Cu-phthalocyanine Coated Hybrid Magnetic Nanoparticles: Preparation and Application in the Synthesis of Mono- and Bis pyrano[2,3-*d*]pyrimidinones and mono- and Bis-2-amino-4*H*-pyrans

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ABSTRACT: *In this research, Cu-phthalocyanine coated hybrid magnetic nanoparticles have been prepared in a simple method and evaluated as an efficient catalyst in the preparation of mono- and bis-pyrano[2,3-d]pyrimidinones and mono- and bis-2-amino-4H-pyrans from the condensation reaction of 1,3-dimethylbarbituric acid or 4-hydroxycumarin with malononitrile and mono- and bis-aldehydes under ultrasonic irradiation. The catalyst could be easily recovered in the presence of the external magnetic field and reused five times without significant loss of activity and mass. The magnetic nanoparticles were characterized using Fourier Transform InfraRed (FT-IR) spectra, X-Ray Diffraction (XRD) spectroscopy, Scanning Electron Microscopy (SEM), Thermal Gravimetric Analysis (TGA). The results showed the spherical structures of hybrid magnetic nanoparticles and the average size is about 37 nm.*

KEYWORDS: *Hybrid magnetic nanoparticles; Phthalocyanine; Pyrano[2,3-d]pyrimidinone; 2-Amino-4H-pyran; Ultrasonic irradiation.*

INTRODUCTION

Phthalocyanines have drawn considerable attention and world-wide interests because of their properties such as the semiconductivity, high thermal stability, photoconductivity, etc.[1] They have been widely used in many fields such as photovoltaic cells,[2] liquid crystals,[3] data storage,[4] non-linear optical applications,[5] optical disks,[6] and photodynamic therapy.[7] Recently phthalocyanines, as a catalyst, have received great attention. Metallophthalocyanines are used, for example, as catalysts in the Merox process for the industrial desulfurization of petroleum[8-9] and they are very well known to catalyze a variety of oxidative transformations.[10-11]

In recent years, major efforts have been focused on investigation and development of effective methods to the preparation of efficient catalysts. There is currently intense interest in the use of magnetic nanoparticles for a wide range of magnetic nanoparticles (MNPs) catalysts applications.[12-13] Some unique properties of magnetic nanoparticles such as their high activity for the reaction challenging in terms of energy, high selectivity for valuable products, a long lifetime and easy separation

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of the catalyst by a simple magnet make them as promising and widely interesting candidates for catalysis applications.[14]

Recently hybrid magnetic nanoparticles have attracted significant interest. However, the efficiency of applications of bar Fe_3O_4 nanoparticles is limited due to their high tendency to aggregation and oxidation, so many attempts have focused on the coating of magnetite nanoparticles to preparation of stable hybrid materials [15-16].

Phthalocyanines have recently emerged as are potential and versatile candidates for construction of magnetic hybrid nanoparticles because of their thermal and chemical stability.[17]

Pyrano[2,3-*d*]- and pyrido[2,3-*d*]pyrimidines and 4*H*-pyrans are the important heterocyclic compounds which have been widely studied over the past years due to their wide range of biological activities. Compounds with pyrano[2,3-*d*]- and pyrido[2,3-*d*]pyrimidines ring systems have diverse pharmacological activities such as antitumour,[18] cardiotonic, hepatoprotactive, antihypertensive,[19] antibronchitic[20] and antifungal activity.[21]

4*H*-Pyrans are constituent of some natural products.[22] They also possess potent biological activities like antibacterial, antiviral, spasmolytic, and antianaphylactic.[23–26] In addition, these compounds are used in the treatment of Alzheimer, Schizophrenia, and Mycolonous diseases.[27] The derivatives of 2-amino-4*H*-pyran are the useful photoactive materials[28]

The synthesis of pyrano[2,3-*d*]pyrimidinones and 2-amino-4*H*-pyrans has been catalyzed by variety of reagents such as: NaOH/piperidine,[29] piperidine,[30] triethylamine,[31] sodium methoxide,[32] 1,1,3,3-tetramethylguanidine,[33] HMTAB,[34] TEBA,[35] $RE(PFO)_3$,[36] NaBr,[37] (*S*)-proline,[38] the use of microwave irradiation,[39] KF-basic alumina under ultrasound irradiation,[40] DAHP,[41] Na_2SeO_4 [42] Mg/La mixed oxide catalyst,[43] TMG-[bmim][X] and [2-aemim][PF_6],[44] morpholine,[45] CTACl (cetyltrimethylammonium chloride),[46] TBAB[47] and aminoalcohol.[48] Recently, it was found that chemical bases could be replaced with an electrogenerated base to promote reactions.[49]

Although pseudo five-component reaction of malononitrile and bis-aldehydes with 4-hydroxycoumarin was previously investigated,[50-51] there is no report on the reaction of malononitrile and bis-aldehydes with barbituric acid for the synthesis of bis-pyrano[2,3-*d*]pyrimidinones.

