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Development of an efficient magnetically separable nanocatalyst: theoretical approach on the role of the ligand backbone on epoxidation capability*

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Three chiral Schiff base ligands H_2L^1 , H_2L^2 , H_2L^3 have been synthesized by treating (R)-1,2-diaminopropane separately with 3,5-dichlorosalicylaldehyde, 3,5-dibromosalicylaldehyde and 3,5-diiodosalicylaldehyde, respectively. Three new asymmetric Fe^{III} complexes, namely, FeL¹Cl (1), FeL²Cl (2), FeL³Cl (3) have been prepared from their corresponding ligands. The crystal structure of 2 reveals that the complexes are mononuclear in nature. Circular dichroism (CD) studies suggest that the ligands and their corresponding This article can be cited before manages were have a sprane sale defendentials allower use inity Chattered and the J. Adhikary, A. Datta, S. Dasgeptaidational rakents nashed in the sugated in the segences of todos all free of the second s 10.1039/C5RA17484H. CH₃CN and CH₂Cl₂. The epoxide yield suggests that the order of their catalytic efficiency is 3 > 2 > 1. This trend as well as the role of substitution on the ligand backbone on alkene epoxidation has also been confirmed by density functional theory (DFT) calculations. For further adaptation, we attached our most efficient homogeneous catalyst, 3, with surface modified magnetic nanoparticles (Fe $_3O_4$ @dopa) and thereby obtained the new magnetically separable nanocatalyst Fe_3O_4 @dopa@FeL³Cl. This catalyst has been characterized and its olefin epoxidation ability investigated in similar conditions to those used for Accepted 22nd October 2015 homogeneous catalysts. The enantiomeric excess of the epoxide yield reveals the retention of chirality of the active site of Fe_3O_4 @dopa@FeL³Cl. The catalyst can be easily recovered by magnetic separation and recycled several times without significant loss of its catalytic activity.

Introduction

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Oxygen activation and transfer by cytochrome P-450 has attracted the attention of organic chemists in particular, since it catalyses the mono-oxygenation of various compounds, both biotic and exobiotic, with high stereo- and regioselectivity under mild conditions. Groves and Nemo proposed that the oxygen transfer reaction proceeds through an oxohaem catalytic intermediate.^{1,2} From these basic results, many optically active complexes have been synthesized and found to be efficient catalysts for the epoxidation of olefins.³⁻⁵ The enantioselective epoxidation of olefins is one of the most important and challenging areas in organic synthesis because the resulting epoxide can be stereospecifically opened by nucleophiles to produce various optically active 1,2-difunctional compounds.^{6,7} Besides, the chiral epoxides play an eminent role as drug intermediates and chiral building blocks in the synthesis of optically active complex molecules.8-11

In the literature, transition metal Schiff base complexes have been extensively used as homogeneous catalysts for epoxidation.¹²⁻¹⁵ They show high efficiency since the active site is easily accessible, but their separation from the reaction mixture is really a difficult task. Heterogeneous catalysts appear to avoid this problems.^{16–18} In heterogeneous catalytic systems, the active catalytic sites and the reactants are in the different phases, so isolation and separation can be readily accomplished. Heterogenization is commonly achieved by entrapment or grafting of the active molecules on surfaces or inside the pores of a solid support, such as silica, alumina, organic nanotube etc.19,20 However, the active sites in heterogeneous catalysts are not as accessible as in a homogeneous system, and thus the activity of such catalysts become lowered. So, a catalytic system showing high activity and selectivity (like a homogeneous system) and ease separation and recovery (like a heterogeneous system) would be highly desirable. This goal can be achieved using magnetic nanoparticles (MNPs), which are able to bridge the

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[†] Electronic supplementary information (ESI) available: FT-IR, UV-Vis spectra of three complexes 1-3, TGA diagram of three complexes 1-3, DFT Cartesian coordinates and absolute energies. CCDC 1025818 contains the supplementary crystallographic data for complexes 1. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ra17484h



gap between homogeneous and heterogeneous catalysis, preserving the desirable attributes of both systems.

The development and growth of nanotechnology has caused a continuous shift in every aspect of modern science. So far, it has changed the perspective of the scientific community towards catalysis and brought remarkable transformations in the synthetic chemical processes. MNPs nowadays have attracted immense scientific and technological interest due to their unique physical and chemical properties which make them an ultimate choice in the field of catalysis.21-23 The preparation and the use of MNPs in organic synthesis has become a subject of intense investigation as they offer advantages in clean and sustainable chemistry.24-27 The use of MNPs as catalysts in chemical synthesis has been extensively studied in recent years as their magnetic properties allow ready separation from the reaction mixture via the aid of an external magnet without cumbersome filtration and centrifugation techniques. The magnetic field-assisted separation can reduce energy consumption, catalyst loss and save the time in achieving catalyst recovery. Besides, these nanosized particles offer a large number of potential active sites for the reactants as a result of a large surface area to volume ratio which eventually results in higher yields.

