Catalysis Science & Technology

Accepted Manuscript

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View Article Online
DOI: 10.1039/C5CY00849B

Journal Name

ARTICLE

Magnetically retrievable magnetite (Fe_3O_4) immobilized ionic liquid: an efficient catalyst for the preparation of 1-carbamatoalkyl-2-naphthols

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Harsh N. Dadhania,[a] Dipak K. Raval[a] and Abhishek N. Dadhania*[b]

Magnetite (Fe_3O_4) supported –SO_3H functionalized benzimidazolium based ionic liquid has been synthesized via covalent grafting of benzimidazole on a (3-chloropropyl)triethoxysilane functionalized magnetic nanoparticle followed by quarternization reaction with 1,4-butane sultone. The obtained magnetic nanoparticle supported ionic liquid (IL@MNP) has been characterized by FT-IR, TGA, TEM, XRD, VSM, EDX and Elemental analysis. The performance of prepared catalyst was evaluated in the preparation of 1-carbamatoalkyl-2-naphthols. The magnetite supported catalyst showed excellent catalytic activity and corresponding products were obtained in high yields in all the tested cases. The heterogeneous nature of the magnetite favoured easy recovery and recyclability of catalyst through magnetic decantation, which makes the protocol highly advantageous over conventional procedures.

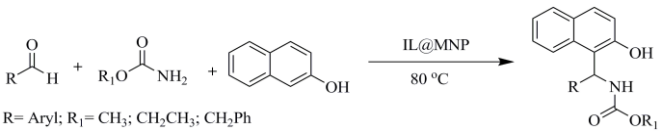
1. Introduction

Ionic liquids have attracted increasing interest of chemists, both in academia and industry due to their unique physical and chemical properties.[1-3] Task-specific ionic liquids have received much attention as catalyst and alternative reaction media for various chemical transformations.[4, 5] We also reported highly efficient methodologies for the synthesis of pharmaceutically important organic moieties using ionic liquid.[6-10] In these methodologies, the ionic liquid not only significantly enhanced the reaction rate by its inherent Brønsted acidity, but also provided the homogeneity to the reaction media. However, due to homogeneous nature of ionic liquid, we encountered a tedious problem of catalyst separation. To overcome this problem an ideal approach was thought worth to immobilize the corresponding ionic liquid on solid support. Such immobilized ionic liquid facilitates the separation process, easy handling and storage.[11, 12]

Magnetically supported catalyst can easily and efficiently be separated from the reaction mixture by an external magnet. It facilitates remarkable catalyst recovery without the need for filtration. Magnetic nanoparticles (MNPs) have emerged as the support to homogeneous catalyst; due to their insoluble and paramagnetic nature.[13, 14]. The ease of separation is one of the most attractive features of MNPs as compared to its homogeneous and heterogeneous counterparts.[15-17]

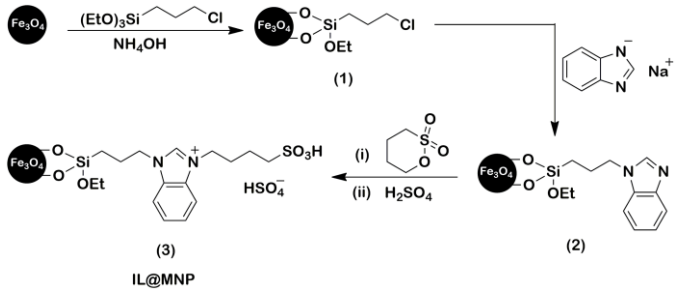
On the other hand, 1-carbamatoalkyl-2-naphthols have emerged as molecules of great interest mainly due to their hydrolyzed product 1-aminoalkyl-2-naphthols, which possess interesting biological activities.[18-21] These derivatives have been evaluated for their hypotensive and bradycardic effects.[22, 23] Many synthetic strategies for the preparation of 1-carbamatoalkyl-2-naphthols have been reported by one-pot multi-component condensation reaction between 2-naphthol, aromatic aldehydes and alkyl carbamates using various catalysts.[24-28] However, some of these methodologies endure one or more drawbacks such as longer reaction time, harsh reaction conditions, poor to moderate yields, large amount of catalyst, use of expensive metal catalysts and tedious work up. The literature survey encouraged us to work in this relatively novel but broadly expanding field.

In this report, we introduce a new magnetic nanoparticle supported –SO_3H functionalized benzimidazolium based acidic ionic liquid, as a highly efficient catalyst for the preparation of 1-carbamatoalkyl-2-naphthols (**Scheme 1**) in good yield with significantly enhanced reaction rate as compared to other reported methods. IL@MNP was easily separated by magnetic decantation and was recycled for six times with retention of activity in the model reaction.