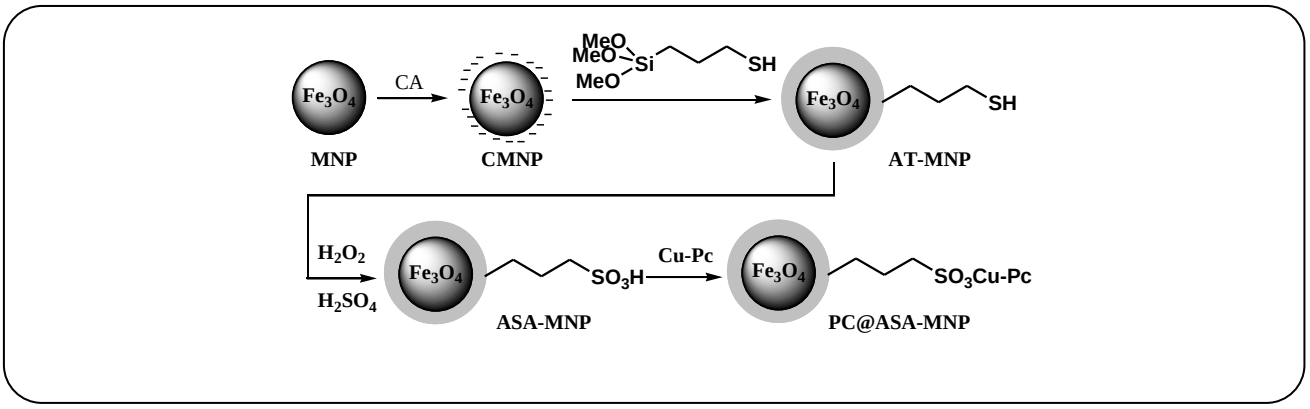
Encouraged with these information and due to our interest in the preparation and catalytic evaluation of new hybrid magnetic nanoparticles,[14] herein, we prepared new Cu-phthalocyanine coated alkyl sulfonic acid-functionalized magnetic nanoparticles (Pc@ASA–MNPs) (Scheme 1) and successfully used them as catalyst in the synthesis of mono- and bis-pyrano[2,3-*d*]pyrimidinones and mono- and bis-2-amino-4*H*-pyrans by condensation reaction of 1,3-dimethylbarbituric acid or 4-hydroxycumarin with malononitrile and mono- and bis-aldehydes under ultrasonic irradiation at 50 °C (Scheme 2).

