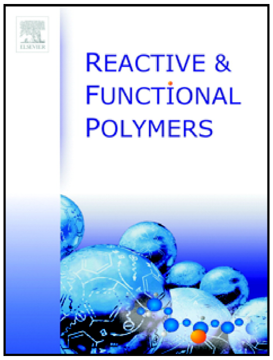

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Synthesis of structurally enhanced magnetite cored poly(propyleneimine) dendrimer nanohybrid material and evaluation of its functionality in sustainable catalysis of condensation reactions

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Abstract: The conventional method of dendrimer synthesis, especially poly(propyleneimine) dendrimer (PPI) involves complicated reaction workup and tedious separation strategies. Since it has greater number of nitrogen atom in the structure, it has numerable applications in different fields. But these dendrimers cannot be recycled for subsequent applications. In order to overcome these issues, for the first time, divergent synthesis of poly(propyleneimine) dendrimer G_3 on silica coated magnetite has been achieved with structurally enhanced PPI dendrimer on core-shell type magnetic silica nanostructure. This nanohybrid material was characterized by using HRTEM, FTIR, XRD, TGA, XPS and VSM studies. Further, nitrogen concentration of PPI dendrimer was quantified by conductometric titration and Prussian blue complex method. The probing of catalytic efficacy of structurally enhanced magnetic cored poly(propyleneimine) dendrimer G_3 as magnetically recyclable heterogeneous organic base catalyst was employed for representative reactions such as Knoevenagel condensation, Knoevenagel- Michael cyclocondensation and Henry reaction at ambient condition. The catalyst was reused for minimum of eight cycles without significant loss of its catalytic activity.

Keywords: magnetic core, PPI dendrimer, nanohybrid, sustainable catalyst, magnetically recoverable

1. **Introduction**

Dendrimers are globular macromolecules with highly branched structure and rich peripheral functional groups which has unique applications in medicine [1], catalysis [2], sensors [3] *etc*. Though dendrimers serve as catalyst in homogenous state with prominent selectivity and catalytic activity, its recoverability is still a challenging task for the chemist [4]. Thus, efforts had been made to improve the recoverability of the dendrimer catalyst using solid supports namely mesoporous silica [5], polymer [6,7], carbon [8], metals [9], metal oxides [10,11] and magnetic nanoparticles [12] *etc*. Among the various solid support, superparamagnetic iron oxide (Fe_3O_4) i.e. magnetite nanoparticle is widely used as a support material due to its specific features like low toxicity, negligible magnetic remanence, high magnetic saturation, minimal aggregation and above all excellent magnetic behavior only in the presence of external magnetic field [13–15]. These magnetic nanoparticle supported dendrimer make a juncture between homogenous and heterogenous catalyst and serve as semiheterogeneous catalyst [16–22]. In recent years, dendrimers anchored on magnetic iron oxide nanoparticle had drawn greater attention due to facile greener and sustainable recovery by magnetic separation method [23]. Alper *et al.*, were the first to report the synthesis of magnetic iron oxide nanoparticle cored poly(amidoamine) (PAMAM) dendrimer with noble metal nanoparticles for selective hydroformylation and hydrogenation catalysis [24]. There are numerous reports available for the synthesis of PAMAM dendrimer on magnetic iron oxide nanoparticle through covalent bonding, but these dendrimers remains unsuitable for catalysis under certain conditions [10,25–27].

Indeed, PPI dendrimer is superior to PAMAM dendrimer due to the availability of more functional nitrogen even in lower generations, greater void space, smaller size, good biocompatibility and more loading capacity [28] *etc*. PPI dendrimer is exclusively chosen for this study as it contains a greater number of amine groups, which can be utilized for base catalysis, better void space to host the guest molecules and easily tunable amine groups. So far intrinsically PPI dendrimers grafted onto magnetite nanoparticle and utilized for various applications [29,30]. Herein for the first time we report the divergent synthesis of PPI dendrimer G_3 on silica coated magnetite core with enhanced dendritic structure with retainment of magnetic behavior for heterogeneous catalysis. Base catalysed condensation reactions using active methylene compounds are most useful due to the formation of new carbon bond. The materials such as pyridine, piperidine, NaOH, K_2CO_3, triethylamine, amino functionalized mesoporous silica, $Fe_3O_4@SiO_2$- pyridine, polyvinylamine coated magnetic microspheres, Nano DAB-PPI G_1 *etc.*, have been used so far in the catalysis of various condensation reactions [31–36]. Unfortunately all are having their own demerits. As far as PPI dendrimer G_3 on silica coated magnetite core material is concerned, it may overcome the above demerits associated with the reported bases.

The formation of PPI dendritic structure with magnetic core is well established in this work and also the structural functions of the nanohybrid material is proved by the probe reactions namely Knoevenagel condensation, Knoevenagel- Michael reaction and Henry reaction even in aqueous phase under ambient condition.

2. Experimental Section

2.1. Reagents and Materials

All the reagents and solvents were purchased from commercial sources. Ferrous sulphate heptahydrate (98%), anhydrous ferric chloride (98%), acrylonitrile (99%), sodium metal was purchased from Spectrochem. Oleic acid, Polyvinylpyrrolidone (Mol. Wt. 40,000 Da) were purchased from LOBA. Tetraethoxysilane (TEOS, 98%), 3-aminopropyltriethoxysilane (APTES, 98%) were purchased from Alfa Aesar. Lithium aluminum hydride (LAH, powder reagent, 95%) was purchased from Sigma Aldrich. Solvents such as methanol, ethanol, THF, toluene (HPLC grade), DCM, DMF were purchased from Fischer, THF and DCM were distilled and used. Deionized water has been used for the reactions wherever is applicable. All the reactions were carried out using Remi digital overhead stirrer with digital rpm controller.

2.2. Synthesis of Oleated Magnetite Nanoparticles

Iron oxide nanoparticles viz., magnetite were prepared via co-precipitation method. The precursors $FeSO_4$ $.7H_2O$ (4.7 g, 16.9 mmol) and $FeCl_3$ (5.5 g, 33.8 mmol) in the ratio 2:1 were dissolved in deionized water and stirred vigorously for 20 min. Then 12.5 mL of 25 % ammonium hydroxide was added rapidly with continuous stirring at room temperature under nitrogen atmosphere. The black Fe_3O_4 nanoparticles was obtained, to this black suspension, 2 mL of oleic acid was added dropwise for 1 h with continuous stirring at 80 ^{o}C. After complete addition, oleated iron oxide nanoparticles were extracted into toluene by adding sodium chloride. The magnetite nanoparticles were separated by magnetic attraction using external magnet and the supernatant solution was decanted. Magnetically separated nanoparticles were washed thrice with deionized water, acetone and dried in vacuum for 24 h. The dried oleated Fe_3O_4 nanoparticles was suspended in toluene for storage.

2.3. Synthesis of Silica Coated Fe_3O_4 Nanoparticles

About 75 mL (4 g) of oleated Fe_3O_4 nanoparticles suspended in toluene was taken in a 1 L three-necked RB flask. 10 g of PVP dissolved in a mixture of 200 mL DCM and 200 mL DMF was added to the iron oxide suspension and then heated at 95 ^oC for about 15 h. Then, PVP stabilized iron oxide nanoparticles were precipitated out by dropwise addition of resultant suspension into diethyl ether, followed by magnetic isolation of PVP coated magnetite nanoparticles. Finally, it was redispersed in ethanol and 1 mL of the suspension contains about 0.1 g of PVP coated Fe_3O_4 nanoparticle.

3 g PVP coated iron oxide nanoparticles were dispersed in 2 L of isopropanol containing 100 mL of 28 % of ammonium hydroxide solution. Then it was sonicated for 1 h followed by dropwise addition of TEOS for a period of 3 h under vigorous stirring. The stirring was continued for another 20 h at room temperature. Finally, silica coated iron oxide nanoparticles were magnetically separated, washed five times with deionized water and dried in vacuum for 24 h. 4.5 g of dry dark yellow colored silica coated iron oxide powder was obtained.

2.4. Synthesis of Amino Silanated Silica Coated Fe_3O_4Nanoparticles

4 g of silica coated iron oxide powder was suspended in 150 mL of dry toluene and sonicated for 45 min. To this suspension, 1.2 mL of APTES was added and stirred continuously for 20 h at 100 ^0C. The reaction mixture was cooled and the amino silane coated iron oxide nanoparticles were separated using an external magnet, washed thrice with methanol and dried in vacuum overnight. The silanated silica coated iron oxide is labelled as Fe_3O_4/SiO_2/PPI-G_0 nanoparticles, which contain approximately 1 mmol/g of amino groups (determined by pre-validated conductometric titration and pre validated Lassaigne's test methods).

2.5. General Procedure for the Synthesis of Magnetite Cored Cyano group Terminated Dendrimer

3 g of Fe_3O_4/SiO_2/PPI-G_0 nanoparticle was dispersed in 100 mL of methanol and sonicated for 30 min. To this suspensions, 16 mL of acrylonitrile (100 mol equivalent per amino group), 2 mL of acetic acid (10 mol equivalent per amino group) were added and mechanically stirred for 40 h at 50 ^0C. The product Fe_3O_4/SiO_2/PPI-$G_{0.5}$ was isolated by using an external magnet,

washed thrice with deionized water, methanol and dried in vacuum for 24 h. Similarly, Fe_3O_4/SiO_2/PPI-$G_{1.5}$, Fe_3O_4/SiO_2/PPI-$G_{2.5}$ were prepared from Fe_3O_4/SiO_2/PPI-G_1, Fe_3O_4/SiO_2/PPI-G_2 respectively, using the same procedure.

