plasma (ICP) analysis (Varian, Vista-pro). The melting points of products were determined with an Electrothermal type 9100 melting point apparatus. Tetrazoles were characterized by their melting points and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra and comparison with literature values.

#### **General procedures**

#### Preparation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles

The Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized by a facile coprecipitation method.<sup>[41,42]</sup> Briefly, FeCl<sub>3</sub>·6H<sub>2</sub>O (1.3 g, 4.8 mmol) was dissolved in 30 ml of water, followed by addition of poly(vinyl alcohol) (PVA 15000, 1 g) as a surfactant and 0.9 g (4.5 mmol) of FeCl<sub>2</sub>·4H<sub>2</sub>O. The mixture was stirred vigorously for 30 min at 80 °C. Then, to this mixture, hexamethylenetetramine (1.0 mol l<sup>-1</sup>) was slowly added under vigorous stirring to produce a black precipitate and the solution pH was maintained at 10.0. The resultant mixture was continuously stirred with nitrogen protection at 60 °C for 2 h and the obtained black magnetite particles were collected with a permanent magnet, and sequentially washed with ethanol and dried at 80 °C for 10 h.

#### Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell nanospheres

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell nanospheres were prepared through a modified Stöber method.<sup>[43-45]</sup> In a typical process, 0.5 g of Fe<sub>3</sub>O<sub>4</sub> nanoparticles were dispersed in a mixture of ethanol (50 ml), deionized water (5 ml) and 5.0 ml of NaOH (10 wt.%). Subsequently, 0.2 ml of tetraethoxysilane (TEOS) was added dropwise under vigorous mechanical stirring. After stirring for 30 min, the products (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>) were collected using an external magnet and washed with deionized water and ethanol three times and then dried under vacuum at 80 °C for 10 h.

#### General procedure for the preparation of $Fe_3O_4@SiO_2$ nanoparticles functionalized with 3-(triethoxysilyl)propylamine ( $Fe_3O_4@SiO_2$ -NH<sub>2</sub>).

 $Fe_3O_4@SiO_2$  nanoparticles (1 g) were dispersed in ethanol (10 ml) and sonicated for 20 min at room temperature. Then, 3-aminopropyl(triethoxy)silane (1 mmol, 0.176 g) was introduced, and the mixture was stirred vigorously and refluxed for 12 h under nitrogen atmosphere. After refluxing, the mixture was cooled to room temperature, separated using an external magnet and washed thoroughly with ethanol and water and dried in an oven at 80 °C for 6 h to afford  $Fe_3O_4@SiO_2-NH_2$ .

Preparation of (4-hydroxy-9,10-dioxo-9,10-dihydroanthracen-1-yloxy)acetic acid ethyl ester (2)

A mixture of 1,4-dihydroxyanthraquinone (1.0 mmol), ethyl 2-bromoacetate (0.5 mmol), *t*-BuOK (0.5 mmol) and dimethylformamide (DMF; 10 ml) was stirred at room temperature for 18 h. After completion of the reaction (monitored by TLC), 20 ml of water was added, the mixture was filtered and the residue was dried. The crude product (**2**) was purified via flash column chromatography using hexane–EtOAc (1:1) as the eluent.

#### Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ nanoparticles

The modification of  $Fe_3O_4@SiO_2-NH_2$  with **2**) was carried out via ligand formation between the amino group and the carbonyl group of ester **2** as presented in Scheme 1.  $Fe_3O_4@SiO_2-NH_2$  (0.5 g) and **2** (1 mmol, 0.325 g) were mixed with 10 ml of ethanol using mechanical stirring to produce a homogeneous suspension. The reaction was refluxed with continuous stirring under inert atmosphere for 24 h. Then, the modified  $Fe_3O_4@SiO_2$  nanoparticles (as  $Fe_3O_4@SiO_2-DAQ$ ) were collected with a magnet, washed several times with ethanol and distilled water, and dried in a vacuum desiccator at 70 °C.

#### Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) nanoparticles

 $Fe_3O_4@SiO_2-DAQ$  (0.5 g) was added to a solution of  $Cu(OAc)_2$  (1 mmol, 0.182 g) in ethanol (10 ml) and the reaction mixture was refluxed for 12 h in nitrogen atmosphere. The resulting  $Fe_3O_4@SiO_2-DAQ-Cu(II)$  nanoparticles were collected using an external magnetic field, then washed with deionized water and ethanol three times and finally dried under vacuum at 80 °C for 10 h.

# General procedure for synthesis of 1-substituted 1*H*-tetrazole derivatives in presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) catalyst

A mixture of amine (1 mmol), triethylorthoformate (1.2 mmol) and sodium azide (1 mmol) was stirred in the presence of  $Fe_3O_4@SiO_2-DAQ-Cu(II)$  (0.035 g, 0.8 mol% of Cu(II)) at 100 °C. After completion of the reaction, as monitored by TLC using *n*-hexane– ethyl acetate, the reaction mixture was diluted with ethyl acetate (20 ml). The catalyst was collected using an external magnet, and then the resulting solution was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The residue was concentrated and recrystallized from EtOAc–hexane (1:10) to afford the pure product.

# General procedure for synthesis of 5-substituted 1*H*-tetrazole derivatives in presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) catalyst

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) (0.04 g, 0.9 mol% of Cu(II)) was added to a mixture of nitrile (1 mmol), sodium azide (1.2 mmol) and DMF (3 ml) and stirred at 100 °C. After completion of the reaction, the resulting mixture was diluted with ethyl acetate (10 ml), the catalyst was separated with an external magnet and washed with ethyl acetate (10 ml) three times. The filtrate was treated with ethyl acetate (10 ml) and 1 N HCI (10 ml) under vigorous stirring for 2 min. The resultant organic layer was separated and the aqueous layer was extracted with ethyl acetate (20 ml). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to give a crude product. The crude product was purified by silica gel column chromatography using appropriate solvent mixture (hexane–EtOAc, 1:1) to afford the pure product.

# **Results and discussion**

FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub>, ester 2, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) are shown in Fig. 1. In Fig. 1(a), the absorption band at 578  $\text{cm}^{-1}$  is assigned to the stretching vibration of the Fe-O bond of Fe<sub>3</sub>O<sub>4</sub>. Also, the peaks at around 3400 and 1620 cm<sup>-1</sup> in Fig. 1(a) are due to the adsorbed water in the sample. The peaks at 1081 and 807 cm<sup>-1</sup> are ascribable asymmetric and symmetric stretching vibration of framework and terminal Si-O-Si groups, suggesting the formation of silica layers (Fig. 1(b)). Figure 1(c) shows the FT-IR spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> nanoparticles: the peaks at 577, 1000-1150, 1400-1410, 1546, 2810-2986 and 3165-3390 cm<sup>-1</sup> are attributed to Fe-O (stretching), Si-O-Si (asymmetric stretching), C-N (stretching), N-H (bending) C-H (stretching) and N-H (stretching), respectively. Figure 1(d) shows the FT-IR spectrum of ester 2. The bands at 2878-3031, 1734, 1665, 1476 and 1355 cm<sup>-1</sup> are attributed to C-H (stretching), C-O (ester stretching), C-O (stretching), CH<sub>2</sub> (bending) and CH<sub>3</sub> (bending), respectively. Also, the bands at 1038 and 1594 cm<sup>-1</sup> are ascribed to the carbonyl group, hydrogen bonded with the hydroxyl group positioned at position 1 in the anthraquinone molecule.<sup>[46]</sup> From the FT-IR spectrum of Fig. 1(e), the peaks at 1645 and 1544 cm<sup>-1</sup> belong to the stretching vibration mode of C-O (amide and anthraquinone stretching) and C-O (hydrogen bonded with hydroxyl group in position 1) bonds in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ, and the absorption peak present at 1000–1150 cm<sup>-1</sup> is due to stretching vibration of framework and terminal Si-O-Si groups. The presence of vibration bands at 3400 (O-H stretching), 2880-3090 (C-H stretching), 1580 (C-O amide stretching), 1531 (C-O non-coordinated stretching), 1436 (C-O coordinated with copper), 1000-1150 (Si-O-Si asymmetric stretching) and 675 cm<sup>-1</sup> (Cu-O stretching) demonstrates the existence of