EXPERIMENTAL SECTION

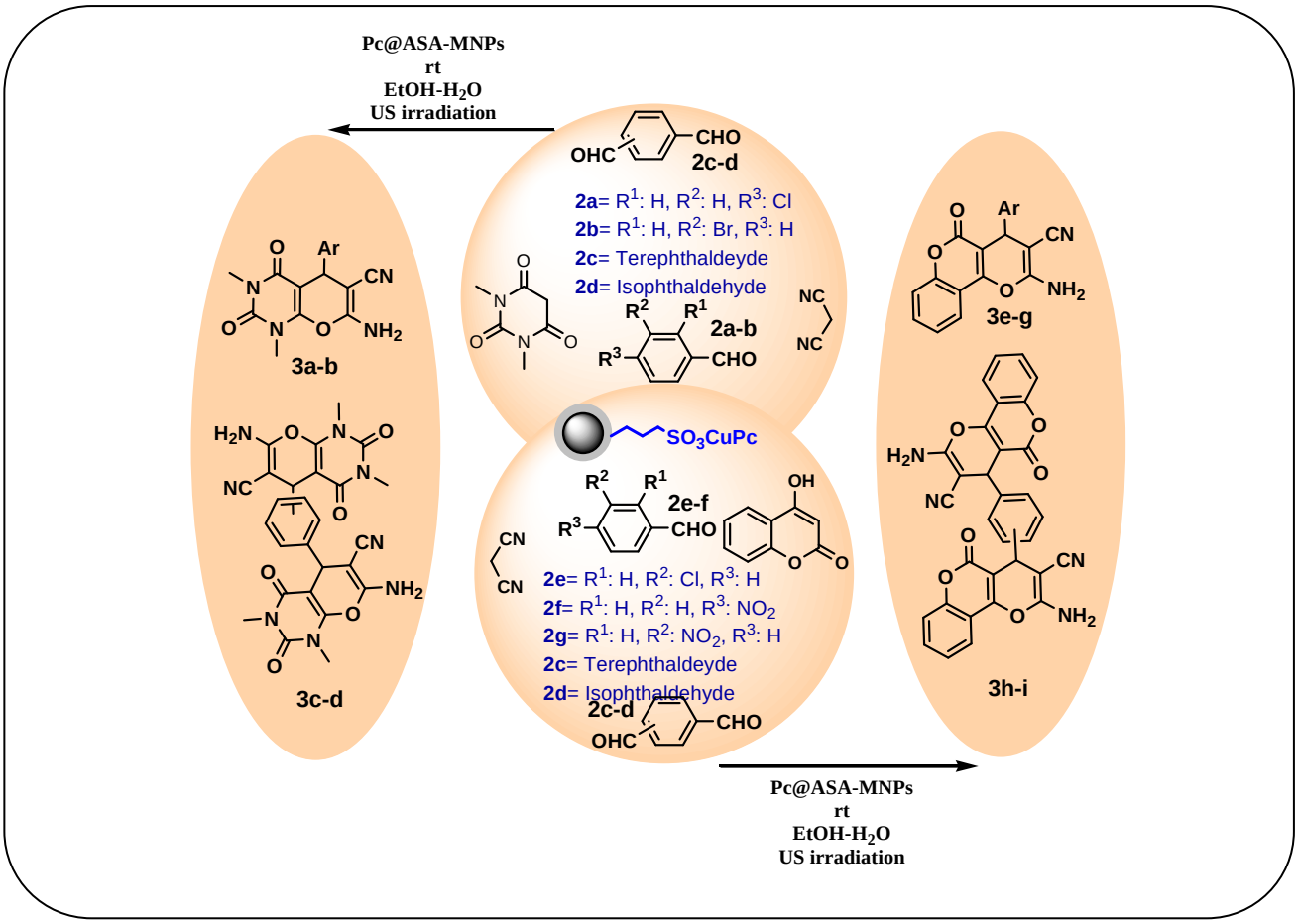
Most of reagents were the best available purity and used without further purification. Fe_3O_4 nanoparticles (MNP), citric acid modified nanoparticles (CMNPs) and alkyl sulfonic acid magnetic nanoparticles (ASA-MNPs) were prepared according to the literature procedure [12, 52-53] Sonication was performed in a Struers Metason 200 HT ultrasonic cleaner with a frequency of 50-60 Hz and an output power of 140 W. The products were characterized by elemental analysis and by IR, ^{1}HNMR, ^{13}CNMR and mass spectroscopy. Fourier-transform IR spectra were recorded by using a Unicom Galaxy Series FTIR 5000 Spectrophotometer. ^{1}H and ^{13}CNMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 300 and 75 MHz, respectively. Mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer operated in the EI mode. Elemental analyses were performed by using Vario EL III elemental analyzer.

General procedure for the preparation of CuPc

At first, dicyano-compound **5** was synthesized by reaction of 4-nitrophthalonitrile 1 (1 mmol), (pyridine-4-yl)methanol **2** (1 mmol) and K_2CO_3 (1 mmol) in 2 mL DMF. The mixture was stirred at room temperature for 24 h. After completion of the reaction, 5 mL acetone and 4 mL water was added respectively to the reaction mixture and the resulting precipitates were separated and washed with 10 mL hot water and 10 mL ethanol. Then mixture of resulting dicyano-compound **5** (3 mmol), CuCl (1 mmol) and DBU (3 drops) in dimethylamino ethanol (DMAE)



Scheme 1: Preparation of Cu-phthalocyanine coated hybrid magnetic nanoparticles (Pc@ASA-MNPs)