Scheme 1 Synthesis of 1-carbamatoalkyl-2-naphthols using IL@MNP

[a]Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388120, Gujarat India.
[b]Department of Chemical Sciences, P. D. Patel Institute of Applied Sciences, Charotar University of Science and Technology, Changa 388421, Gujarat India.
E-mail: abhishekdadhania.bt@charusat.ac.in



Scheme 2 Synthesis of magnetically supported ionic liquid (IL@MNP)

2. Results and Discussion

2.1 Preparation and characterization of catalyst (IL@MNPs)

The catalyst was prepared according to the procedure shown in **scheme 2**. We used Fe_3O_4 nanoparticles of approximately 8-10 nm for solid support, which were prepared via co precipitation method[29]. Subsequently, these particles were functionalized using (3-chloropropyl)triethoxysilane in ammonia solution by surface capping method[30] to produce **(1)**. Functionalization provided good stability to nano Fe_3O_4 against aggregation and acid corrosion. Furthermore, it also offered suitable binding sites for further modification. Then, **(1)** was reacted with sodium salt of benzimidazole in benzene to yield the precursor **(2)**. This was further subjected to quarternization reaction with 1,4-butane sultone followed by treatment with one equivalent H_2SO_4 to yield the magnetically retrievable acidic ionic liquid IL@MNP **(3)**.

The morphology of IL@MNP was checked by transmission electron microscopy (TEM) (**Figure 1**). TEM images displayed the dark magnetite core surrounded by benzimidazolium linkers and the core-shell structure of catalyst with an average size of 20-22 nm. In addition, the XRD study of the silane functionalized magnetic nanoparticle was carried out to confirm the crystalline nature and surface state. The XRD pattern (**Figure 2**) of the silane functionalized nanoparticles showed the diffraction peak positions and the relative intensities of the peaks matched well with the standard Fe_3O_4 sample (JCPDS file No. 19-0629).

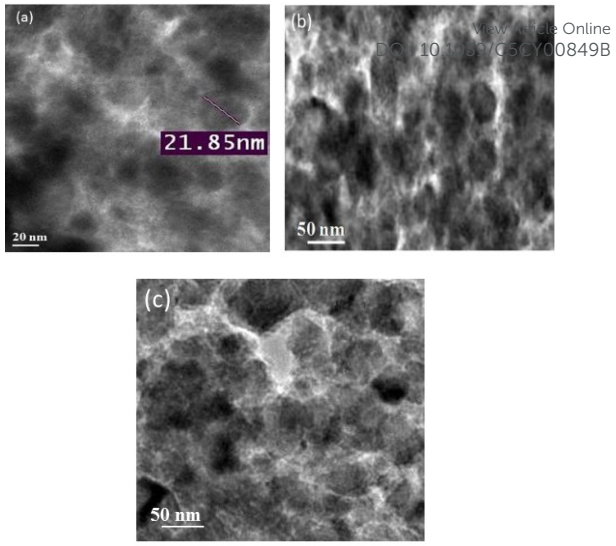


Figure 1 Transmission electron microscope (TEM) images of IL@MNP [fresh **(a) & (b),** recycled **(c)]**

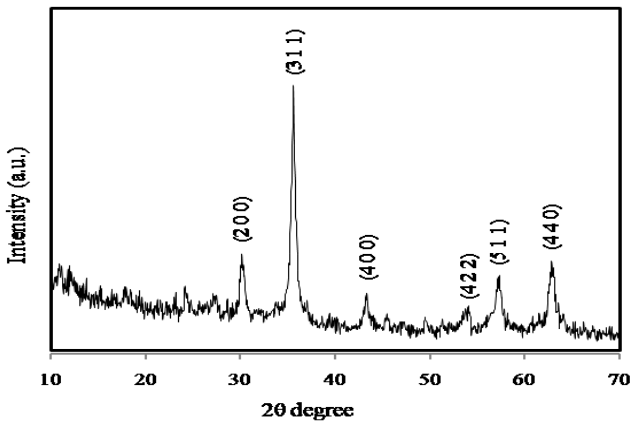


Figure 2 X-Ray diffraction pattern of silane functionalized magnetic nanoparticles

The detailed investigation about functionalization of magnetic nanoparticle was done by FT-IR spectroscopy (**Figure 3**). All spectra showed characteristic broad band around 3420 cm^{-1} due to Si-OH group and adsorbed water. Spectrum (3a) shows the characteristic band of the Fe–O bond vibration of iron oxide core at 585 cm^{-1} [31]. The strong band observed at around 1095 cm-1 is due to Si–O–Si stretching modes of the silica shell[32]. Additionally, the band at 2955 cm^{-1}, corresponds to the $–CH_2$ group of the chloro-propyl group. Spectrum (3b) shows typical bands at 1565 and 1635 cm^{-1} due to C=N and C=C vibration of benzimidazole ring respectively[33]. Additionally, the band observed at 3145 cm^{-1} is due to sp^2 C–H stretching vibrations of benzimidazole ring revealed the grafting of benzimidazole moiety. Spectrum (3c) shows the strong bands at 1041 and 1137 cm^{-1} due to S=O stretching vibration[34].