Fe_3O_4/SiO_2/PPI-$G_{0.5}$: 3 g of Fe_3O_4/SiO_2/ PPI-G_0 was dispersed in 100 mL of methanol, 16 mL of acrylonitrile and 2 mL of acetic acid

Fe_3O_4/SiO_2/PPI-$G_{1.5}$: 3 g of Fe_3O_4/SiO_2/ PPI-G_1 was dispersed in 100 mL of methanol, 32 mL of acrylonitrile and 4 mL of acetic acid

Fe_3O_4/SiO_2/PPI-$G_{2.5}$: 3 g of Fe_3O_4/SiO_2/ PPI-G_2 was dispersed in 100 mL of methanol, 64 mL of acrylonitrile and 4 mL of acetic acid

2.6. General Procedure for the Synthesis of Magnetite Cored Amino Group Terminated Dendrimer

3 g of magnetite cored cyano group terminated nanohybrid material Fe_3O_4/SiO_2/PPI-$G_{0.5}$ were dispersed using sonication bath in 100 mL THF taken in a three necked RB flask fitted with water condenser and dropping funnel. 114 mg of LAH in dry THF (twice the mole equivalence per amino group) was added dropwise for 1 h under continuous stirring at 0 ^{0}C. After complete addition of LAH, stirring was continued for 15 h at 60 ^{0}C. The resulting nanohybrid material Fe_3O_4/SiO_2/PPI-G_1 was separated by an external magnet, excess LAH was decomposed by the addition of ethyl acetate, washed thrice with THF, deionized water, dil. HCl, deionized water, dil. NaOH, deionized water, methanol, acetone and dried in vacuum for 24 h. Fe_3O_4/SiO_2/PPI-G_2, Fe_3O_4/SiO_2/PPI-G_3 were prepared from Fe_3O_4/SiO_2/PPI-$G_{1.5}$ and Fe_3O_4/SiO_2/PPI-$G_{2.5}$ respectively, using the same procedure.

Fe_3O_4/SiO_2/PPI-G_1:3 g of Fe_3O_4/SiO_2/PPI-$G_{0.5}$ was dispersed in 100 mL of THF and 114 mg of LAH in THF was added dropwise.

Fe_3O_4/SiO_2/PPI-G_2: 3 g of Fe_3O_4/SiO_2/PPI-$G_{1.5}$ was dispersed in 100 mL of THF and 230 mg of LAH in THF was added dropwise.

Fe_3O_4/SiO_2/PPI-G_3: 3 g of Fe_3O_4/SiO_2/PPI-$G_{2.5}$ was dispersed in 100 mL of THF and 460 mg of LAH in THF was added drop wise.

2.7. General Procedure for Quantitative Analysis of Amino Group

2.7.1. Conductometric Titration Method

Exactly 10 mg of the Fe_3O_4/SiO_2/PPI-G_3 nanohybrid material was dispersed in 20 mL of standardized hydrochloric acid (1 mmol) and stirred mechanically for 30 min. After stirring, the nanomaterial was separated by magnet and 5 mL of supernatant solution was titrated against standardized sodium hydroxide solution, conductance was measured for each 0.2 mL addition of NaOH solution. The HCl consumed by the magnetite cored PPI dendrimer nanomaterial is equivalent to the concentration of amine groups present in the dendritic moiety. This experiment was carried for all the three nanohybrid materials namely Fe_3O_4/SiO_2/PPI-G_0, G_1, G_2 and the amount of nitrogen present in the dendrimers have been estimated.

2.7.2. Lassaigne's Prussian Blue Complex Method

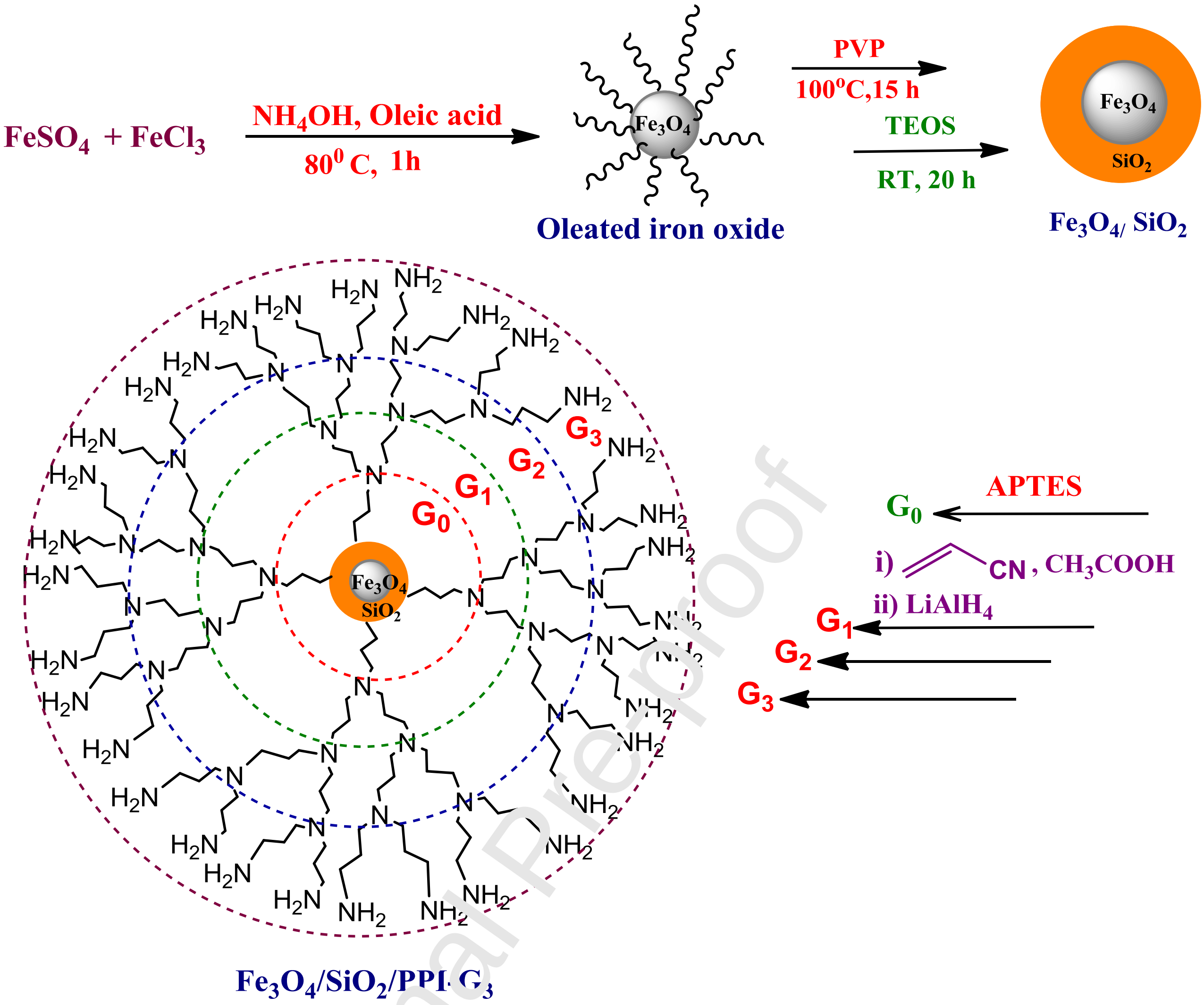
25 mg of the dried Fe_3O_4/SiO_2/PPI-G_3 nanohybrid material was added to fused sodium metal and heated to red hot condition, the mixture was cooled and 5 mL of deionized water was added and then boiled. The sodium fusion extract was cooled and freshly prepared ferrous sulphate solution was added in excess, boiled and cooled. To this solution conc. sulphuric acid was added, resulting Prussian blue complex was diluted to 50 mL in standard volumetric flask and the absorbance was recorded through UV-Vis spectrophotometer. This experiment has been carried out individually for all the three magnetite cored dendrimers

2.8. General Procedure for Catalysis

10 mg of Fe_3O_4/SiO_2/PPI-G_3 catalyst was dispersed in 5 mL ethanol and sonicated for 30 s, 1 mmol of aldehyde, 1 mmol of active methylene compound were added to the above suspension and stirred at room temperature under nitrogen atmosphere. The completion of condensation reaction was monitored using TLC with hexane and ethyl acetate as eluent (4:1). After completion of the reaction, the product was decanted by arresting the catalyst with external magnet. The obtained product was recrystallised and the yields were noted. Similarly, the condensation reactions have also been established in aqueous medium and the yields were compared.