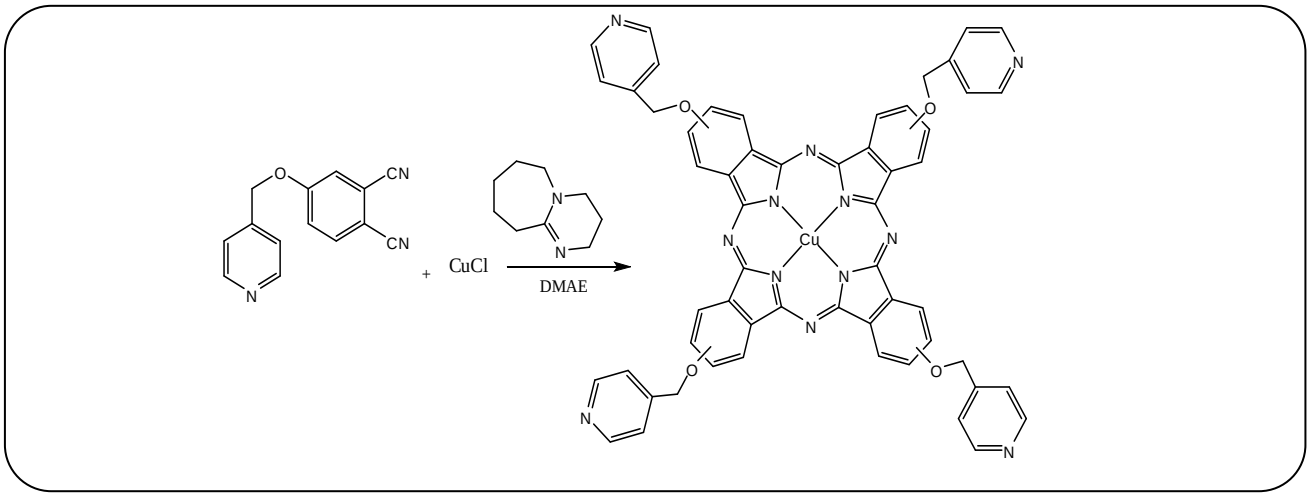


Scheme 2. Synthesis of (mono- and bis-pyrano[2,3-d]pyrimidinones) (3a-d) and (mono- and bis-2-amino-4H-pyrans) (3e-i) catalyzed by Pc@ASA-MNPs.

(10 mL) was refluxed under nitrogen atmosphere for 18 h. The reaction mixture was then cooled to room temperature. In the next step ethanol was added and the product was filtered under reduced pressure. The green solid was washed several times with hot ethanol.

General procedure for the preparation of (ASA-MNPs)

Citric acid modified magnetic nanoparticles (250 mg) were dispersed in 50 mL ethanol/water (1:1) and the mixture was sonicated for 30 min to maintain proper dispersion. Then, under continuous mechanical stirring,



Scheme 3. Preparation of CuPc.

1 mL 3-mercaptopropyltrimethoxysilane was added. After mechanical stirring at room temperature for 4 h, black precipitate (AT-MNPs) was isolated by magnetic decantation and washed with de-ionized water and ethanol and dried at room temperature. In order to preparation of ASA-MNPs, 10 mL H_2O_2 (30%) was added to the mixture of AT-MNPs in MeOH/water (1:1) and the mixture was stirred at room temperature overnight. After completion of oxidation, the resulting ASA-MNPs were collected with magnet and washed with deionized water and aqueous solution of H_2SO_4 (1 molar). After that the resulting ASA-MNPs washed with deionized water and finally dried under vacuum.

General procedure for the preparation of (Pc@ASA-MNPs)

ASA-MNPs (0.1 gr) were dispersed in 5 mL DMF and the mixture was sonicated for 30 min to maintain proper dispersion. Then CuPc(I) (0.05 gr dissolved in 3 mL DMF) added to the mixture of ASA-MNPs in DMF and sonicated for 20 min. After completion of reaction the resulting Pc@ASA-MNPs were collected with magnet and washed with ethanol, chloroform and deionized water and finally dried under vacuum.

General procedure for the preparation of mono- and bis-2-amino-4H-pyrans (3e-i)

A mixture of aromatic aldehyde (**2a-b** or **2e-g**), 1,3-dimethylbarbituric acid (or 4-hydroxycoumarin) (1 mmol), malononitrile (1 mmol) and Pc@ASA-MNPs (0.05 g) in ethanol–water (4:1) was exposed to ultrasonic irradiation at 50 °C for the appropriate time according to Table 2. Upon completion of the reaction as monitored by TLC, the Pc@ASA-MNPs was removed under applied external magnetic field. The solid products that obtained were collected by filtration, washed with hot C_2H_5OH and hot water. Same procedure was followed for the preparation of bis-pyrano[2,3-*d*]pyrimidinones (**3a-d**) or bis-2-amino-4*H*-pyrans (**3e-i**) except two mmol of 1,3-dimethylbarbituric acid or 4-hydroxycoumarin and 2 mmol of malononitrile were subjected to reaction with one mmol of their corresponding bis-aldehydes (**2c-d**).

Spectral data of the selected products

7-Amino-5-(4-chlorophenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile (3a)

White; solid; isolated yield 89%, MP: 243-247 °C. IR (KBr) (ν_{max}, cm^{-1}): 3416, 3373, 3306, 3190, 2960, 2883, 2195, 1707, 1633, 1493, 1390, 1226, 1190, 1085, 1035, 968, 837. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 3.08 (3H, s, CH_3), 3.35 (3H, s, CH_3), 4.35(1H, s, CH), 7.34-7.38 (3H, m, H_{arom} and NH_2), 7.54-7.56 (1H, d, *J*=8.8, H_{arom}), 7.72-7.74 (1H, d , *J* =8.4, H_{arom}), 7.95-7.97 (1H, d, J=8.4, H_{arom}).