**Figure 1.** FT-IR spectra: (a)  $Fe_3O_4$ ; (b)  $Fe_3O_4$ @SiO<sub>2</sub>; (c)  $Fe_3O_4$ @SiO<sub>2</sub>-NH<sub>2</sub>; (d) ester **2**; (e)  $Fe_3O_4$ @SiO<sub>2</sub>-DAQ; (f)  $Fe_3O_4$ @SiO<sub>2</sub>-DAQ-Cu(II) nanoparticles.

1,4-dihydroxyanthraquinone–copper(II) supported on  $Fe_3O_4@SiO_2$  nanoparticles (Fig. 1(f)).  $^{\rm [47]}$ 

The crystalline structures of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) were determined using powder XRD. As shown in Fig. 2(a), the XRD pattern of Fe<sub>3</sub>O<sub>4</sub> is in agreement with JCPDS card no. 19-0629 (cubic spinel structure).<sup>[48]</sup> As shown in Figs 2(b) and (c), the peak positions of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) do not show any changes. This confirms that the surface modification and conjugation of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles do not lead to a phase change. The patterns of  $Fe_3O_4@SiO_2$ and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) show an obvious diffusion peak around  $2\theta = 10-25^{\circ}$  attributable to amorphous silica (Figs 2(b) and (c)). For Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) nanoparticles, the broad peak is transferred to lower angles due to the synergetic effect of amorphous silica and ligand. Also, the XRD pattern of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) nanocatalyst shows the peaks of both Fe<sub>3</sub>O<sub>4</sub> and Cu, and the diffraction peaks at  $2\theta$  around  $28^\circ$ ,  $65^\circ$  and  $78^\circ$  are correlated to the different copper phases of Cu(111), Cu(331) and Cu(220), respectively (Fig. 2(c)).<sup>[47]</sup>

The morphology of  $Fe_3O_4$  and  $Fe_3O_4@SiO_2$  particles was observed using FE-SEM, as shown in Fig. 3. The FE-SEM images indicate the successful coating of the magnetic  $Fe_3O_4$  particles (Figs 3(a) and (b)).

The morphologies and structures of the nanoparticles at various synthetic steps were observed using TEM (Figs 3(c)–(e)). The TEM image reveals that the diameter of the pure Fe<sub>3</sub>O<sub>4</sub> is uniform at about 10 nm (Fig. 3(c)). After coating with thin SiO<sub>2</sub>, the diameter of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> increases to approximately 20 nm,



Figure 2. XRD patterns: (a) Fe<sub>3</sub>O<sub>4</sub>; (b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>; (c) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II).

corresponding to a 10 nm thick SiO<sub>2</sub> layer on the Fe<sub>3</sub>O<sub>4</sub> (Fig. 3 (d)).<sup>[48]</sup> Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> -DAQ-Cu(II) is also observed as having well shaped spherical or ellipsoidal particles. The diameter of the nanoparticles is found to be approximately 50 nm (Fig. 3(e)).

Figures 3(f)–(h) show the particle size distributions of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) nanoparticles. This size distribution is centred at a value of 12, 20 and 50 nm for Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II), respectively. The result is in good agreement with the size of particles shown in TEM images.