3. Results and Discussion

Rational design for divergent synthesis of PPI G_3 dendrimer on silica coated superparamagnetic iron oxide nanoparticles is discussed (**scheme 1**). Initially Fe_3O_4 was prepared by conventional coprecipitation method, subsequently controlled silica coating was carried out on Fe_3O_4 nanoparticle for better protection and to achieve spherical morphology with sustainable magnetic retentivity. It was further functionalized with APTES to develop dendrimer on it. The amino silanated material was labeled as Fe_3O_4/SiO_2/PPI-G_0 nanohybrid material with propylamine surface groups. Subsequently, Fe_3O_4/SiO_2/PPI-G_1 was synthesized in two steps namely Michael addition of acrylonitrile to the amine group using acetic acid as catalyst, followed by reduction of the nitrile group in to amine group with LAH [37]. The amount of amine group present in Fe_3O_4/SiO_2/PPI-G_0, G_1, G_2, G_3 were determined by conductometric titration method and Lassaigne's Prussian blue complex test.



Scheme 1. Synthesis of magnetite cored poly(propylene imine) dendrimer.

HRTEM images of the Fe_3O_4/SiO_2/PPI-G_3 dendrimer nanoparticles at different resolutions clearly indicates the formation of spherical shaped single core shell type silica coated iron oxide nanoparticles (**Fig.1A and 1B**). The particle size obtained from HRTEM images of magnetic cored PPI-G_3 dendrimer shows the size distribution of 10 ± 4 nm for Fe_3O_4 core and 25±5 nm for silica coated Fe_3O_4 nanoparticles. The Dynamic Light Scattering analysis in the Zeta analyzer was carried out in ethanol, the average particle size of the materials was found to be 71 nm and 105 nm for Fe_3O_4/SiO_2 and Fe_3O_4/SiO_2/PPI-G_3 respectively (**Fig. S1.**). The hydrodynamic size of Fe_3O_4/SiO_2/PPI-G_3 was found to be greater than Fe_3O_4/SiO_2, which attributes the formation of dendritic entities on silica coated iron oxide nanoparticles.

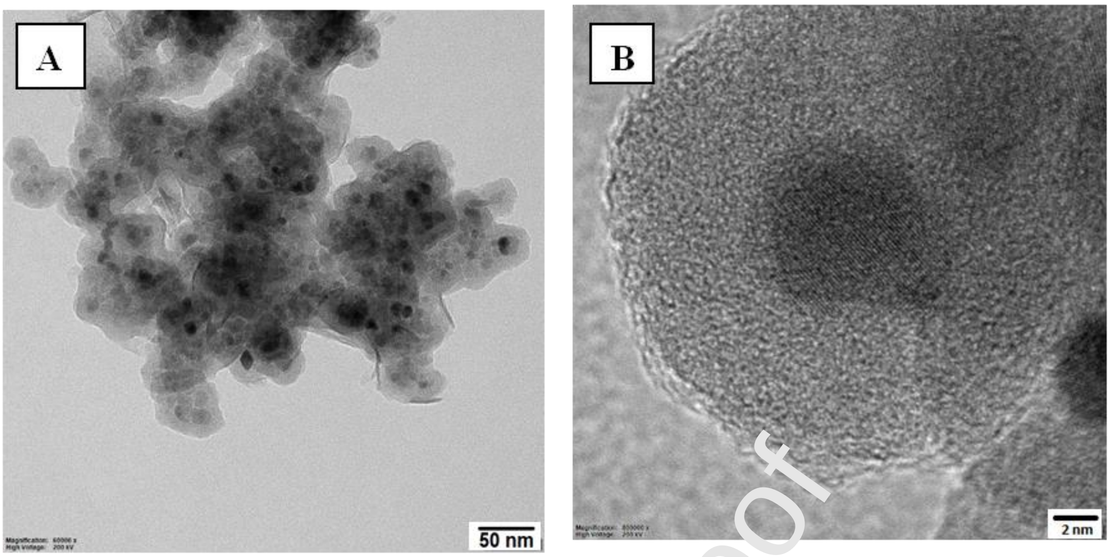


Fig. 1. (A) HRTEM images of Fe_3O_4/SiO_2/PPI-G_3 nanohybrid material (B) Core- shell type silica coated iron oxide nanoparticle.

X-ray Photoelectron spectroscopy for the Fe_3O_4/SiO_2/PPI-G_3 confirms the presence of elements *viz.*, iron, silicon, carbon and nitrogen through the peaks obtained from the wide spectra with binding energies 751eV, 105 eV, 397 eV and 285 eV for respective elements. The ratio of peak area for carbon to nitrogen was observed to be 3:7:1 which is closer to the theoretical value of PPI dendrimer. Si 2p, C1s, N $2p^{3/2}$ spectra were also confirmed (**Fig. S2 and S3**). The crystal structure and phase composition of the synthesized nanoparticles were investigated through X-Ray diffraction method (**Fig. 2**), the XRD patterns for the oleated superparamagnetic Fe_3O_4 nanoparticles matched well with the patterns of magnetite (inverse Spinel cubic structure) obtained from JCPDS data. XRD data showed sharp peaks at 2θ values of 30.25^0, 35.66^0, 45.34^0, 57.37^0, 62.7^0 which corresponds to the lattice planes (220), (311), (400), (511), (440) respectively for magnetite nanoparticle. The lattice parameters of the superparamagnetic iron oxide nanoparticle remained unaltered throughout the divergent synthesis of PPI dendrimer on to it. The crystallite size of Fe_3O_4 nanoparticles has been determined using Scherrer equation and it was found to be 12±1 nm which shows good agreement with the size obtained from HRTEM images.

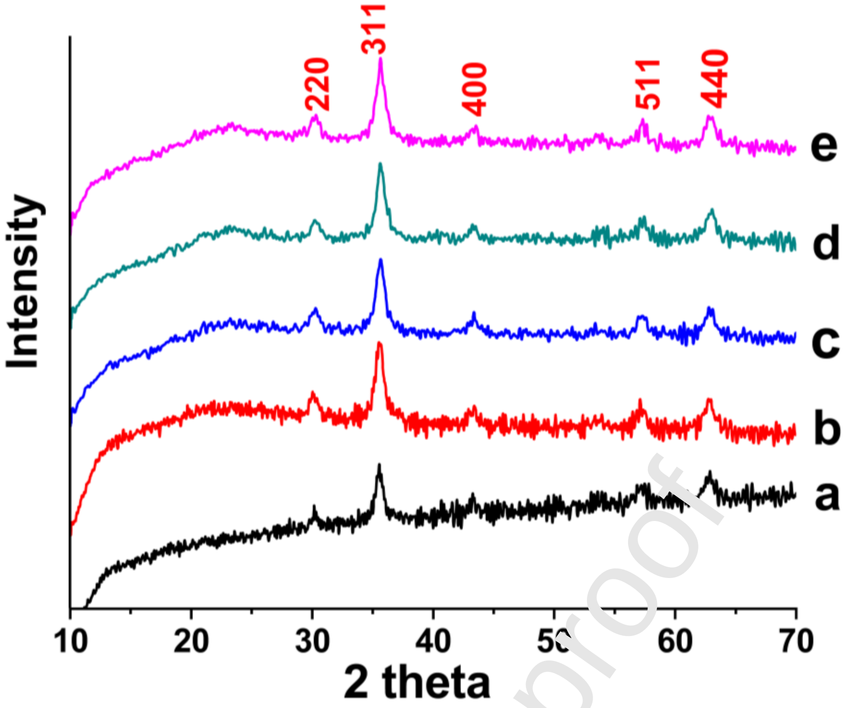


Fig. 2. X-Ray diffraction pattern of (a) oleated iron oxide (b) Fe_3O_4/SiO_2 (c) Fe_3O_4/SiO_2/PPI-G_0 (d) Fe_3O_4/SiO_2/PPI-G_1 (e) Fe_3O_4/SiO_2/PPI-G_3

Superparamagnetic behavior of nanohybrid material studied at room temperature using VSM analysis proves that iron oxide nanoparticle and the dendrimer grafted silica coated iron oxide nanomaterials behaves as super paramagnets. They exist with negligible magnetic retention and attains magnetic saturation when high magnetic field was applied in the order of 14 KOe. The saturation magnetization for oleated iron oxide, Fe_3O_4/SiO_2 and Fe_3O_4/SiO_2/PPI-G_3 were 53.292 emu/g, 15.932 emu/g and 12.797 emu/g respectively. The decrease in the magnetization values from 53.292 emu/g to 15.932 emu/g (**Fig. 3a and 3b**) incorporates the occurrence of silica shell with sufficient thickness and subsequently slight decrease from 15.932 emu/g to 12.797 emu/g (**Fig. 3b and 3c**) confirms the presence of PPI dendritic layer on the magnetic cored silica surface; these observation authenticates the presence of silica shell as well as PPI dendrimer layer on the Fe_3O_4 nanoparticle.