7-Amino-5-(3-bromophenyl)-1,3-dimethyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-pyrano[2,3-d]pyrimidine-6-carbonitrile(3b)

Yellow; solid; isolated yield 90%, MP: 278-280 °C. IR (KBr) (ν_{max}, cm^{-1}): 3377, 3311, 3267, 3200, 2202, 1714, 1685, 1637, 1489, 1392, 1226, 1186, 1026, 972, 852. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 3.20 (3H, s, CH_3), 3.42 (3H , s, CH_3), 4.46 (1H, s, CH) 7.13-7.15 (1H, d, *J*=8 Hz, H_{arom}), 7.19 (2H, s, NH_2), 7.21-7.28 (1H, m,

H_{arom}), 7.26-7.27 (1H, t, H_{arom}), 7.30-7.32 (1H, m, H_{arom}). Anal. calc. for $C_{16}H_{13}N_4O_3Cl$: C, 55.74; H, 3.80; N, 16.25%. Found: C, 55.84; H, 3.96; N, 16.53%.

5,5'-(1,4-Phenylene)bis(7-amino-1,3-dimethyl-2,4-dioxo-2,3,4,5 -tetrahydro -1H- pyrano[2,3-d]pyrimidine-6-carbonitrile (3c)

Yellow; solid; isolated yield 85%, MP: 297 ˚C. IR (KBr) (ν_{max}, cm^{-1}): 3456, 3333, 3202, 2964, 2885, 2198, 1697, 1637, 1493, 1386, 1230, 1186, 1089, 968, 796. ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H (ppm): 3.07 (6H, s, CH_3), 3.14 (6H, s, CH_3), 4.45 (2H, s, CH), 7.46 (4H, s, NH_2), 7.51-7.53 (2H, d, *J*=8.4 Hz, H_{arom}), 7.89-7.91 (2H, d, *J*=8 Hz, H_{arom}) ppm. ^{13}C-NMR (DMSO-d_6, 75 MHz) δ: 27.6, 27.7, 36.5, 55. 9, 87.6, 127.0, 127.1, 127.1, 128.5, 130.7, 157.6, 157.9, 160.4, 161.1. Anal. calc. for $C_{26}H_{22}N_8O_6$: C, 57.56; H, 4.09; N, 20.65%. Found: C, 57.61; H, 4.31; N, 20.79%.

5,5'-(1,4-Phenylene)bis(7-amino-1,3-dimethyl -2,4-dioxo-2,3,4,5- tetrahydro -1H- pyrano[2,3-d]pyrimidine-6-carbonitrile (3d)

Yellow; solid; isolated yield 90%, MP: >300 °C. IR (KBr) (ν_{max}, cm^{-1}): 3364, 3327, 3190, 2962, 2200, 1716, 1678, 1635, 1493, 1396, 1226, 1182, 1143, 1080, 754. ^{1}H NMR (DMSO-d_6, 400 MHz) δ_H (ppm): 3.07-3.16 (12H, s, CH_3), 4.42 (2H, s, CH), 7.37 (2H, s, NH_2), 7.43 (2H, s, NH_2) 7.56-7.64 (2H, m, H_{arom}), 7.81-7.83 (2H, m, H_{arom}). ^{13}C NMR (DMSO-d_6, 75 MHz) δ_C (ppm): 27.6, 27.9, 28.59, 29.0, 36.2, 57.7, 88.0, 114.1, 128.7, 129.3, 129.4, 131.5, 133.5, 144.1, 145.6, 151.2, 151.3, 155.2, 157.6, 160.4, 161.2. Anal. calc. for $C_{26}H_{22}N_8O_6$: C, 57.56; H, 4.09; N, 20.65%. Found: C, 57.68; H, 4.28; N, 20.81%.

2-Amino-4-(3-chlorophenyl) -5- oxo -4,5- dihydropyrano [3,2-c]chromene-3-carbonitrile (3e)

White; solid; isolated yield 92%, MP: 253-256 °C. IR (KBr) (ν_{max}, cm^{-1}): 3383, 3323, 3256, 3196, 2206, 1697, 1668, 1608, 1383, 760. ^{1}H NMR (DMSO-d_6, 300 MHz) δ_H (ppm): 4.51(1H, s, CH), 7.23-7.35 (4H, m, H_{arom}), 7.48 (2H, bs, NH_2), 7.46-7.53 (2H, m, H_{arom}), 7.72 (1H, dt, *J*=8.1 and 1.6 Hz, H_{arom}), 7.90 (1H, dd, J=7.9 and 1.4 Hz, H_{arom}). Anal. calc. for $C_{19}H_{11}N_2O_3Cl$: C, 65.06; H, 3.16; N, 7.99%. Found: C, 65.27; H, 3.29; N, 8.13%.