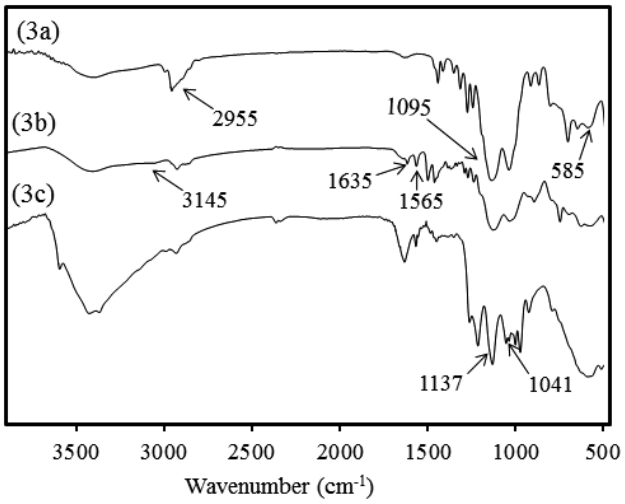


Figure 3 FT-IR spectra of (a) ClPr-Si@Fe_3O_4, (b) 3-(1-benzimidazole) Pr-Si@Fe3O4 and (c) IL@MNP

Thermal stability of the catalyst was determined by thermogravimetric (TG) analysis (**Figure 4**). The loss of adsorbed water on the support and silanol groups resulted into initial weight loss of 3.79% up to 105 ºC. The complete loss of covalently attached organic moiety was observed in the temperature range from 200 to 600 ºC. The amount of organic moiety was found to be about 27% against total solid catalyst. The organic loading in the catalyst was found to be 0.573 mmol·g^{-1}. The loading of IL obtained from TG analysis was found in good agreement with elemental analysis. Elemental analysis of catalyst showed 6.75% S, which is equal to IL loading 0.56 mmol·g^{-1}.

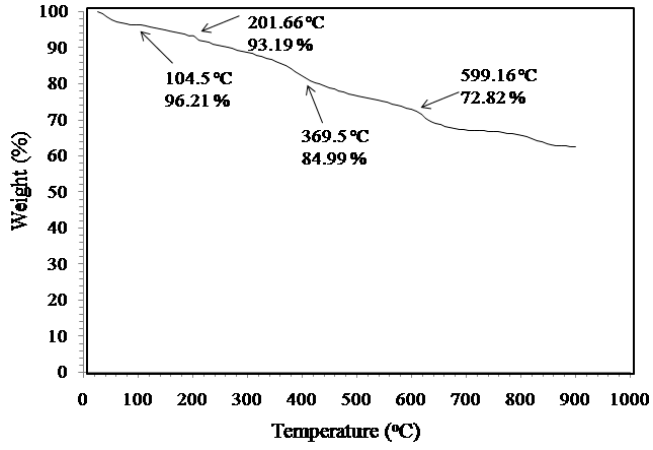


Figure 4 TG analysis of IL@MNP

The magnetic properties of the IL@MNP and the neat Fe_3O_4 were checked by vibrating sample magnetometry (VSM). The field dependent magnetization curves measured at room temperature with the field sweeping from -10 000 to 10 000 Oe are depicted in **Figure 5**. The saturation magnetization of the sample was found to reduce from 8.95 to 5.88 emu.g^{-1}, due to the functionalization of Fe_3O_4. However, it was still sufficient for magnetic separation of the catalyst from reaction mixture using external magnet. Moreover, no hysteresis was observed before and after functionalization which demonstrated its superparamagnetic characteristics[35, 36].