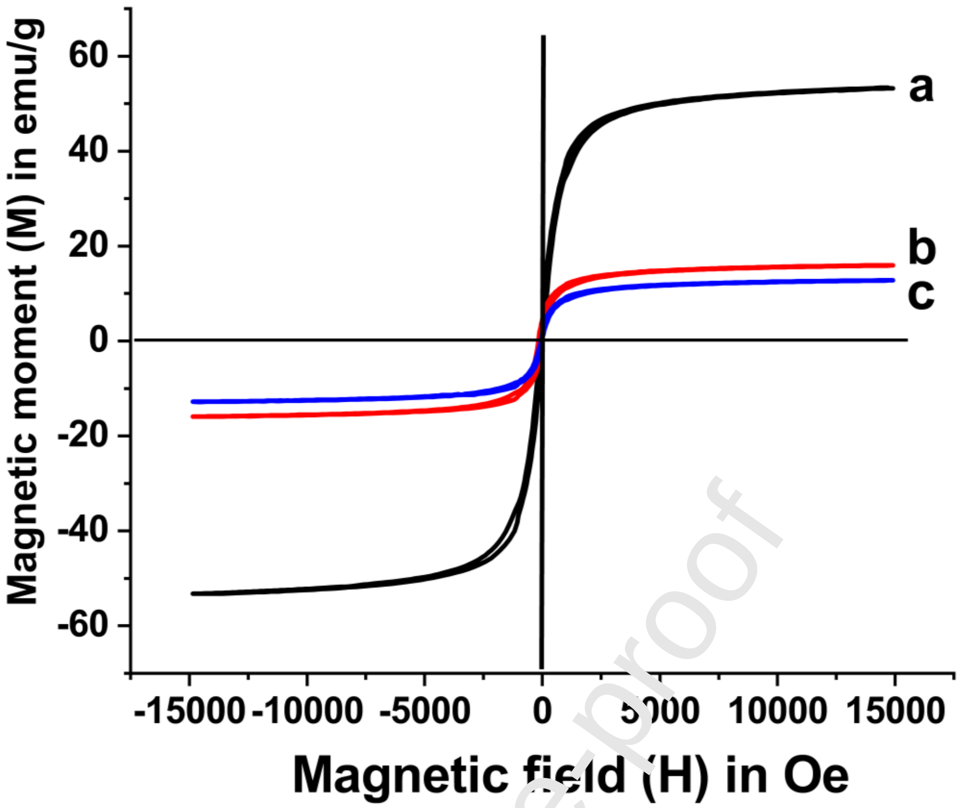


Fig. 3.VSM curve at RT for (a) oleated Fe_3O_4 (b) Fe_3O_4/SiO_2 (c) $Fe_3O_4/SiO_2/PPI\text{-}G_3$

Thermogravimetric analysis strongly proves the stepwise growth of dendrimer on the silica coated iron oxide nanoparticles (**Fig. 4 and S4**). The weight loss around 100 ^{0}C is due to the release of the adsorbed water, weight loss between 100 ^{0}C - 500 ^{0}C is attributed to decomposition of the organic matrix namely PPI dendrimer, interstitial water molecule present in the nanohybrid material and above 500 ^{0}C should be due to the decomposition of silica shell. Quantitative weight loss was observed for $Fe_3O_4/SiO_2/PPI\text{-}G_0$, $Fe_3O_4/SiO_2/PPI\text{-}G_1$, $Fe_3O_4/SiO_2/PPI\text{-}G_2$ and $Fe_3O_4/SiO_2/PPI\text{-}G_3$ between 100 ^{0}C -500 ^{0}C were 6.7%, 9.5%, 11.3% and 16.9% respectively. These observations conclude the growth of poly (propylene imine) onto the magnetite cored silica particles. The difference in weight loss indicated by curve A, B, C, D (**Fig. 4**) corresponds to the stepwise formation of dendritic entity onto Fe_3O_4/SiO_2 nanoparticles

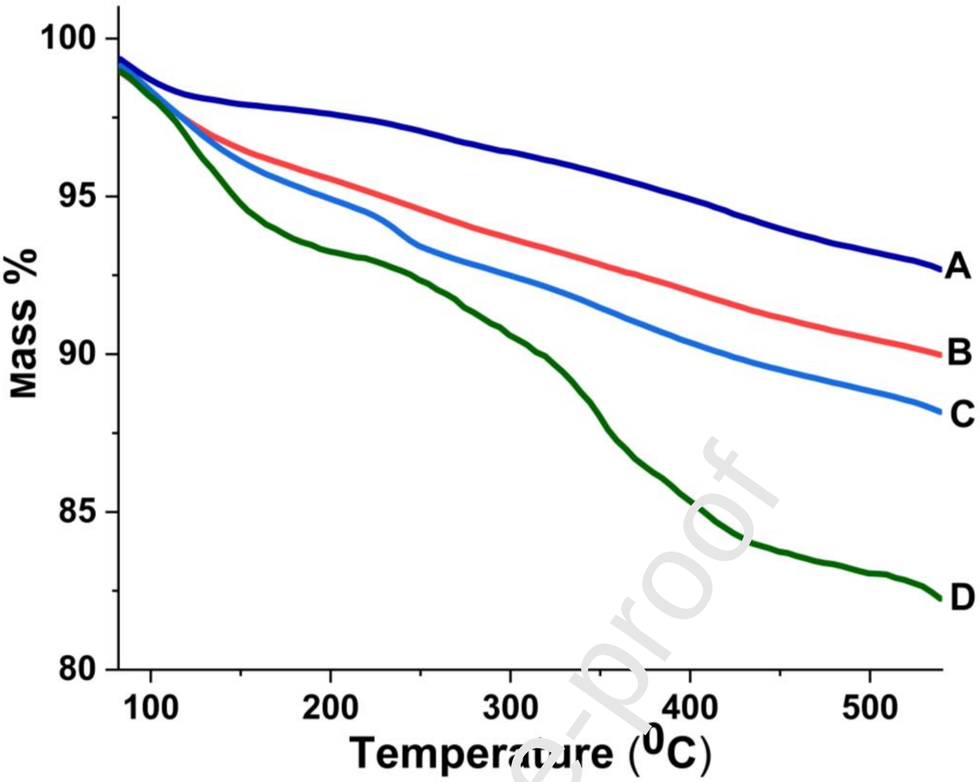


Fig. 4. TGA curves of (A) Fe_3O_4/SiO_2/PPI-G_0 (B) Fe_3O_4/SiO_2/PPI-G_1 (C) Fe_3O_4/SiO_2/PPI-G_2 (D) Fe_3O_4/SiO_2/PPI-G_3

FTIR spectral analysis results are presented in **Fig. 5**, where the spectrum a designates iron oxide nanoparticle with very strong band at 580 cm^{-1} for Fe-O-Fe and absorption band at 3450 cm^{-1} corresponds to the peripheral -OH stretching of iron oxide nanoparticle. Further, the intensity of Fe-O-Fe band at 580 cm^{-1} decreases with respect to the stepwise modification of Fe_3O_4 with PVP, silica and PPI dendrimer (**5b-5i**). Similarly, appearance of new absorption band at 1080 cm^{-1} confirms the formation of silica shell around the magnetite core and a broad intensive band at 3450 cm^{-1} indicates -OH bond stretching due to peripheral -OH on the silica shell. A small decrease in the band intensity of Si-O- Si from **5c** to **5i** represents the growth of the dendrimer which is shielding the silica coating. Absorption peak around 1640 cm^{-1} increase from **5c** to **5i** because of C-N bond stretching frequencies. A shift of the broad absorption band from 3450 cm^{-1} to 3420 cm^{-1} was observed from **5d** to **5i**, which confirms the growth of dendrimer with enriched peripheral amino groups.

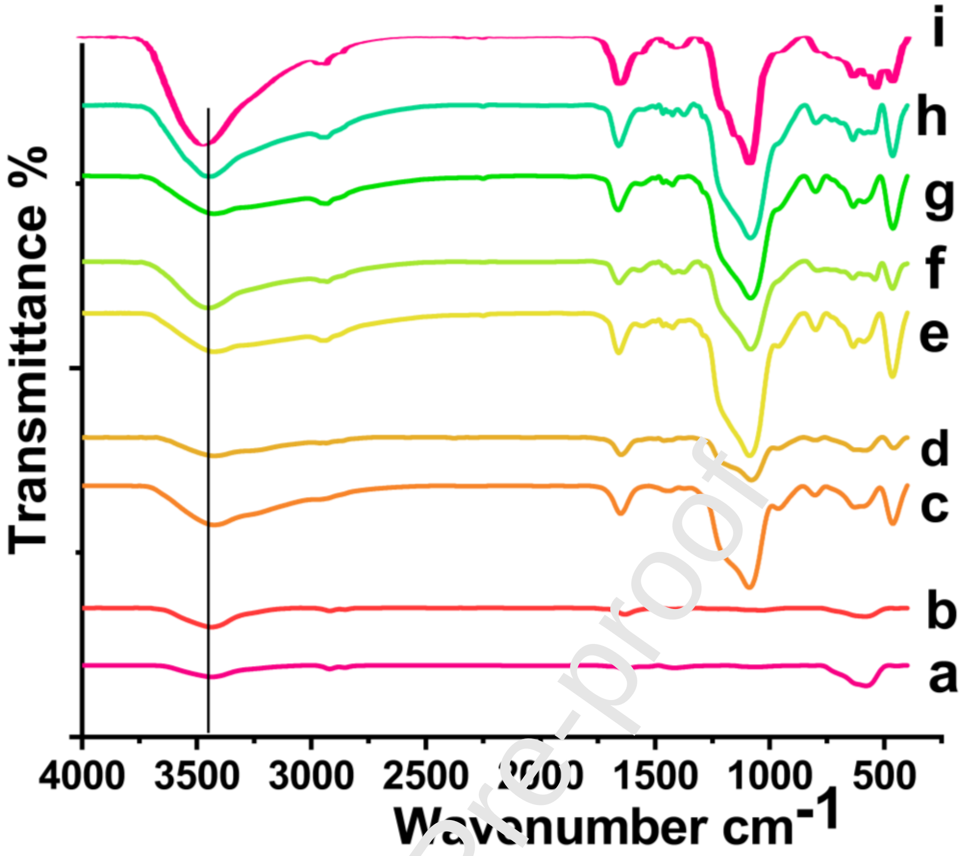


Fig. 5. FTIR spectra of (a) Oleated Fe_3O_4 (b) PVP coated Fe_3O_4 (c) Fe_3O_4/SiO_2 (d) $Fe_3O_4/SiO_2/PPI\text{-}G_0$ (e) $Fe_3O_4/SiO_2/PPI\text{-}G_{0.5}$ (f) $Fe_3O_4/SiO_2/PPI\text{-}G_1$ (g) $Fe_3O_4/SiO_2/PPI\text{-}G_{1.5}$ (h) $Fe_3O_4/SiO_2/PPI\text{-}G_2$ (i) $Fe_3O_4/SiO_2/PPI\text{-}G_3$