Magnetization curves of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) magnetic samples show no hysteresis and the saturation magnetization values are 64.8, 40.3 and 30.7 emu g<sup>-1</sup>, respectively, revealing their superparamagnetism (Fig. 4(A)). Obviously, the saturation magnetization of Fe<sub>3</sub>O<sub>4</sub> gradually decreases with the increase of SiO<sub>2</sub> and ligand complex.

Nevertheless, the magnetism of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) is still high enough to allow it be magnetically separated by applying an external permanent magnet, which can facilitate the separation of catalyst from reaction solutions. With a magnet placed beside the vial, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) nanoparticles dispersed in DMF are quickly attracted to the side of the vial within a few seconds without the need for a filtration step, and then can be readily redispersed with slight shake, which illustrates their magnetic nature (Fig. 4(B)).

Results of TGA analyses for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu (II) nanoparticles are shown in Fig. 4(C) obtained at a heating rate of 20 °C min<sup>-1</sup> from 50 to 700 °C. According to Fig. 4(C) curve (a), the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles exhibit a weight loss in the range 50–200 °C due to evaporation of surface-adsorbed water and ethanol, while weight loss between 200 and 560 °C is associated with the release of the structure water.<sup>[49]</sup> As shown in Fig. 4(C) curve (b), the TGA curve of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) shows a weight loss of 5.1% below 200 °C due to the loss of the surface hydroxyl groups.



**Figure 3.** SEM images of (a)  $Fe_3O_4$  and (b)  $Fe_3O_4@SiO_2$ . TEM images of (c)  $Fe_3O_4$ , (d)  $Fe_3O_4@SiO_2$  and (e)  $Fe_3O_4@SiO_2-DAQ-Cu(II)$ . Size distributions of (f)  $Fe_3O_4$ , (g)  $Fe_3O_4@SiO_2$  and (h)  $Fe_3O_4@SiO_2-DAQ-Cu(II)$ .

The weight loss of about 24.8% in the range 200–700  $^\circ\!C$  is attributed to the decomposition of organic moieties on the surface.

Figure 5 shows the XPS spectrum of the synthesized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) particles. For a better understanding of the oxidation state of copper, the binding energy obtained from the catalyst was compared with the Cu<sup>2+</sup> 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peak positions. From Fig. 5, it can be seen that the main peaks of Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) nanoparticles are about 934.61 eV and 942.67 eV indicating that Cu is in the formal +2 valance state.<sup>[50]</sup>

Determination of the Cu content was carried out using ICP analysis of the digested catalyst. The obtained results reveal that 0.23 mmol per gram of Cu is immobilized on  $Fe_3O_4@SiO_2-DAQ$ .

The specific surface area and pore diameter were calculated based on standard BET and Barrett–Joyner–Halenda methods, respectively. According to the BET isotherms, the active surface area of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) is estimated at 480, 430 and 362 m<sup>2</sup> g<sup>-1</sup>, respectively (Table 1).



**Figure 4.** (A) Magnetization curves at 300 K for (a)  $Fe_3O_4$ , (b)  $Fe_3O_4@SiO_2$  and (c)  $Fe_3O_4@SiO_2-DAQ-Cu(II)$  nanoparticles. (B) Separation process of  $Fe_3O_4@SiO_2-DAQ-Cu(II)$  nanoparticles using a magnet. (C) TGA of (a)  $Fe_3O_4@SiO_2$  and (b)  $Fe_3O_4@SiO_2-DAQ-Cu(II)$  nanoparticles.



Figure 5. XPS spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) nanoparticles.

In order to optimize the reaction conditions and performance of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) as a catalyst, the reaction between aniline (1 mmol), triethylorthoformate (1.2 mmol) and sodium azide (1 mmol) was selected as a model reaction (Table 2).