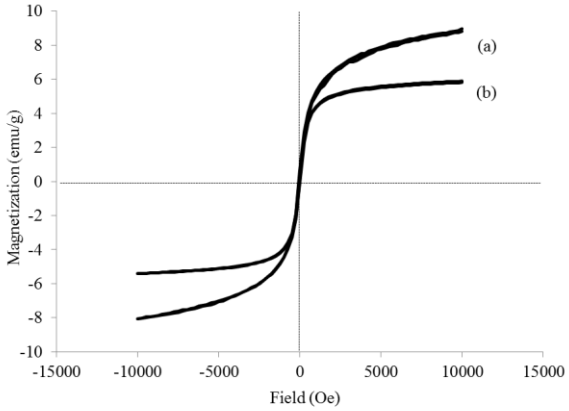


Figure 5 Magnetization curves obtained by VSM at room temperature for (a) Fe3O4 and (b) IL@MNP

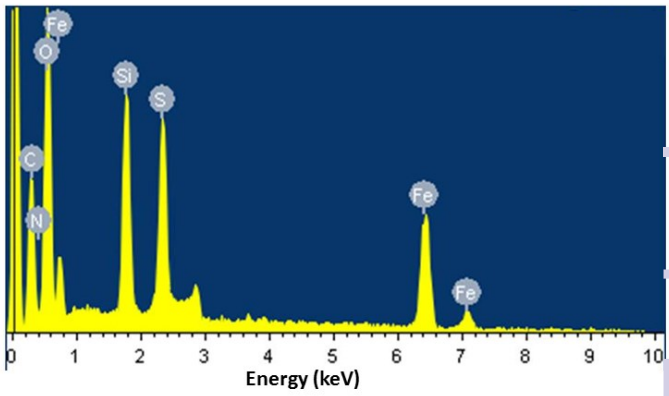


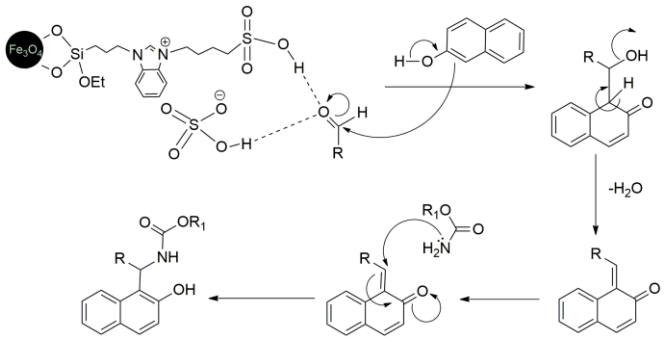
Figure 6 EDX spectrum of IL@MNP

The energy-dispersive X-ray (EDX) spectrum of the IL@MNP **(Figure 6)** show the presence of elements C, N, O, Si, S and Fe in the catalyst, which revealed the grafting of benzimidazolium ionic liquid on the surface of magnetic nanoparticles.

2.2 Catalytical activity of IL@MNPs for the preparation of 1-carbamatoalkyl-2-naphthols

The efficacy of the prepared catalyst in preparation of 1-carbamatoalkyl-2-naphthols was checked. The reaction condition was optimized on model reaction between 2-naphthol, benzaldehyde and methyl carbamate under solvent free condition to yield **4a** (**Table 1**). Initially, the model reaction without any catalyst or sole Fe_3O_4 as catalyst showed no reaction over a period of 60 min (**Entry 1**). From the results of subsequent reactions with different amount of catalyst at various temperatures (**Entry 2 to 7**), the reaction at 80 ºC with 1.5 mol% of catalyst was found to be the most optimum reaction condition with 96% yield after 5 min (**Entry 5**). The

efficiency of prepared catalyst was also compared with some other reported catalysts for the synthesis of **4a**. Present catalyst is found better than other reported catalysts in terms of catalyst recovery, reaction temperature, reaction time and yield. To check the efficiency and generality of the catalyst, the reaction of 2-naphthol was carried out with a variety of aryl aldehydes and alkyl carbamates to yield the corresponding 1-carbamatoalkyl-2-naphthol derivatives under optimal reaction condition derived from the model reaction. In all the tested cases, excellent yields of corresponding 1-carbamatoalkyl-2-naphthol derivatives were obtained in short reaction time (**Table 2**). The plausible mechanism for the formation of 1-carbamatoalkyl-2-naphthols catalyzed by IL@MNPs is proposed in **Scheme 3**.



Scheme 3 Plausible mechanism for the synthesis of 1-carbamatoalkyl-2-naphthols using IL@MNP

Table 1 Optimization of reaction condition for the synthesis of 4a[a] and comparison with the reported catalysts.