The persistence of dendrimer onto the silica coated magnetite has been proved by conductance measurement and Prussian blue complex formation. Prussian blue complex formation method was adapted to justify the generation wise increase of nitrogen from PPI-G_1 to PPI-G_3. Prussian blue complex was prepared from $Fe_3O_4/SiO_2/PPI\text{-}G_1$, $Fe_3O_4/SiO_2/PPI\text{-}G_2$, $Fe_3O_4/SiO_2/PPI\text{-}G_3$ individually by taking 25 mg of each material and prepared under identical experimental conditions. UV-Vis absorption spectra were recorded for each solution and the observed data proves the increase in amount of nitrogen from PPI-G_1 to PPI- G_3. The absorption intensity at 735 nm for Prussian blue complex obtained from $Fe_3O_4/SiO_2/PPI\text{-}G_1$,

$Fe_3O_4/SiO_2/PPI-G_2$, $Fe_3O_4/SiO_2/PPI-G_3$ manifestly shows the increase in nitrogen content with respect to generation (**Fig. 6, Table 1**)

Similarly, the formation of dendrimer on the silica coated iron oxide nanoparticle has also been proved by conductometric titrations for stepwise increase in amino group concentration (Table 1). As described in the experimental part, fixed concentration of HCl was mixed with 10 mg of $Fe_3O_4/SiO_2/PPI-G_0$, $Fe_3O_4/SiO_2/PPI-G_1$, $Fe_3O_4/SiO_2/PPI-G_2$ and $Fe_3O_4/SiO_2/PPI-G_3$ individually under mechanical stirring for 30 min and finally the nanohybrid materials were arrested by using external magnet. Subsequently, the representative volume of supernatant solutions was titrated against standardized sodium hydroxide solution using conductometric method. The result evidences the increasing concentration of nitrogen from PPI-G_0 to PPI-G_3 with respect to dendritic growth.

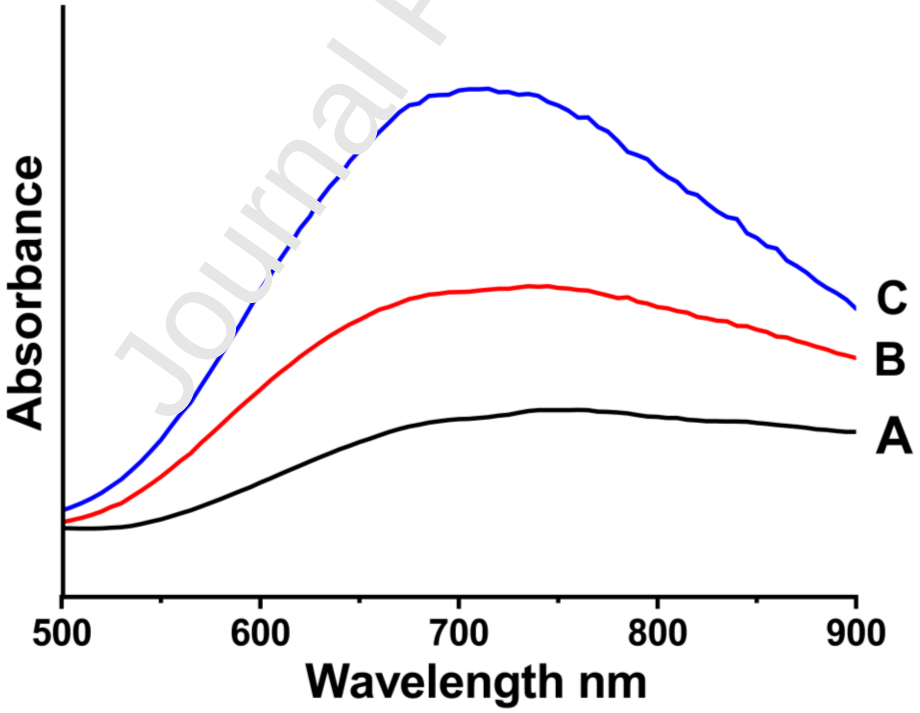


Fig. 6. UV-Vis absorption spectra of Prussian blue complex obtained for (A) $Fe_3O_4/SiO_2/PPI-G_1$ (B) $Fe_3O_4/SiO_2/PPI-G_2$ (C) $Fe_3O_4/SiO_2/PPI-G_3$

Table 1. Amount of amine groups determined by conductometric titrations and Lassaigne's Tests

Magnetic cored PPI dendritic Nanohybrid material	**Amount of amine group (mmol/g)**	
	Conductometric titration method	**Lassaigne's Prussian blue complex test**
Fe_3O_4/SiO_2/PPI-G_0	1.32	1.28
Fe_3O_4/SiO_2/PPI-G_1	2.14	1.92
Fe_3O_4/SiO_2/PPI-G_2	3.11	2.85
Fe_3O_4/SiO_2/PPI-G_3	4.86	4.63

The current approach (divergent strategy) comprises the synthesis of dendrimer from the magnetic core to which the arms (dendron) are built by step-wise manner. The above process lead the magnetic cored dendrimer which is structurally perfect, symmetrical, well defined, thermally stable, highly dispersed with stochiometric functional atoms as designed. The magnetic cored stepwise synthesis of PPI dendrimer eliminates the complicated reaction workup and tedious isolation and purification process. Since, the core is superparamagnetic material, the reaction intermediates and the products are isolated by using external magnet. Similarly we can remove the absorbed impurities by washing with suitable solvents and the final material can be recovered magnetically without any loss.

In the case of regular synthesis of PPI dendrimer in homogeneous medium require tedious work set up coupled with complicated purification techniques at each step. The separation and purification techniques normally adopted are nanofiltration, gel permeation, column chromatography, centrifugation etc that makes the material (PPI dendrimer) to higher cost. This dendrimer is used to attach with magnetic support. The conventional attachment of commercial PPI dendrimer on magnetic core may not yield symmetrical product and also the steric factor will decide the extent of grafting and ultimately we may not get desired magnetic nanoparticle supported PPI dendrimer material as expected. These factors will also increase the cost of material to higher side. If we adopt the method reported in this work, it will resolve all the issues pertaining with conventional grafting of dendrimer on magnetic material. Divergent synthesis approach of magnetic cored PPI dendrimer is generally a commercial viable method for industrial application via simple method of preparation, consumes less work and economic.

3.1. Catalysis of condensation reacting using nanohybrid materials

The catalytic efficiency of the synthesized Fe_3O_4/SiO_2/PPI-G_3 nanohybrid material was examined for Knoevenagel condensation between benzaldehyde and malononitrile in ethanol at room temperature to yield the desired product 2-benzylidene malononitrile as a model reaction (**Scheme 2**). It was observed that 10 mg (5 mol%) of Fe_3O_4/SiO_2/PPI-G_3 catalyst is sufficient to accelerate the Knoevenagel condensation reaction (**Table 2**). Knoevenagel condensation reaction was also employed to ascertain the comparative efficiency of other nanohybrid materials *viz.*, Fe_3O_4/SiO_2/PPI-G_0 (10 mg, i.e. 1 mol%; calculated from conductometric measurement and Prussian blue complex method), Fe_3O_4/SiO_2/PPI-G_1 (10 mg, 2 mol%) & Fe_3O_4/SiO_2/PPI-G_2 (10 mg, 3 mol%), in ethanol at room temperature to yield the desired product with variations in reaction time (**Table 3, entry 1**). Results shows that Fe_3O_4/SiO_2/PPI-G_3 with more amino group accelerates the reaction to rapidly and enhances the product yield in shorter time compared with other nanohybrid material catalyst. The better void space available at the dendritic entity to host the guest molecules, presence of a greater number of nitrogen atom in the single molecular entity leads multivalent interaction with the substrate and fine dispersion of dendritic nanohybrid material in the reaction medium enhanced the catalytic activity drastically. The condensation reactions were also carried out with different aldehydes such as aromatic, aliphatic, heterocyclic etc., which favorably yields the corresponding products (entry 1-6). Knoevenagel condensation in aqueous medium also gave appreciable amount of the product with quite increase in reaction time.