As a first stage, the reactions were conducted in EtOH, MeOH, CI  $(CH_2)_2CI$ ,  $CH_3CN$ , DMF, DMSO and water as solvents and under

Table 1. BET results for Fe $_3O_4$ , Fe $_3O_4$ @SiO $_2$ and Fe $_3O_4$ @SiO $_2$ -DAQ-Cu(II)						
Entry	Sample	Specific surface area $(m^2 g^{-1})$	Pore volume (cm <sup>3</sup> g <sup><math>-1</math></sup> )	Average pore radius (nm)		
1	Fe <sub>3</sub> O <sub>4</sub>	480	0.803	1.254		
2	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	430	0.755	1.787		
3	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -	362	0.730	1.833		
	DAQ-Cu(II)					

$ \qquad \qquad$					
Entry	Catalyst amount (mol%)/solvent	Temp. (°C)	Time (h)	Yield (%) <sup>b</sup>	
1	0.8/EtOH	Reflux	2	67	
2	0.8/MeOH	Reflux	3	62	
3	0.8/CICH <sub>2</sub> CH <sub>2</sub> CI	Reflux	3	43	
4	0.8/CH <sub>3</sub> CN	Reflux	4	64	
5	0.8/DMF	100	3	76	
6	0.8/DMSO	100	4	70	
7	0.8/H <sub>2</sub> O	Reflux	5	9	
8	0.8/solvent-free	100	1	96	
9	None/solvent-free	130	12	0	
10	0.3/solvent-free	100	4	48	
11	0.6/solvent-free	100	2	70	
12	0.7/solvent-free	100	1	89	
13	0.9/solvent-free	100	1	94	
14	0.8/solvent-free	r.t.	6	26	
15	0.8/solvent-free	80	2	83	
16	0.8/solvent-free	110	1	95	
<sup>a</sup> Reaction conditions: aniline (1 mmol), triethylorthoformate (1.2 mmol) and sodium azide (1 mmol). <sup>b</sup> Isolated yield.					

solvent-free conditions. As evident from Table 2, solvent-free condi-

tions at 100 °C with 0.8 mol% of catalyst are obviously the best choices for this reaction (Table 2, entry 8).

We also evaluated the amount of catalyst required for the reaction. As evident from Table 2, with no catalyst, the reaction does not proceed even at a high temperature (entry 9). The best result is achieved by carrying out the reaction with the catalyst (0.8 mol %), aniline (1 mmol), triethylorthoformate (1.2 mmol) and sodium azide (1 mmol) under solvent-free conditions at 100°°C (Table 2, entry 8). Decreasing the catalyst concentration results in lower yields under the same conditions (Table 2, entries 10–12). Further increase in catalyst concentration does not show any significant effect on reaction time and yield of product (Table 2, entry 13).

Furthermore, the effect of temperature was also studied by carrying out the model reaction. At room temperature a useful conversion is not observed (Table 2, entry 14). However the productivity increases on raising the temperature. Thus, the best results for this reaction are obtained with 0.8 mol% of catalyst under solvent-free conditions at 100  $^{\circ}$ C (Table 2, entry 8).

After optimization of the reaction conditions, the reaction of triethylorthoformate and sodium azide with various amines was

Table 3. Preparation of 1-substituted 1/H-tetrazoles in the presence of  $Fe_3O_4@SiO_2\text{-}DAQ\text{-}Cu(II)$  catalyst^