Entry	Catalyst (mol %)	Temperature (°C)	Time (min)	Yield (%)[b]
1	None/ Fe_3O_4 (1.5)	80	60	NR[c]
2	IL@MNP (1.0)	60	15	81
3	IL@MNP (1.0)	80	11	89
4	IL@MNP (1.0)	100	9	90
5	**IL@MNP (1.5)**	**80**	**5**	**96**
6	IL@MNP (1.5)	70	9	85
7	IL@MNP (2.0)	80	5	97
8	4-(1-Imidazolium)-butanesulfonate	80	120	78[24]
9	Preyssler nanoparticles/SiO_2	90	3	84[25]
10	[Dsim]HSO_4	80	11	98[27]
11	$NaHSO_4/SiO_2$	100	3.5	81[26]
12	$SnCl_4.5H_2O$	60	12	83[37]

[a] Reaction condition: 2-naphthol (2 mmol), benzaldehyde (2 mmol) and methyl carbamate (2.2 mmol), solvent free. [b] Isolated yield. [c] No reaction was observed.

Table 2 Solvent free synthesis of 1-carbamatoalkyl-2-naphthols using IL@MNPs at 80°C

Entry	R	R_1	Time (min)	Yield %	M. P. (°C) Found	M. P. (°C) Reported
4a	C_6H_5	CH_3	5	96	224 - 226	222 - 225[25]
4b	4-$NO_2C_6H_4$	CH_3	4	97	202 -204	200 - 202[25]
4c	3-$NO_2C_6H_4$	CH_3	4	97	248 - 250	253 - 255[25]
4d	4-BrC_6H_4	CH_3	10	94	214 - 216	172 - 174[27]
4e	4-ClC_6H_4	CH_3	7	96	196 – 198	198 - 200[25]
4f	C_6H_5	CH_3CH_2	5	93	202 – 204	-
4g	4-FC_6H_4	CH_3CH_2	6	92	210 – 212	-
4h	4-$NO_2C_6H_4$	CH_3CH_2	4	95	226- 228	-
4i	4-BrC_6H_4	CH_3CH_2	7	91	218 - 220	-
4j	4-ClC_6H_4	CH_3CH_2	7	93	208 – 210	-
4k	C_6H_5	$PhCH_2$	12	94	182 – 184	180 – 182[38]
4l	4-FC_6H_4	$PhCH_2$	10	90	206 – 208	202 – 203[38]
4m	4-$MeOC_6H_4$	$PhCH_2$	12	90	166 - 168	165 – 167[38]
4n	4-$NO_2C_6H_4$	$PhCH_2$	5	94	194 - 196	200[38]
4o	3-$NO_2C_6H_4$	$PhCH_2$	5	92	186 - 188	196 - 197[38]

2.3 Catalyst recyclability and leaching study

Recyclability and leaching, important factors to judge the sustainability of any catalyst, were checked on model reaction between 4-nitrobenzaldehyde, ethyl carbamate and 2-naphthol. The catalyst was easily recovered by magnetic decantation after the reaction and was reused in the same model reaction for next five consecutive cycles with comparable retention in its activity (**Figure 7**). The FT-IR spectrum **(Figure 8)** and TEM image **(Figure 1)** of the recovered catalyst also suggest no significant change in functionality.

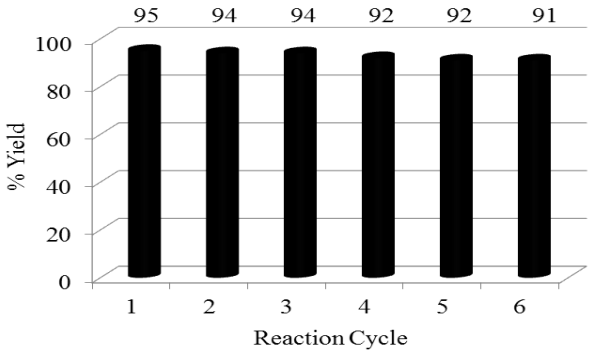


Figure 7 Recyclability test of catalyst

To check leaching of the catalyst, hot EtOH (15 mL) was added after 2 min of reaction time and the catalyst was easily removed using external magnet. The same reaction was continued for another 30 min and was monitored using TLC, Further conversion was not observed during this period and the overall yield was found to be 52%. It proved that leaching of the catalyst was not occurring during the process.

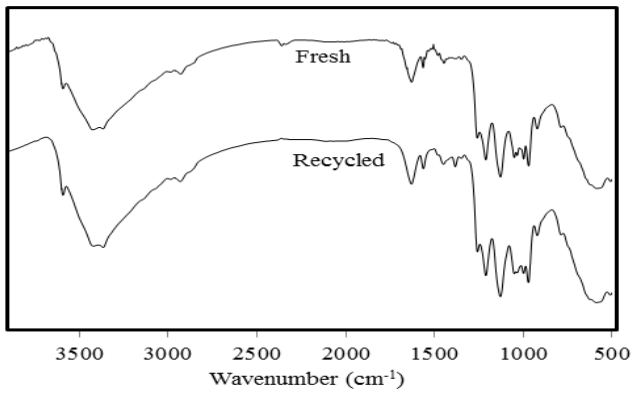


Figure 8 FT-IR spectra of fresh and used catalyst.