2-Amino-4-(4-nitrophenyl)-5-oxo-4,5- dihydropyrano [3,2-c]chromene-3-carbonitrile (3f)

Yellow; solid; isolated yield 80%, MP: 278-280 °C. IR (KBr) (ν_{max}, cm^{-1}): 3481, 3433, 3369, 3335, 3149, 3070, 2195, 1718, 1672, 1606, 1504, 1348, 765. ^{1}H NMR (DMSO-d_6, 300 MHz) δ_H (ppm): 4.67 (1H, s, CH), 7.46-7.61 (4H, m, H_{arom}), 7.58 (2H, bs, NH_2), 7.74 (1H, t, *J*=8.0 Hz, H_{arom}), 7.91 (1H, d, *J*=7.8 Hz, H_{arom}), 8.18 (1H, d, *J*=8.4 Hz, H_{arom}). Anal. calc. for $C_{19}H_{11}N_3O_5$: C, 63.16; H, 3.07; N, 11.63%. Found: C, 63.34; H, 3.35; N, 11.86%.

2-Amino-4-(3-nitrophenyl)-5-oxo-4,5-dihydropyrano[3,2-c] chromene-3-carbonitrile (3g)

Withe; solid; isolated yield 80%, MP: 264-266 °C. FT- IR (KBr) (ν_{max}, cm^{-1}): 3398, 3323, 3211, 3088, 2876, 2195, 1699, 1674, 1602, 1531, 1456, 1379, 1062, 760. ^{1}H NMR (DMSO-d_6, 300 MHz) δ_H (ppm): 4.73 (1H, s, CH), 7.45-7.65 (3H, m, H_{arom}), 7.56 (2H, bs, NH_2), 7.70-7.82 (2H, m, H_{arom}), 7.91 (1H, dd, *J*=7.90 and 1.4 Hz, H_{arom}), 8.10-8.14 (2H, m, H_{arom}). Anal. calc. for $C_{19}H_{11}N_3O_5$: C, 63.16; H, 3.07; N, 11.63%. Found: C, 63.28; H, 3.31; N, 11.91%.

4,4`-(1,4-Phenylene)bis(2-amino-5-oxo-4,5-dihydropyrano [3,2-c]chromene-3-carbonitrile (3h)

Withe; solid; isolated yield 91%, MP: >300 °C. FT- IR (KBr) (ν_{max}, cm^{-1}): 3468, 3393, 3325, 3256, 3192, 2198, 1709, 1674, 1606, 1494, 1379, 1058, 760. ^{1}H NMR (DMSO-d_6, 300 MHz) δ_H (ppm): 4.42 (2H, s, CH), 7.20-7.41 (4H, m, H_{arom}), 7.36 (4H, s, NH_2), 7.41-7.50 (4H, m, H_{arom}), 7.69 (2H, m, H_{arom}), 7.87-7.90 (2H, m, H_{arom}). ^{13}C-NMR (DMSO-d_6, 75 MHz) δ: 37.0, 58.3, 104.4, 113.3, 115.5, 116.9, 119.7, 125.1, 128.2, 131.3, 133.3, 142.5, 152.5, 153.9, 158.5, 160.0. Anal. calc. for $C_{32}H_{18}N_4O_6$: C, 69.31; H, 3.27; N, 10.10%. Found: C, 69.54; H, 3.65; N, 10.31%.

4,4`-(1,4- Phenylene)bis(2-amino-5-oxo-4,5-dihydropyrano [3,2-c]chromene-3-carbonitrile (3i)

Withe; solid; isolated yield 80%, MP: 294-296 °C. FT- IR (KBr) (ν_{max}, cm^{-1}): 3408, 3319, 3215, 3190, 2193, 1714, 1672, 1606, 1494, 1379, 1055, 761. Anal. calc. for $C_{32}H_{18}N_4O_6$: C, 69.31; H, 3.27; N, 10.10%. Found: C, 69.61; H, 3.58; N, 10.23%.

Table 1: The optimization of reaction for the synthesis of 3a under ultrasonic irradiation.

Entry[a]	Pc@ASA-MNPs	Time	Solvent	Yield
1	(0.01 gr)	30 min	EtOH-H_2O	30%
2	(0.02 gr)	30 min	EtOH-H_2O	35%
3	(0.05 gr)	30 min	EtOH-H_2O	88%
4	(0.1 gr)	30 min	EtOH-H_2O	89%
5	(0.05 gr)	30 min	EtOH	80 %
6	(0.05 gr)	30 min	CH_3CN	30%
7	(0.05 gr)	30 min	THF	47%
8	(0.05 gr)	30 min	CH_2Cl_2	20%

[a]4-Chlorobenzaldehyde (1 mmol) , 1,3-dimethylbarbituric acid (1 mmol) and malononitrile (1 mmol) at r.t. EtOH-H_2O (ratio 4:1).

RESULT AND DISCUTION

In order to our initial optimization studies, 1,3-dimethylbarbituric acid (1 mmol), 4-chlorobenzaldehyde (1 mmol) and *malononitrile* (1 mmol) were selected as representative reactants and reaction was investigated under different conditions (Table 1).