Scheme 2. Knoevenagel Condensation

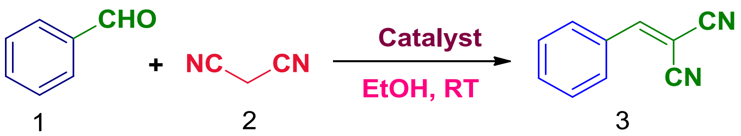


Table 2. Optimization of catalyst concentration in Knoeveagel condensation[a]

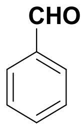
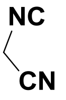
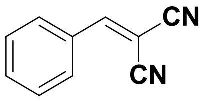
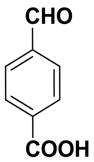
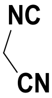
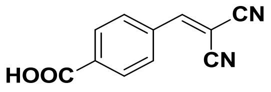
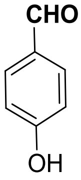
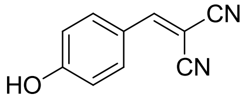
S.No.	Amount of Catalyst (mg)	Time (min)	Yield[b] %
1	Without catalyst	360	NR

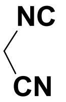
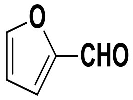
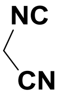
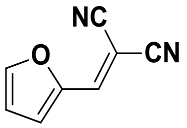
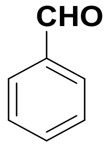
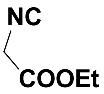
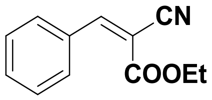
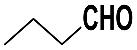
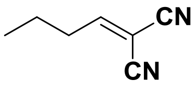
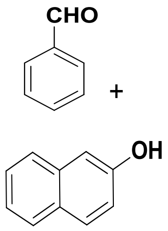
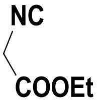
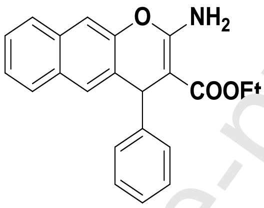
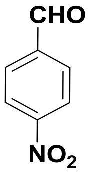
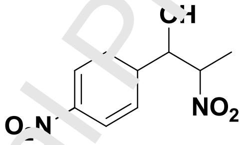
2	3	120	40
3	5	60	55
4	7	45	75
5	**10**	**30**	**95**
6	10	45	95
7	17	30	95
8	17	45	95

[a] benzaldehyde (1 mmol), malononitrile (1 mmol), ethanol (5 mL), catalyst: Fe_3O_4/SiO_2/PPI-G_3
[b] Isolated yield of the product 2-benzylidenemalononitrile after recrystallisation

From entry 1 (table 1), without catalyst no condensation reaction has been taken place. At the same time, amount of catalyst is influencing the reaction and it has been optimized as given in the Table 2. It was observed that 10 mg (5 mol% with respect to amine concentration) of Fe_3O_4/SiO_2/PPI-G_3 catalyst is sufficient to accelerate the Knoevenagel condensation reaction at ambient condition (entry 5).

Table 3 Catalytic efficiency of the magnetic cored PPI for various base catalyzed reactions [a]

Entry	**Substrate**		**Product**	**Catalyst**	**Time min**	**Yield[c] %**
	A	**B**				
1				G_0	150	90
				G_1	90	93
				G_2	45	95
				G_3	**30**	**95**
				G_3	**60***	**82***
2				G_3	30	90
					45*	82*
3				G_3	35	94

					45*	84*
4				G_3	60 75*	94 73*
5				G_3	45	92^b
6				G_3	25*	95*
7				G_3	120	89^b
8		CH_3NO_2		G_3	450	86

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[a] Substrates (1 mmol); solvent (5 mL) ethanol, * water; Catalyst (10 mg) at room temperature [b] temperature at 50 ^{0}C; [c] Isolated yield by recrystallisation; Catalyst G_0-Fe_3O_4/SiO_2/PPI-G_0, G_1-Fe_3O_4/SiO_2/PPI-G_1 and G_2- Fe_3O_4/SiO_2/PPI-G_2, G_3- Fe_3O_4/SiO_2/PPI-G_3

All the products were purified by recrystallisation process and products were confirmed by ^{1}H and ^{13}C NMR spectroscopic studies using the solvent $CDCl_3$ (see supporting information).

- The feasibility of chemical conversions such as Knoevenagel- Michael cyclocondensation (entry 7) and Henry reaction (entry 8) were also evaluated by using Fe_3O_4/SiO_2/PPI-G_3. The holistic evaluation of catalyst for all the three different condensations reactions inevitably proves that magnetite core PPI dendritic nanohybrid material is a promising catalyst material when compared to the magnetite cored base catalysts reported by others (**Table 4**) [38–41]. The reason behind the efficiency is the multiple number of nitrogen in single molecular entity, fine accessible voids to host the guest molecules, the multivalent interaction exerted by dendritic molecules towards the substrates and the enhanced dispersibility in the reaction medium.

Table 4. Comparison of the catalyst for Knoevenagel Condensation

S.No.	**Catalyst**	**Catalyst weight**	**Reaction conditions**	**Time**	**Product yield**
1	piperidine, pyridine	0.3, 4 mol eq	water/reflux	2 h	88[36]
2	NaOH	10 mol%	Water/RT	2 h	55[35]
3	K_2CO_3	10 mol %	Water/RT	2 h	44[35]
4	Triethylamine	1.3 mol eq	Toulene/ reflux	2h	90[33]
5	Amine functionalized mesoporous silica	20 mg	Ethanol/RT	6 h	90[42]
6	Fe_3O_4@SiO_2-Py	100 mg	100 °C	4h	94[34]
6	Fe_3O_4@SiO_2- PVA	50 mg	Ethanol/RT	0.5 h	95[32]
7	**Fe_3O_4/SiO_2/PPI-G_3**	**10 mg**	**Ethanol/RT**	**0.5 h**	**93(this work)**

Recycle efficacy of the catalyst holds good up to eight cycles with minimal loss in their activity for the Knoevenagel condensation reaction (**Fig. 7**). The use of solvent for isolation and regeneration of catalyst material is because of the magnetic separation method compared to other solid supported catalyst.

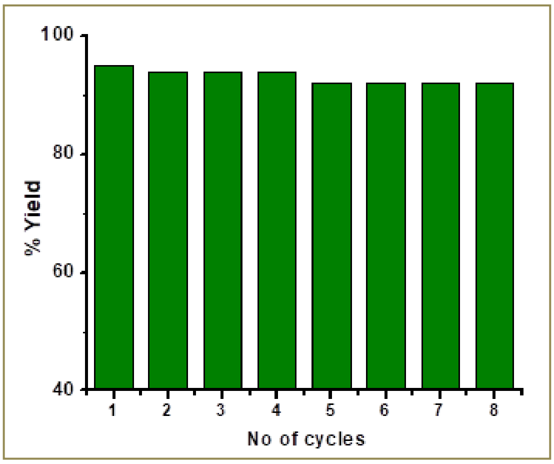

Fig. 7. Recycle efficiency of Fe_3O_4/SiO_2/PPI-G_3 for Knoevenagel condensation reactions

HRTEM image (**Fig. 8**) of the recycled Fe_3O_4/SiO_2/PPI-G_3 catalyst demonstrates the spherical morphology with core- shell and size of the nanohybrid material seems to be alike with fresh catalyst. The HRTEM image is prominently supporting the stability of magnetic PPI dendrimer. Additionally, FTIR spectrum (Fig. S6), VSM data (Fig.S7) and XRD pattern (Fig. S8) obtained for recycled Fe_3O_4/SiO_2/PPI-G_3 catalyst evidences that no significant changes occurs when compared with fresh Fe_3O_4/SiO_2/PPI-G_3 catalyst. The FTIR spectrum reveals either the PPI dendrimer or the silica coated magnetite nanoparticles is unaltered even after eighth cycle of catalysis. The XRD spectrum of the recycled Fe_3O_4/SiO_2/PPI-G_3 catalyst proves the lattice planes of the magnetite nanoparticles is retained, even after exposing the catalyst to diverse chemical environment. VSM curves at room temperature for the fresh and recycled catalyst confirms the paramagnetic behavior of the catalyst remains unaffected

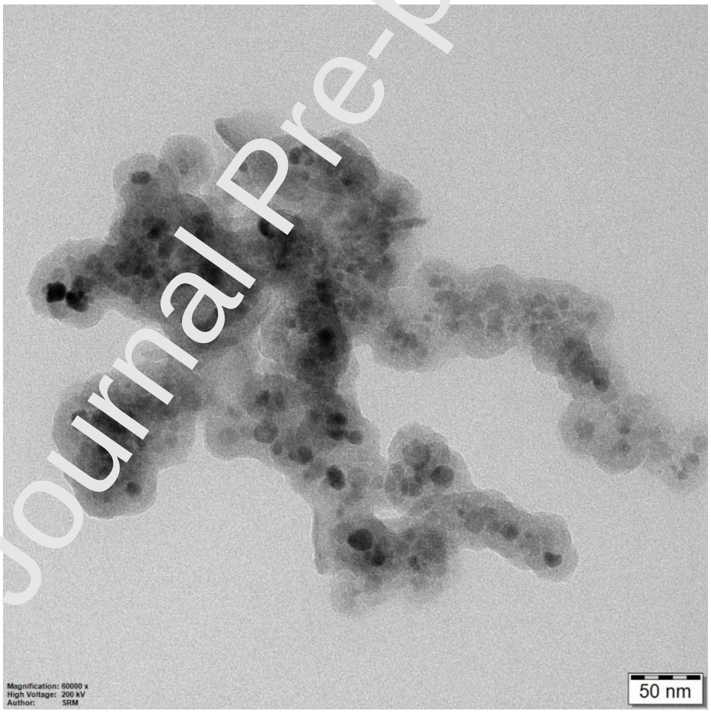

Fig. 8. HRTEM image of Fe_3O_4/SiO_2/PPI-G_3 catalyst after eight cycles

A leaching test was carried out to examine the leaching and stability of magnetic supported heterogeneous catalyst [43]. For this purpose, the catalyst Fe_3O_4/SiO_2/PPI-G_3 was magnetically separated from the model Knoevenagel condensation reaction medium (scheme 2) at different time intervals such as 10 min, 20 min and 30 min and the catalytic activity of filtrate was monitored every 5 min (**Fig. 9**).. The product yield during this continuous assessment after the removal of catalyst from the reaction mixture seems to be unaffected.