3. Conclusions

We have synthesized and applied a novel magnetic nanoparticle supported $–SO_3H$ functionalized benzimidazolium based ionic liquid (IL@MNP), as a highly efficient and environmentally benign catalyst for the synthesis of 1-carbamatoalkyl-2-naphthols. The notable advantages of this methodology are magnetic separability and reusability of the catalyst, ease of reaction, short reaction times, high yields and solvent-free greener protocol. Thus, it provides an attractive alternative to the existing methodologies.

4. Experimental

4.1 Materials and methods

Magnetite (Fe_3O_4) was prepared according to a procedure reported in literature[29] and was used for the support. (3-chloropropyl)triethoxysilane, benzimidazole, 1,4-butane sultone, were purchased from Sigma–Aldrich, India and were used without further purification. FT-IR spectra were recorded on Thermo Nicolet 6700 spectrophotometer using KBr pellets. Thermal gravimetric analysis (TGA) was performed at a heating rate of 10°C/min on a Mettler-Toledo TGA. X-ray diffraction (XRD) study was done on Bruker, D2 Phaser. The magnetization curves were obtained by a vibrating sample magnetometer (VSM-7400, LAKE SHORE, USA). Transmission electron microscopy (TEM) was done on JEOL, JEM 2100 model. The EDX was performed using a JOEL JSM-5610 scanning electron microscope. C, H, N elemental analysis was carried out on PerkinElmer 2400 series-II elemental analyzer (PerkinElmer, USA). All the synthesized compounds were characterized by ^1H NMR (400 MHz Bruker Avance, Switzerland). Melting points were determined on µThermoCal10 (Analab Scientific Pvt. Ltd) melting points apparatus and were uncorrected.

4.2 Synthesis of (3-chloropropyl)triethoxysilane coated Fe_3O_4 nanoparticles (ClPr-Si@Fe_3O_4).

Magnetite (Fe_3O_4) nanoparticles were synthesized using a coprecipitation method[29]. Initially, $FeCl_3 \cdot 6H_2O$ (5.4 g) and urea (3.6 g) were dissolved in water (200 mL) at 90 °C. The temperature was maintained for 2 h. After the solution turned brown, it was cooled to room temperature and $FeSO_4 \cdot 7H_2O$ (2.8 g) was added. The pH of resultant solution was adjusted to 10 by adding 0.1 M NaOH solution. The obtained precipitates were subjected to ultrasonic irradiation at 30 to 35 °C for 30 min. Black powder (Fe_3O_4) was obtained after 5h which was washed several times with water and dried under vacuum. Coating of Fe_3O_4 nanoparticles with (3-chloropropyl)triethoxysilane was performed via surface capping method[30]. A dispersion of Fe_3O_4 (6 g) was prepared in ethanol (200 mL) under sonication for 30 minutes. After that (3-chloropropyl)triethoxysilane (15 mL) and ammonia solution (15 mL) were added to the dispersed ethanolic solution of Fe_3O_4 and stirred for 24 h at room temperature. The resulting (3-chloropropyl)triethoxysilane coated Fe_3O_4 nanoparticles were washed 4 times with aliquot of 10 mL ethanol each time and dried under vacuum.

4.3 Synthesis of 3-(1-benzimidazole)propyltriethoxysilane@ Fe_3O_4 (3-(1-benzimidazole)Pr-Si@Fe_3O_4)

For covalent grafting of benzimidazole on (3-chloropropyl)triethoxysilane coated Fe_3O_4 nanoparticles, sodium salt of benzimidazole was prepared by reacting benzimidazole (1.17 g) with 50% sodium hydride in mineral oil (0.479 g) in dry benzene (25 mL) under inert atmosphere for 3 h. The resultant solution of sodium benzimidazole was mixed with ClPr-Si@Fe_3O_4 (5 g) and refluxed for 24 h to get the precursor 2. It was separated by external magnet, washed thoroughly with ethanol and dried under vacuum.

4.4 Synthesis of IL@MNP

3-(1-benzimidazole)Pr-Si@Fe_3O_4 (3g) and 1,4-butane sultone (0.34 g) were dispersed in toluene (30 mL) and stirred at 100 ºC for 6 h. The resultant particles were further treated with conc. H_2SO_4 (0.133 mL) at 50 ºC for 8 h and then washed with toluene. After cooling, the resultant IL@MNP was collected magnetically, washed thoroughly with ethanol and dried in a vacuum oven at 100°C.