Initially the effect of catalyst quantity on the yield of reaction was evaluated by varying the amounts of catalyst from 0.01 to 0.1 gr under ultrasonic irradiation. After 1 h, with 0.01, 0.02, 0.05 and 0.1 gr of Pc@ASA–MNPs, yields of 30%, 35%, 88% and 89%, were obtained respectively (Table 1, entries 1-4). The solvents also played an important role in this reaction. Several solvents such as EtOH, EtOH-H_2O, THF, MeCN and CH_2Cl_2 were tested for the reaction (Table 1, entries 5-8). The reaction hardly proceeded in CH_2Cl_2. However, the reaction in EtOH-H_2O (ratio 4:1) afforded the product in high yield with nearly complete conversion. Hence, the best reaction conditions were obtained by using 0.05 gr of Pc@ASA–MNPs in EtOH-H_2O (4:1) (Table 1, entry 3) at room temperature.

We next examined a some variety of mono- and bis-aldehydes **2a-g** to establish the scope of this catalytic transformation (Table 2). The synthesis of mono- and bis-pyrano[2,3-d]pyrimidinone **3a-d** were obtained by condensation of aromatic aldehydes **2a-b** or bis-aldehydes **2c-d** (1 mmol) with 1,3-dimethylbarbituric acid (1 mmol for **2a-b** or 2 mmol for **2c-*d***) and malononitrile (1 mmol for **2a-b** or 2.2 mmol for **2c-d**) in the presence of 0.05 g Pc@ASA–MNPs as heterogeneous catalyst. The reaction was carried out in ethanol-H_2O (10 mL, 4:1) under ultrasonic conditions to give products **3a-d** in high yields. The synthesis of mono- and bis-2-amino-4*H*-pyrans **3e-i** were similarly obtained by the condensation of aromatic aldehydes **2e-g** or bis-aldehydes **2c-d** (1 mmol) with 4-hydroxycoumarin (1 mmol for **2e-g** or 2 mmol for **2c-d**) and malononitrile (1 mmol for **2e-g** or 2.2 mmol for **2c-d**) in the presence of Pc@ASA–MNPs (0.05 g) in ethanol-H_2O (10 mL, 4:1) under ultrasonic irradiation at 50 °C. We found that the catalyst Pc@ASA-MNPs showed high catalytic activity and could be recovered and recycled several times without significant loss of activity (Table 2, entry 1).

Cu-phthalocyanine coated alkyl sulfonic acid-functionalized magnetic nanoparticles (Pc@ASA–MNPs) were obtained by reaction of tetra-amino Cu-phthalocyanine with alkyl sulfonic acid functionalized Fe_3O_4 (ASA-MNPs). For this purpose, prior to reaction of tetra-amino Cu-phthalocyanine with ASA-MNPs, magnetic nanoparticles of Fe_3O_4 were synthesized and surface modification of the resulted nanoparticles with negatively charged citrate groups was done and then the surface of them were functionalized by grafting with 3-mercaptopropyltrimethoxysilane. In continues, alkyl sulfonic acid coated Fe_3O_4 nanoparticles were obtained *via* oxidation of the thiol groups by H_2O_2.

The bands at 3000-3500, 561 and 578 cm-1 which appear in all the FTIR spectra, are assigned to the –OH and the Fe–O bonds stretching, respectively. The absorptions at 1558 and 1396 cm^{-1} can be assigned to binding of CA to the iron oxide nanoparticle surfaces.[54] The bands at 2577 cm^{-1} corresponded to the S–H stretching. The formation of alkyl sulfonic acid functionalized Fe_3O_4 was confirmed by the presence

Table 2. Pc@ASA-MNPs catalyzed synthesis of (mono- and bis-pyrano[2,3-d]pyrimidinone) and (mono- and bis-2-amino-4H-pyran) at 50 °C under ultrasonic irradiation.

Entry	Aldehyde	Product	Time/Yield	Mp (°Ca0)	M.p ^{Lit} (°C)
1	2a	(3a)	30 min / 95% (93, 92, 90, 90%)[a]	243-247	
2	2b	(3b)	30min / 90%	278-280	
3	2c	(3c)	30min / 85%	297	
4	2d	(3d)	30min / 90%	>300	
5	2e	(3e)	30min / 92%	253-256	253-256 [50]
6	2f	(3f)	30min / 80%	278-280	264-266 [50]
7	2g	(3g)	30minh / 80%	264-266	
8	2c	(3h)	1h / 91%	>300	307 [50]
9	2d	(3i)	1h / 80%	294-296	296 [50]

a) Yield after recycling of catalyst.

Table 3: Comparison of the efficiency of various catalysts for the synthesis of Pyran derivatives.