R- (3	NH <sub>2</sub> + HC(OEt) <sub>3</sub> + 3) (4)	NaN <sub>3</sub> (5)	Fe <sub>3</sub> O₄@SiO₂-DAQ-Cu(II) Solvent-free, 100 °C R−N / N 6 (a-m)			
Entry	R	Product	Time (h)	Yield (%) <sup>b</sup>	M.p. (lit.) (°C) <sup>c</sup>	
1	C <sub>6</sub> H₅	ба	1	96	61-62 (63-64) <sup>[28]</sup>	
2	4-MeC <sub>6</sub> H <sub>4</sub>	6b	1	91	92–93 (92) <sup>[51]</sup>	
3	2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	6с	0.75	95	131–132 (133) <sup>[52]</sup>	
4	4-MeOC <sub>6</sub> H <sub>4</sub>	6d	0.75	93	114–116 (115) <sup>[52]</sup>	
5	$4-BrC_6H_4$	бе	1.5	89	170–172 (170) <sup>[52]</sup>	
6	4-CIC <sub>6</sub> H <sub>4</sub>	6f	1.5	86	150–152 (153) <sup>[52]</sup>	
7	$4-NO_2C_6H_4$	6 g	2	84	199–200 (200–201) <sup>[28]</sup>	
8	4-MeCOC <sub>6</sub> H <sub>4</sub>	6 h	1.5	85	178–179 (177) <sup>[15]</sup>	
9	3-Pyridyl	<b>6i</b>	3	84	77–79 (77) <sup>[28]</sup>	
10	6-Methyl-2-pyridyl	бј	2	90	107–108 (106) <sup>[52]</sup>	
11	$C_6H_5CH_2$	6 k	1.25	88	132–133 (130–132) <sup>[15]</sup>	
12	$CH_3CH_2CH_2CH_2$	6 I	2.5	79	141–142 (143) <sup>[15]</sup>	
13	Cyclohexyl	6 m	3	85	168–169 (170) <sup>[52]</sup>	

<sup>a</sup>Reaction conditions: amine compounds (1 mmol), NaN<sub>3</sub> (1 mmol), triethylorthoformate (1.2 mmol), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) (0.8 mol%), solvent-free, 100 °C.

<sup>b</sup>Isolated yield.

<sup>c</sup>Melting points reported in parentheses refer to literature melting points.

Table 4. Effect of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) as catalyst, solvent and tem-

perature on the formation of 5-phenyl-1H-tetrazoles<sup>a</sup>

$ \begin{array}{c c} \hline \\ \hline $						
Entry	Catalyst amount (mol%)/solvent	Temp. (°C)	Time (h)	Yield (%) <sup>b</sup>		
1	0.9/EtOH	Reflux	12	38		
2	0.9/MeOH	Reflux	12	27		
3	0.9/H <sub>2</sub> O	Reflux	16	18		
4	0.9/CH <sub>3</sub> CN	Reflux	24	14		
5	0.9/CHCl <sub>3</sub>	Reflux	12	0		
6	0.9/CH <sub>2</sub> Cl <sub>2</sub>	Reflux	12	0		
7	0.9/1,4-dioxane	Reflux	12	0		
8	0.9/toluene	100	6	54		
9	0.9/NMP	100	4	61		
10	0.9/DMSO	100	8	58		
11	0.9/DMF	100	2.5	96		
12	None/DMF	140	24	0		
13	0.3/DMF	100	6	27		
14	0.6/DMF	100	6	71		
15	0.7/DMF	100	3	82		
16	0.8/DMF	100	3	85		
17	1.0/DMF	100	3	94		
18	0.9/DMF	r.t.	8	Trace		
19	0.9/DMF	80	4	63		
20	0.9/DMF	110	2.5	95		

<sup>a</sup>Reaction conditions: benzonitrile (1 mmol) and sodium azide (1.2 mmol). <sup>b</sup>Isolated yield. carried out in the presence of 0.8 mol% Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II). As evident from Table 3, high yields of the relevant products are obtained for the 1-substituted 1*H*-tetrazoles with electron-withdrawing or electron-donating groups (e.g. Br, Cl, NO<sub>2</sub>, COMe, Me, OMe; Table 3, entries 2–10). Heterocyclic compounds such as aminopyridines efficiently react to give the corresponding tetrazoles (Table 3, entries 9 and 10). Also, the reactions with aliphatic amines such as benzylamine, *n*-butylamine and cyclohexanamine give the desired products in good yields of 88, 79 and 85%, respectively (Table 3, entries 11–13).