4.5 General procedure for the synthesis of 1-carbamatoalkyl-2-naphthols

A mixture of aldehyde (2 mmol), 2-naphthol (2 mmol), alkyl carbamate (2.2 mmol) and IL@MNP (1.5 mol %) was stirred magnetically and after solidification with a small glass rod at 80 ºC in an oil bath. After completion of reaction as indicated by TLC, the crude reaction mass was washed with hot water to remove unreacted water soluble starting material. Ethanol was added to the solid reaction mass and the catalyst was separated by external magnet from the product solution. Recovered IL@MNP was washed with ethanol, and used for subsequent cycles after drying under vacuum. Pure 1-carbamatoalkyl-2-naphthols were obtained by evaporation of solvent followed by recrystallization. The synthesized 1-carbamatoalkyl-2-naphthols were characterized by the physical and spectral data.

4.5.1 Methyl(2-hydroxynaphthalen-1-yl)(phenyl)methyl carbamate (4a) : Yield 96% ; mp 224-226 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.58 (s, 3H), 6.88 (d, *J* = 8.8 Hz, 1H), 7.15–7.41 (m, 8H), 7.68 (d, *J* = 7.4 Hz, 1H, NH), 7.76–7.82 (m, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 10.13 (s, 1H, OH); Anal. Calcd for: $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56%. Found: C, 74.25; H, 5.55; N, 4.52%.

4.5.2 Methyl(2-hydroxynaphthalen-1-yl)(4-nitrophenyl) methyl carbamate (4b) : Yield 97% ; mp 202-204 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.60 (s, 3H), 6.95 (d, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.79–7.89 (m, 4H), 8.15 (d, *J* = 7.6 Hz, 2H), 10.22 (s, 1H, OH); Anal. Calcd for: $C_{19}H_{16}N_2O_5$: C, 64.77; H, 4.58; N, 7.95%. Found: C, 64.70; H, 4.56; N, 7.93%.

4.5.3 Methyl(4-Bromophenyl)(2-hydroxynaphthalen-1-yl) methyl carbamate (4d) : Yield 94% ; mp 214-216 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) : 3.57 (s, 3H), 6.82 (d, *J* = 8.8 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 6.0 Hz, 2H), 7.73-7.82 (m, 3H), 7.88 (d, *J* = 6.8 Hz, 1H), 10.15 (s, 1H, OH); Anal. Calcd for $C_{19}H_{16}BrNO_3$: C, 59.08; H, 4.18 ; N, 3.63%. Found: C, 59.05; H, 4.15; N, 3.65%.

4.5.4 Methyl(4-chlorophenyl)(2-hydroxynaphthalen-1-yl) methyl carbamate (4e) : Yield 96% ; mp 196-198 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.57 (s, 3H), 6.85 (d, *J* = 8.4 Hz, 1H), 7.21–7.42 (m, 7H), 7.77–7.82 (m, 3H), 7.89 (d, *J* = 7.2 Hz, 1H), 10.17 (s, 1H, OH) ppm; Anal. Calcd for $C_{19}H_{16}ClNO_3$: C, 66.77; H, 4.72; N, 4.10%. Found: C, 66.75; H, 4.69; N, 4.07%.

4.5.5 Ethyl(2-hydroxynaphthalen-1-yl)(phenyl)methyl carbamate (4f) : Yield 93% ; mp 202-204 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.17 (t, *J* = 6.8, 3H), 4.01 (d, *J* = 7.2, 1H), 4,04 (d, *J* = 7.2, 1H), 6.88 (d, *J* = 8.8, 1H), 7.17-7.30 (m, 7H), 7.40 (t, *J* = 7.2, 1H), 7.59 (S, 1H), 7.76-7.82 (m, 2H), 7.93 (d, *J* = 7.2 Hz, 1H, NH), 10.13 (s, 1H, OH) ppm ; Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36%. Found: C, 74.66; H, 5.92; N, 4.34%.

4.5.6 Ethyl(4-Fluorophenyl)(2-hydroxynaphthalen-1-yl) methyl carbamate (4g) : Yield 92% ; mp 210-212 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.16 (t, *J* = 6.8, 3H), 3.99 (d, *J* = 6.8, 1H), 4.03 (d, *J* = 6.8, 1H), 6.82 (d, *J* = 8.4, 1H), 7.08 (t, *J* = 8.8, 2H), 7.19-7.30 (m, 4H), 7.40 (t, *J* = 6.8, 1H), 7.70 (d, *J* = 8.8, 1H), 7.80-7.89 (m, 2H), 7.92 (d, *J* = 8.0, 1H), 10.15 (s, 1H, OH)ppm; Anal. Calcd for $C_{20}H_{18}FNO_3$: C, 70.78 ; H, 5.35 ; N, 4.13%. Found: C, 70.75; H, 5.34; N, 4.13%.