Recent reports have shown that the mechanism of epoxidation of alkenes catalyzed by metal complexes, and the yield of products depends on several factors: the nature of the alkenes, oxidant, counter-ion of the catalyst, structure of the ligand moiety of catalyst and the added Lewis base.²⁸ Steric and electronic effects of catalyst and olefinic substrates on epoxidation property have been investigated by several research groups also.²⁹ However, the role of the halogen substituent present at the ligand back bone in transition metal Schiff base complexes on the epoxide yield is yet to be explored. Thus we are prompted to look at this issue. For this purpose we have designed and synthesized Fe^{III} complexes of H_2L^1 , H_2L^2 and H_2L^3 (Scheme 1), characterized them and investigated their catalytic efficiencies as epoxidation catalysts, in presence of terminal oxidant PhIO and in two solvents, CH_3CN and CH_2Cl_2 under mild conditions. The order of their experimental catalytic efficiency has also been ratified by theoretical calculations. Finally, we attached the most efficient catalyst to surface modified nanoparticles (MNPs) and investigated its catalytic behavior. In this way we have developed an efficient magnetically separable asymmetric nanocatalyst for alkenes epoxidatation that preserve its activity after several catalytic cycles.

Results and discussion

Preparation and characterization of complexes (1-3)

Three purposely selected Schiff bases H_2L^1 , H_2L^2 and H_2L^3 have been prepared by treating 3,5-dichlorosalicylaldehyde, 3,5dibromosalicylaldehyde and 3,5-diiodosalicylaldehyde separately with (*R*)-1,2-diaminopropane in ethanolic medium, respectively. Further treatment of H_2L^1 , H_2L^2 and H_2L^3 with iron(m) chloride gives complexes **1**, **2** and **3**, respectively. We failed to get X-ray diffractable single crystals of **1** and **3**; only a single crystal of **2** is obtained from DMF solvent. The complexes are characterized by regular physiochemical methods. All of them exhibit characteristic IR bands at the range of ~1609–1638 cm⁻¹ and ~1498–1526 cm⁻¹ assigned to C=N and skeletal vibrations (Fig. S1, ESI†), respectively. Electronic absorption spectra of the complexes in acetonitrile medium show multiple intense bands in the UV and visible regions (Fig. S2, ESI†). In these complexes, the absorption maxima observed in the near-UV regions (below 300 nm) are caused by $\pi \to \pi^*$ transitions involving the phenolate units. Intense, high energy bands are also observed in the region between 300 and 350 nm, which are assigned to charge transfer transitions from the out-of-plane $p\pi$ orbital (HOMO) of the phenolate oxygen to the half-filled $d_{x^2-v^2}/d_{z^2}$ orbital of high spin iron(III). The lowest energy bands (around 500 nm) are proposed to arise from charge-transfer transitions from the in-plane $p\pi$ orbital of the phenolate to the half-filled $d\pi^*$ orbital of iron(III).30 Molar conductance of three complexes in acetonitrile medium are 2.3, 4.5, 5.8 Ω^{-1} cm² M⁻¹, which implies that all are nonelectrolyte in solution. Thermogram of the complexes (Fig. S3, ESI[†]) reveal that 1, 2 are stable up to 80 °C where 3 is stable upto 255 °C. Initial weight loss for both 1 and 2 are \sim 3.1% (theoretical wt. loss are 3.4% and 2.6% for 1 and 2 respectively) may be due to loss of one absorbed water molecule. On further heating all three species generate Fe₂O₃ as the thermally stable end product (for complex 1, expt. wt loss = 58.33%, theo. wt loss = 56.51%; for complex 2 expt. wt loss = 69.74%, theo. wt loss = 67.5% and for complex 3 expt. wt loss = 75.3%, theo. wt loss = 73.82%). Circular dichroism (CD) measurements for all the ligands and their corresponding complexes have been performed. The CD spectra of ligand (H_2L^3) and 3 (FeL³Cl) are presented in Fig. 1 (as representative of all ligands and their corresponding complexes). Interestingly, the nature of CD spectra for FeL³Cl is the reverse of H_2L^3 . suggesting the inversion of configuration after complexation.

Description of crystal structure of complex 2

The X-ray structure of complex 2 has been depicted in Fig. 2. Selected bond lengths and bond angles are listed in Table S1 (ESI[†]). According to the X-ray structure the Schiff base ligand coordinates to one iron atom in a tetradentate mode. The metal center is five-coordinated and the geometrical index (τ_5) is equal to 0.18, slightly shifted from zero, implying the geometry is slightly distorted square-pyramid. The two phenolic O atoms



Fig. 1 Circular dichroism (CD) spectra of the chiral ligand (H_2L^3) and the chiral complex 3 (FeL³Cl).