These observations suggest that the catalyst remains stable and no significant destruction of organic functionalities present on the magnetite core was observed.

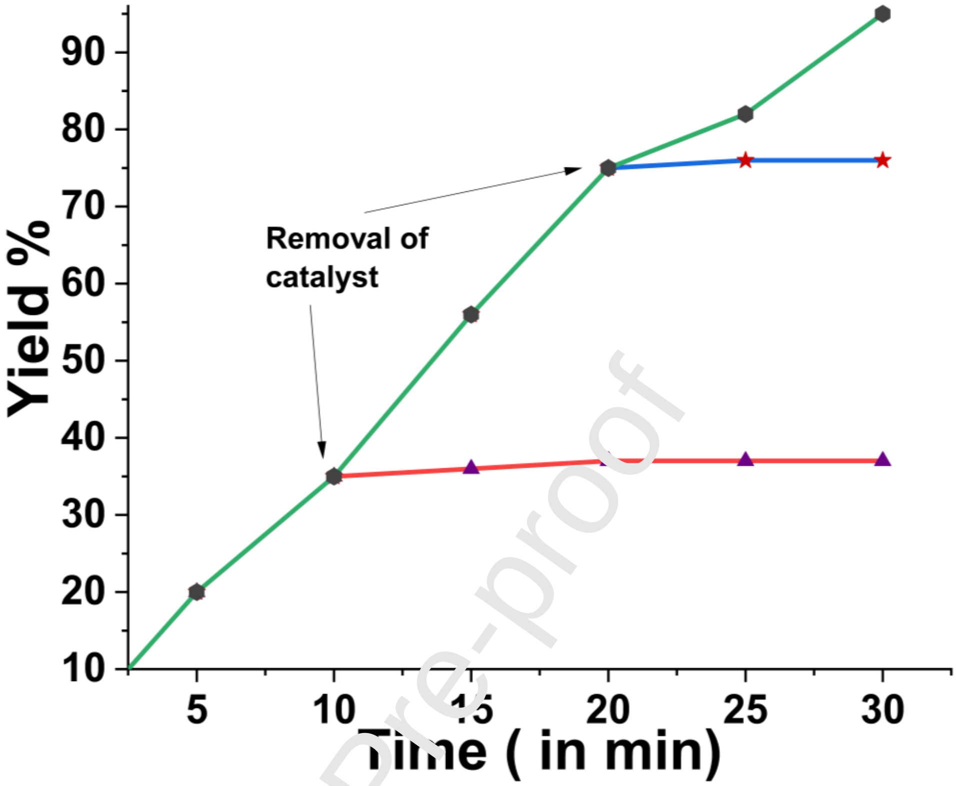

Figure 9. Test for the leaching study of Fe_3O_4/SiO_2/PPI-G_3 catalyst

4. **Conclusions**

Based on the rationale, the structurally enhanced magnetite cored PPI core shell nanohybrid material has been developed successfully to serve as multivalent organic base catalyst with enriced activity and facile magnetic recyclability. Though it is magnetic supported synthesis, the analytical data strongly supports the expected nano architecture as much as possible. The catalytic activity of magnetite cored PPI dendrimer was studied for Knoevenagel condensation, Knoevenagel- Michael cyclocondensation and Henry reactions at ambient conditions and found to be superior to the conventional magnetic cored base catalyst of previous report. The condensation reaction was also accomplished even in aqueous medium with good yield. The catalyst was reused for eight times without any significant loss in their activity. As a preliminary study we have examined the utility of the new nanohybrid material for various condensations reactions. The further application of this material is explored with numerous modifications to green and sustainable organic transformation for the perspectives of industrial purposes, this material may exploit other fields such as biomedical, sensor, environmental *etc*.

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Keywords: magnetic core, PPI dendrimer, nanohybrid, sustainable catalyst, magnetically recoverable

References

[1] L.M. Bronstein, Z.B. Shifrina, Nanoparticles in dendrimers: From synthesis to application, Nanotechnologies Russ. 4 (2009) 576–608.

[2] D. Astruc, F. Chardac, Dendritic catalysts and dendrimers in catalysis, Chem. Rev. 101 (2001) 2991–3023.

[3] C.D. and J.L. Xiao Yang, Hui Shang, Recent developments and applications of bioinspired dendritic polymers, Polym. Chem. 33 (2014) 1125–1133.

[4] D. Wang, D. Astruc, Dendritic catalysis — Basic concepts and recent trends, Coord. Chem. Rev. 257 (2013) 2317–2334.

[5] S.C. Bourque, H. Alper, M. Curie, C. Kn, L.E. Manzer, Hydroformylation Reactions Using Recyclable Rhodium-Complexed Dendrimers on Silica, J. Am. Chem. Soc. 122 (2000) 956–957.

[6] E. Murugan, R. Rangasamy, Synthesis, Characterization, and Heterogeneous Catalysis of Polymer-Supported Poly(propyleneimine) Dendrimer Stabilized Gold Nanoparticle Catalyst, J. Polym. Sci. Part A Polym. Chem. 48 (2010) 2525–2532.

[7] G.R. Krishnan, K. Sreekumar, First example of organocatalysis by polystyrene-supported PAMAM dendrimers: Highly efficient and reusable catalyst for knoevenagel condensations, European J. Org. Chem. (2008) 4763–4768.

[8] G. Vijayaraghavan, K.J. Stevenson, Synergistic assembly of dendrimer-templated platinum catalysts on nitrogen-doped carbon nanotube electrodes for oxygen reduction, Langmuir. 23 (2007) 5279–5282.

[9] S. Hwang, C.D. Shreiner, N. Moorefield, G.R. Newkome, Recent progress and

applications for metallodendrimers, New J. Chem. 31 (2007) 1192–1217.

[10] Z. Lotfi, H.Z. Mousavi, S.M. Sajjadi, Amino-terminated hyper-branched polyamidoamine polymer grafted magnetic graphene oxide nanosheets as an efficient sorbent for the extraction of selective serotonin reuptake inhibitors from plasma samples, Anal. Methods. 9 (2017) 4504–4513.

[11] K. Lakshmi, R. Rangasamy, E. Prathibha, A. Sridhar, Immobilization of Pt nanoparticles on magnetite–poly (epoxyamine) nanocomposite for the reduction of p-nitrophenol, SN Appl. Sci. 1 (2019)..

[12] Q.M. Kainz, O. Reiser, Polymer- and Dendrimer-Coated Magnetic Nanoparticles as Versatile Supports for Catalysts, Scavengers, and Reagents, Acc. Chem. Res. 47 (2013) 667–677.

[13] A. Pourjavadi, S.H. Hosseini, S.T. Hosseini, S.A. Aghayeemeibody, Magnetic nanoparticles coated by acidic functionalized poly(amidoamine) dendrimer: Effective acidic organocatalyst, Catal. Commun. 28 (2012) 86–89.

[14] P.D. Stevens, J. Fan, H.M.R. Gardimalla, M. Yen, Y. Gao, Superparamagnetic nanoparticle-supported catalysis of Suzuki cross-coupling reactions, Org. Lett. 7 (2005) 2085–2088. https://doi.org/10.1021/ol050218w.

[15] A. Baykal, M.S. Toprak, Z. Durmus, M. Senel, H. Sozeri, A. Demir, Synthesis and characterization of dendrimer-encapsulated iron and iron-oxide nanoparticles, J. Supercond. Nov. Magn. 25 (2012) 1541–1549. https://doi.org/10.1007/s10948-012-1454-z.

[16] S. Shylesh, V. Schünemann, W.R. Thiel, Magnetically separable nanocatalysts: Bridges between homogeneous and heterogeneous catalysis, Angew. Chemie - Int. Ed. 49 (2010) 3428–3459.

[17] M.B. Gawande, P.S. Branco, R.S. Varma, Nano-magnetite (Fe3O4) as a support for recyclable catalysts in the development of sustainable methodologies, Chem. Soc. Rev. 42 (2013) 3371–3393.

[18] R.S.V. and M.B.G. Rakesh K. Sharma,*Sriparna Dutta, Shivani Sharma, Radek Zboril, Fe3O4 (Iron Oxide)-Supported Nanocatalysts: Synthesis, Characterization and Applications in Coupling Reactions, Green Chem. 18 (2016) 3184–3209.