4.5.7 Ethyl(2-hydroxynaphthalen-1-yl)(4-Nitrophenyl) methyl carbamate (4h) : Yield 95% ; mp 226-228 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.18 (t, *J* = 7.2, 3H), 4.02 (d, *J* = 6.8, 1H), 4.06 (d, *J* = 6.8, 1H), 6.94 (d, *J* = 8.4, 1H), 7.21 (d, *J* = 8.8 1H), 7.29 (t, *J* = 7.2, 1H), 7.39-7.47 (m, 3H), 7.79-7.91 (m, 3H), 8.14 (d, *J* = 2.8 Hz, 1H), 8.16 (d, *J* = 2.8 Hz, 2H) 10.21 (s, 1H) ppm; Anal. Calcd. for $C_{20}H_{18}N_2O_5$: C, 65.57 ; H, 4.95 ; N, 7.65%. Found: C, 65.60; H, 4.86; N, 7.62%.

4.5.8 Ethyl(4-Chlorophenyl)(2-hydroxynaphthalen-1-yl) methyl carbamate (4j) : Yield 93% ; mp 208-210 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 1.17 (t, *J* = 6.8, 3H), 4.02 (d, *J* = 6.8 1H), 4.05 (d, *J* = 6.8, 1H), 6.83 (d, *J* = 8.4, 1H), 7.20-7.42 (m, 7H), 7.64-7.83 (m,3H), 7.90 (d, *J* = 5.6, 1H), 10.14 (s, 1H, OH) ppm; Anal. Calcd for $C_{20}H_{18}ClNO_3$: C, 67.51; H, 5.10; N, 3.94%. Found: C, 67.50; H, 5.05; N, 3.94%.

4.5.9 Benzyl(2-hydroxynaphthalen-1-yl)(phenyl)methyl carbamate (4k) : Yield 94% ; mp 182-184 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 5.08 (d, *J* = 12.8 Hz, 1H), 5.15 (d, i = 12.8 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 7.07–7.59 (m, 13H), 7.79–7.84 (m, 3H), 7.98 (d, *J* = 6.4 Hz, 1H, NH), 10.19 (s, 1H, OH); Anal. Calcd for $C_{25}H_{21}NO_3$: C, 78.31; H, 5.52; N, 3.65%. Found: C, 78.28; H, 5.57; N, 3.63%.

4.5.10 Benzyl(4-fluorophenyl)(2-hydroxynaphthalen-1-yl) methyl carbamate (4l) : Yield 90% ; mp 206-208 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 5.03 (d, *J* = 12.8 Hz, 1H), 5.09 (d, *J* = 12.8 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 7.01–7.16 (m, 2H), 7.21–7.36 (m, 10H), 7.77–7.90 (m, 4H), 10.16 (s, 1H, OH) ppm; Anal. Calcd for $C_{25}H_{20}FNO_3$: C, 74.80; H, 5.02; N, 3.49%. Found: C, 74.70; H, 5.01; N, 3.47%.

4.5.11 Benzyl(2-hydroxynaphthalen-1-yl)(3-Nitrophenyl) methyl carbamate (4o) : Yield 92% ; mp 186-188 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 5.05 (d, *J* = 12.0 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 6.98 (d, *J* = 8.8 Hz,1H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.25-7.43 (m, 7H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.80-7.84 (m,2H), 7.94 (d, *J* = 7.6 Hz, 1H), 8.06-8.17 (m, 3H), 10.22 (s, 1H, OH) ppm; anal. calcd for $C_{25}H_{20}N_2O_5$: C, 70.08; H, 4.71; N, 6.54%. Found: C, 70.05; H, 4.72; N, 6.55%.

Acknowledgements

We gratefully acknowledge the research facilities provided by Department of Chemistry, Sardar Patel University and P. D. Patel Institute of Applied Sciences, CHARUSAT. Authors also thankful to CSMCRI, Bhavnagar and SICART, Vallabh Vidyanagar for providing analysis facilities at concessional rates. H.N.D. thanks the University Grant Commission, New Delhi for research fellowship under UGC BSR Scheme 2013 - 2015.

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View Article Online
DOI: 10.1039/C5CY00849B