Also, the catalytic activity of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) was studied in order to optimize the protocol for formation of 5-substituted 1*H*-tetrazoles using benzonitrile and NaN<sub>3</sub> as model reaction. Our optimization data are: 1 mmol of benzonitrile, 1.2 mmol of sodium azide, 0.9 mol% of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) catalyst and 3 ml of DMF at 100 °C (Table 4, entry 11).

After optimizing the reaction conditions, we next examined the generality of the reaction using sodium azide and various benzonitriles. The results are summarized in Table 5. Aromatic nitriles containing both electron-donating and electron-withdrawing groups undergo conversion smoothly in high to excellent yields. The nature of the substituents on the benzonitriles had a significant effect on the reaction time. Reactions of electron-poor aromatic and heteroaromatic nitriles are completed within a few hours (Table 5, entries 6–12). Nitriles having electron-donating substituents require longer reaction time (Table 5, entries 2–4). The *ortho*-substituted nitriles render lower yields (Table 5, entry 8) due to steric hindrance. Benzyl nitriles require longer reaction times than benzonitriles because of absence of conjugated electron withdrawing aromatic ring in benzyl nitrile (Table 5, entries 15 and 16).

<b>Table 5.</b> $Fe_3O_4@SiO_2-DAQ-Cu(II)$ -catalysed synthesis of 5-substituted 1 <i>H</i> -tetrazoles <sup>a</sup>						
R <sup>1</sup> -CN + NaN <sub>3</sub> (7) (5) Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -DAQ-Cu(II) DMF, 100 °C H H 8 (a-p)						
Entry	Substrate	Product	Time (h)	Yield (%) <sup>b</sup>	M.p. (lit.) (°C) <sup>c</sup>	
1	C <sub>6</sub> H <sub>5</sub>	8a	2.5	96	215–217 (215) <sup>[52]</sup>	
2	4-MeC <sub>6</sub> H <sub>4</sub>	8b	4	91	249–250 (248–249) <sup>[53]</sup>	
3	4-MeOC <sub>6</sub> H <sub>4</sub>	8c	5	87	230–231 (231–233) <sup>[53]</sup>	
4	4-OHC <sub>6</sub> H <sub>4</sub>	8d	5	93	235–236 (234) <sup>[52]</sup>	
5	$4-BrC_6H_4$	8e	4	93	266–268 (266–267) <sup>[15]</sup>	
6	4-CIC <sub>6</sub> H <sub>4</sub>	8f	3	88	260–261 (261–263) <sup>[28]</sup>	
7	$4-NO_2C_6H_4$	8 g	2	95	217–218 (219–220) <sup>[51]</sup>	
8	2-CNC <sub>6</sub> H <sub>4</sub>	8 h	4.5	83	209–211 (208–210) <sup>[51]</sup>	
9	3-CNC <sub>6</sub> H <sub>4</sub>	8i	3	92	210–212 (213) <sup>[52]</sup>	
10	$4-CNC_6H_4$	8j	3	95	255 (254–256) <sup>[15]</sup>	
11	2-Pyridyl	8 k	3.5	94	211–212 (210–211) <sup>[28]</sup>	
12	3-Pyridyl	81	4	92	237–238 (239) <sup>[28]</sup>	
13	1-Naphthalene	8 m	3	95	261–262 (264) <sup>[52]</sup>	
14	9-Phenanthrenyl	8n	6	88	216 (214–216) <sup>[15]</sup>	
15	$C_6H_5CH_2$	80	6	84	121–122 (123–124) <sup>[51]</sup>	
16	$4-NO_2C_6H_5CH_2$	8p	4	90	181–183 (184) <sup>[52]</sup>	

<sup>a</sup>Reaction carried out with nitrile (1.0 mmol), NaN<sub>3</sub> (1.2 mmol) and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) (0.9 mol%) in 3 ml of DMF at 100 °C. <sup>b</sup>Isolated yield.

<sup>c</sup>Melting points reported in parentheses refer to literature melting points.