[19] B. Maleki, O. Reiser, E. Esmaeilnezhad, H.J. Choi, SO3H-dendrimer functionalized magnetic nanoparticles (Fe3O4@D–NH–(CH2)4–SO3H): Synthesis, characterization and its application as a novel and heterogeneous catalyst for the one-pot synthesis of polyfunctionalized pyrans and polyhydroquinolines, Polyhedron. 162 (2019) 129–141.

[20] T. Kanti, D. Sayan, G. Poushali, B. Sanjay, R. Subhadip, M.N.C. Das, Mussel inspired green synthesis of silver nanoparticles ‐ decorated halloysite nanotube using dopamine : characterization and evaluation of its catalytic activity, Appl. Nanosci. (2018).

[21] M. Tarahomi, H. Alinezhad, B. Maleki, Immobilizing Pd nanoparticles on the ternary hybrid system of graphene oxide, Fe3O4 nanoparticles, and PAMAM dendrimer as an efficient support for catalyzing sonogashira coupling reaction, Appl. Organomet. Chem. 33 (2019) 1–13.

[22] H. Alinezhad, M. Tarahomi, B. Maleki, A. Amiri, SO 3 H-functionalized nano-MGO-D-NH 2 : Synthesis, characterization and application for one-pot synthesis of pyrano[2,3-d]pyrimidinone and tetrahydrobenzo[b]pyran derivatives in aqueous media, Appl. Organomet. Chem. 33 (2019) 1–14.

[23] D. Wang, C. Deraedt, L. Salmon, C. Labrugère, L. Etienne, J. Ruiz, D. Astruc, Efficient and magnetically recoverable "click" PEGylated γ-Fe 2 O 3 -Pd nanoparticle catalysts for Suzuki-Miyaura, Sonogashira, and Heck reactions with positive dendritic effects, Chem. - A Eur. J. 21 (2015) 1508–1519.

[24] R. Abu-reziq, H. Alper, D. Wang, M.L. Post, Metal Supported on Dendronized Magnetic Nanoparticles : Highly Selective Hydroformylation Catalysts, J. Am. Chem. Soc. 128 (2006) 5279–5282.

[25] Q.H. and C.J. Wei Wu, Magnetic Iron Oxide Nanoparticles : Synthesis and Surface Functionalization Strategies Synthesis of Iron Oxide NPs, Nanoscale Res. Lett. 3 (2008) 397.

[26] M.R. Knecht, R.M. Crooks, Magnetic properties of dendrimer-encapsulated iron nanoparticles containing an average of 55 and 147 atoms, New J. Chem. 31 (2007) 1349–1353

[27] J. Chiou, B. Lai, K. Hsu, D. Chen, One-pot green synthesis of silver / iron oxide composite nanoparticles for 4-nitrophenol reduction, J. Hazard. Mater. 248–249 (2013) 394–400.

[28] D.K.. K.J.. N.K.M.. P.K.. N.K. Jain, A review on comparative study of PPI and PAMAM dendrimers, J. Nanoparticle Res. (2016) 146.

[29] B. González, E. Ruiz-Hernández, M.J. Feito, C. López De Laorden, D. Arcos, C. Ramírez-Santillán, C. Matesanz, M.T. Portolés, M. Vallet-Regí, Covalently bonded dendrimer-maghemite nanosystems: Nonviral vectors for in vitro gene magnetofection,

J. Mater. Chem. 21 (2011) 4598–4604.

[30] E. Murugan, N.J. J, M. Ariraman, S. Rajendran, J. Kathirvel, C.R. Akshata, K. Kumar, Core − Shell Nanostructured Fe 3 O 4 − Poly (styrene- co -vinylbenzyl chloride) Grafted PPI Dendrimers Stabilized with AuNPs / PdNPs for E ffi cient Nuclease Activity, ACS Omega. 3 (2018) 13685–13693.

[31] E. Knoevenagel, Ueber Derivate des 1, 3- Diketocyclohexans (Dihydroresorcins), Berichte Der Dtsch. Chem. Gesellschaft. 27 (1894) 2337–2345.

[32] F. Zamani, E. Izadi, Polyvinyl amine coated Fe3O4@SiO2 magnetic microspheres for Knoevenagel condensation, Cuihua Xuebao/Chinese J. Catal. 35 (2014) 21–27.

[33] H.S. Pawar, A.S. Wagh, A.M. Lali, Triethylamine: A potential N-base surrogate for pyridine in Knoevenagel condensation of aromatic aldehydes and malonic acid, New J. Chem. 40 (2016) 4962–4968.

[34] K. Tarade, S. Shinde, S. Sakate, C. Rode, Pyridine Immobilised on magnetic silica as an efficient solid base catalyst for Knoevenagel condensation of furfural with acetyl acetone, Catal. Commun. 124 (2019) 81–85

[35] F. Poyafar, M. Fallah-mehrjardi, S. Hossein, APreparation and characterization of polyethylene glycol-bis(N- methylimidazolium) dihydroxide as a basic phase-transfer catalyst and its application in Knoevenagel condensation under aqueous media, Asian J. Green Chem. 2 (2018) 96–105.

[36] C.J. Simpson, M.J. Fitzhenry, N.P.J. Stamford, Preparation of vinylphenols from 2- and 4-hydroxybenzaldehydes, Tetrahedron Lett. 46 (2005) 6893–6896.

[37] M. Golshan, M. Salami-Kalajahi, H. Roghani-Mamaqani, M. Mohammadi, Synthesis of poly(propylene imine) dendrimers via homogeneous reduction process using lithium aluminium hydride: Bioconjugation with folic acid and doxorubicin release kinetics, Appl. Organomet. Chem. 31 (2017) 1–7.

[38] K. Tarade, S. Shinde, S. Sakate, C. Rode, Pyridine Immobilised on Magnetic Silica as an Efficient Solid Base Catalyst for Knoevenagel Condensation of Furfural with Acetyl acetone, Catal. Commun. 128 (2019) 85.

[39] B. Maleki, S. Sheikh, Nano polypropylenimine dendrimer (DAB-PPI-G1): as a novel nano basic-polymer catalyst for one-pot synthesis of 2-amino-2-chromene derivatives, RSC Adv. 5 (2015) 42997–43005.

[40] A. V Davis, M. Driffield, D.K. Smith, V. Uni, A Dendritic Active Site : Catalysis of the Henry Reaction, Org. Lett. 3 (2001) 3075–3078.

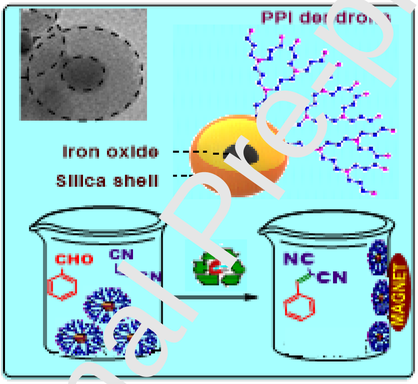
[41] F. Adibian, A.R. Pourali, B. Maleki, M. Baghayeri, A. Amiri, One- pot synthesis of

dihydro-1H-indeno[1,2-b] pyridines and tetrahydrobenzo[b] pyran derivatives using a new and efficient nanocomposite catalyst based on N- butylsulfonate- functionalized MMWCNTs-D-NH2, Polyhedron. 175 (2020) 114179.

[42] J.B.M. de Resende Filho, G.P. Pires, J.M.G. de Oliveira Ferreira, E.E.S. Teotonio, J.A. Vale, Knoevenagel Condensation of Aldehydes and Ketones with Malononitrile Catalyzed by Amine Compounds-Tethered Fe3O4@SiO2 Nanoparticles, Catal. Letters. 147 (2017) 167–180.

[43] E. Prathibha, R. Rangasamy, A. Sridhar, K. Lakshmi, Synthesis and Characterization of Fe3O4/Carbon Dot Supported MnO2 Nanoparticles for the Controlled Oxidation of Benzyl Alcohols, ChemistrySelect. 5 (2020) 988–993.

Graphical Abstract



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Declaration of interests

☐The authors declare that they have no known competing financial interestsor personal relationships that could have appeared to influence the work reported in this paper.

Synthesis of structurally enhanced magnetite cored poly(propyleneimine) dendrimer nanohybrid material and evaluation of its functionality in sustainable catalysis of condensation reactions

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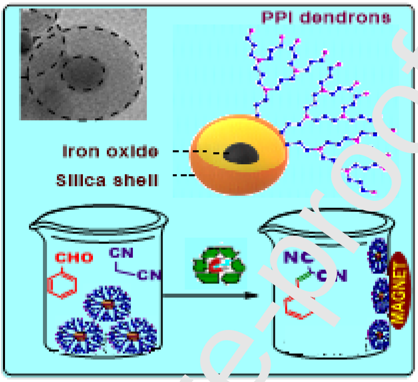

HIGHLIGHTS

- First time, we report the magnetic cored synthesis of PPI dendrimer
- Fine core-shell magnetite dendritic structure was accomplished at 25±5 nm size
- Semi-heterogeneous, multivalent base catalysis explored for active methylene compound
- Better efficacy observed at ambient conditions even in aqueous medium
- Its' magnetic recyclability was proved 8 times with retained activity