Entry	Catalyst	Temp(°C)	Time	Yield
1	AHST-MNP[55]	60	1:45h	94
2	Alum[56]	60	2h	93
3	Alum[56]	60	15h	86
4	SSA-MNP[57]	60	1:20h	95
5	AVOPc –MNPs[58]	Room temperature	20h	92
6	ACoPc-MNPs[59]	Room temperature	15h	93

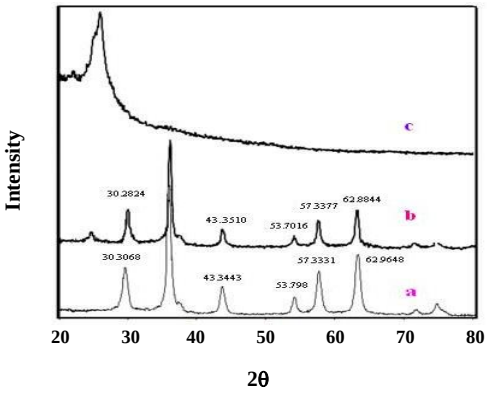


Fig. 1: FT-IR Spectra of (a)MNP (b)CMNP (c) AT-MNP (d) ASA-MNP (e) Pc@ASA-MNPs.

of SO_2 bands at 1043 and 1136 cm^{-1}. Also, the absorption at 1481 and 1604 cm^{-1} related to the C═C stretching aromatic group. Formation of Cu-phthalocyanine was confirmed by complete disappearance of the sharp band for CN vibration in the IR spectra at 2233. The IR spectrum of Cu-phthalocyanine is as follow: 3028, 2918, 2849, 1604, 1483, 1413, 1384, 1342, 1232, 1093, 1058 cm^{-1}.

The sizes of nanoparticles were determined by scanning electron microscopy (SEM). SEM image of Pc@ASA–MNPs is shown in Fig. 2. The SEM photograph illustrated that the Pc@ASA–MNPs is spherical in shape and the average size is about 37 nm. The thermal properties of Pc@ASA–MNPs were analyzed by thermal gravimetric analysis (TGA) in the temperature range of 50-1000 °C under a nitrogen atmosphere. The primary weight loss up to 200 °C was related to the removal of physically adsorbed solvent. The rate of weight loss between 200 and 836 °C is relatively slow that represent the high thermal stability of the Pc@ASA–MNPs. Pc@ASA–MNPs generally is thermally stable until 540 °C and the maximum rate of lost weight for these nanoparticles was started from 540 °C. There is a well-defined mass weight loss of 39%

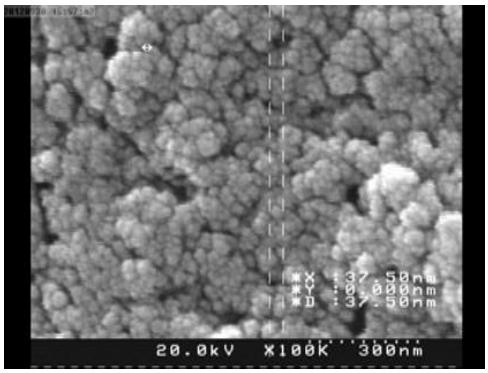


Fig. 2: SEM images of Pc@ASA-MNPs.

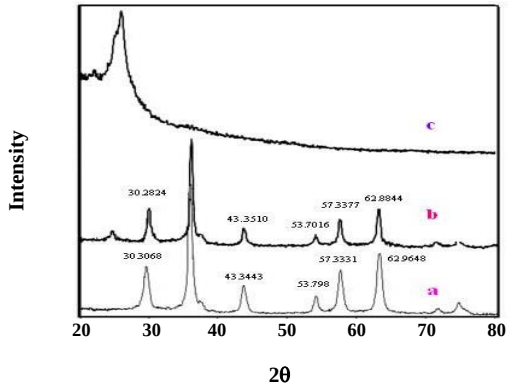


Fig. 3: XRD patterns of (a) ASA-MNPs (b) Pc@ASA-MNPs (c) CuPc.

between 160 and 670 °C related to the breakdown of the alkyl sulfonic acid and phthalocyanine moieties.

XRD patterns of the Pc@ASA–MNPs showed that the cubic structure of the magnetite was well preserved after introduction of the sulfonic acid and Pc functionality. Intensity of the 35.7 reflection of the Pc@ASA–MNPs was decreased after introduction of Pc (I) group.

CONCLUSIONS

In conclusion, we have described the preparation of magnetically recyclable Cu-Phthalocyanine supported on sulfonic acid-functionalized magnetic nanoparticles (Pc@ASA–MNPs) and its catalytic activity has been investigated. The Pc@ASA–MNPs are dispersed into solvents and can be isolated easily with magnet. Its application in the synthesis of mono- and bis-pyrano [2,3-*d*]pyrimidinones and mono- and bis-2-amino-*4H*-pyrans) showed that the short reaction time coupled with the simplicity of the reaction procedure and reusable catalyst make this method one of the most efficient methods for the synthesis of this class of compounds.

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