**Table 6.** Comparison of various catalysts used in synthesis of

 5-substituted 1*H*-tetrazole from benzonitrile

Entry	Catalyst	Conditions	Time (h)	Yield (%)	Ref.
1	Cu–Zn alloy nanopowder	DMF/120 °C	10	95	[54]
2	SiO <sub>2</sub> -H <sub>2</sub> SO <sub>4</sub>	DMF/130 °C	12	88	[55]
3	Nano-CuFe <sub>2</sub> O <sub>4</sub>	DMF/120 °C	12	82	[26]
4	CoY zeolite	DMF/120 °C	14	90	[56]
5	FeCl <sub>3</sub> -SiO <sub>2</sub>	DMF/120 °C	12	79	[57]
6	ZnS nanospheres	DMF/120 °C	36	96	[1]
7	Sulfated zirconia	DMF/110-120 °C	24	90	[58]
8	ZnWO <sub>4</sub>	DMF/120 °C	24	75	[23]
9	Zn/Al-HT	DMF/120-130 °C	12	84	[22]
10	Nano-ZnO/Co <sub>3</sub> O <sub>4</sub>	DMF/120 °C	12	90	[25]
11	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -DAQ-Cu(II)	DMF/100 °C	2.5	96	This work

A comparison among Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) and other catalysts reported in the literature, in the synthesis of 5-phenyl-1*H*-tetrazoles, reveals advantages of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) over the most of them in terms of higher yield and shorter reaction time (Table 6, entry 11).

In order to confirm the reusability and stability of this magnetic catalyst in the synthesis of 1- and 5-phenyl-1*H*-tetrazoles, it was recovered by applying a magnetic field and reused six times without observation of appreciable loss in its catalytic activity (Fig. 6(A)).

Also, to confirm if any aggregation of the nanoparticles occurs, TEM analysis of the reused catalyst was performed (Fig. 6(B)). After





**Figure 6.** (A) Recyclability of  $Fe_3O_4@SiO_2-DAQ-Cu(II)$  in the synthesis of (a) 1-phenyl-1*H*-tetrazole and (b) 5-phenyl-1*H*-tetrazole. (B) TEM image of  $Fe_3O_4@SiO_2-DAQ-Cu(II)$  nanoparticles after six reaction cycles.

six repeat reaction cycles, we do not observe significant change in the morphology of the catalyst, but some nanoparticles might have aggregated onto the surfaces of the matrices.

To further confirm the robustness of the catalyst and to measure the extent of Cu leaching after the reactions, we carried out a hot filtration experiment.<sup>[42]</sup> For this, we studied the condensation of benzonitrile and sodium azide in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) catalyst under optimized conditions. When the reaction was half complete, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-DAQ-Cu(II) nanoparticles were removed *in situ* at the reaction temperature, and the reactants were allowed to undergo further reaction in the solution. These results indicate that after removal of the heterogeneous catalyst, the clear filtrate was weakly active suggesting that only slight leaching had occurred during the reaction.

Also, leaching of Cu into the reaction mixture of benzonitrile and sodium azide under optimized conditions was tested, using ICP analysis. The results show that the difference between the Cu content of the fresh catalyst and the reused catalyst, in the sixth run, is only 2.66%. Therefore, the analysis of the reaction mixture using the ICP technique shows that the leaching of Cu is negligible.

## Conclusions

In summary, we have reported that 1,4-dihydroxyanthraquinonecopper(II) supported on superparamagnetic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles can be an efficient and reusable catalyst for one-pot syntheses of 1- and 5-substituted 1*H*-tetrazoles from nitriles and amines in good to excellent yields. This method has notable advantages such as thermal stability, heterogeneous nature, easy preparation and easy separation of catalyst, short reaction time, clean and simple procedure, excellent yields, easy product separation and purification and lower loading of catalyst compared with other methods. These factors make this method an alternative to the previous methodologies for the scale-up of these reactions. In addition, the catalyst could be successfully recovered and recycled at least six times without a noticeable decrease in catalytic activity.

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