Fig. 2 Crystal structure of complex 2 with atom numbering scheme having 50% ellipsoid probability.

and the two imines N atoms of Schiff-base constitute the basal plane and one chlorine atom is occupying the axial position. Two Fe–O (phenolic) have almost similar bond distance, 1.888(6) and 1.890(6) Å, respectively. Two Fe–N (imine) distances of 2.093(8) and 2.088(8) Å, are also comparable whereas Fe–Cl bond distance is 2.222(3) Å. The methyl group on the 1,2-diaminopropane is disordered over two positions, C10a and C10b with refined occupancies of 0.65/0.35 respectively. This is intended to avoid steric clashes with the lattice dimethylformamide (DMF) molecule, which is also positionally disordered and refined with restraints on its geometry. The crystal is low diffracting (theta max = 21.80°) for the disorder detected. The atoms at lower occupancies (methyl C10b and DMF molecule) have been isotropically refined.

Optimization of the catalytic epoxidation conditions

In all cases, we have followed the same procedure to study the epoxidation reaction catalyzed by the three homogeneous catalysts (1–3). In a typical reaction, (*E*)-stilbene (30 mmol) (as representative), **3** (0.1 mmol) and PhIO (30 mmol) are mixed in 25 mL dichloromethane/acetonitrile and stirred for 4 h at room temperature (see Scheme 2). The progress of the reaction is monitored by TLC. After usual work up and chromatographic purification, the isolated yields of epoxide are found to be 74% in acetonitrile and 62% when dichloromethane used as a solvent. From this initial experiment we proceed to further optimization of the catalysis conditions, *viz.* amount of catalyst and terminal oxidant, along with the time required to obtain the maximum



Scheme 2 Model epoxidation reaction where (E)-stilbene is oxidized by iodosylbenzene, PhIO, in the presence of catalyst 3 (FeL³Cl).

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epoxide yield. To optimize the amount of catalyst, its concentration is varied between 0.05 and 0.2 mmol per 30 mmol of (E)stilbene. Epoxide yield increases when the amount of catalyst is increased from 0.05 mmol to 0.1 mmol but the yield remains the same with further increment of catalyst amount up to 0.2 mmol. Then, the reaction has been studied with varying amounts of PhIO between 25 and 35 mmol per 30 mmol of (E)-stilbene. The yield of the epoxide also is studied by varying the time period between 2 and 6 h. We observe the epoxide yield attains the peak after 4 h of reaction and remain the same even after 6 h. An optimum of 87.84 mg (0.1 mmnol) of catalyst, PhIO (30 mmol) and 4 h reaction time are ideal for achieving the best yield. Table S2 (ESI[†]) represents the (E)-stilbene epoxide yields under different conditions using 3 as catalyst. The optimum reaction conditions thus determined have been followed in 1 and 2 catalyzed epoxidation reactions. The essential role played by the catalyst is evident from the extremely low (<2%) yield of epoxide found in a blank reaction carried out in absence of the catalyst.

Catalytic epoxidation with PhIO

Here we investigate the epoxidation of three alkenes [(*E*)-stilbene, (*Z*)-stilbene, or styrene] catalyzed by complexes 1–3 in CH_3CN or CH_2Cl_2 , with PhIO as oxidant (Table 1). From Table 1 three main features may be drawn. First, in all cases CH_3CN solvent renders higher conversions and yields than CH_2Cl_2 . Second, using the same catalyst for the epoxidation of the three olefins, all of them produce similar epoxide yields, with a very slight preference for (*E*)-stilbene. Finally, complex 3 emerges as the best catalyst for the epoxidation reaction under study, rendering yields close to 70% in CH_3CN . However, complex 2 and complex 1 show average yields of 65% and 54% in CH_3CN , respectively. The epoxidation process has also been monitored by UV-Vis spectroscopy. The isolated Fe(m) complex has two



Scheme 3 Schematic presentation of the generation of Fe(v) oxo species during epoxidation of alkenes.

peaks at 306 and 487 nm. But, after addition of PhIO both disappear and a shoulder around 377 nm emerges (Fig. S4, ESI[†]). This observation clearly suggests the generation of higher valent Fe^{V} =O species as previously reported (see Scheme 3).^{15c,d} The generation of Fe^{V} =O species is very common that were confirmed previously both experimentally an theoretically.³¹⁻³⁶

Theoretical investigation

Theoretical investigation on the effect of halogen substituent on the oxidation of iron complex catalysts

Geometry and charge distribution of the non-oxidized Fe(m) complexes. All the initial complexes are electrically neutral and only differ in the halogen at the *ortho* and *para* positions of the two benzene rings of the Schiff base bonded to the Fe(m) center (Fig. 3). The non-oxidized initial complexes could present low (2S + 1 = 2) or high (2S + 1 = 6) spin depending of the distribution of the 5 most external iron electrons over the non-degenerate d orbitals of the metal in the complexes. We have

Catalyst ^a	Substrate	Solvent	Conversion (%)	TON^b	Yield ^c (%)	$ee^{d,f}$ (%)
1	(E)-Stilbene	CH ₃ CN	58	43.5	55	Trace ^e
		CH_2Cl_2	55	41.4	50	Trace ^e
	(Z)-Stilbene	CH ₃ CN	61	45.9	55 (cis: trans = 70: 30)	18 (trans)
		CH_2Cl_2	52	39	48 (cis: trans = 80: 20)	15 (trans)
	Styrene	CH ₃ CN	60	45	53	20
		CH_2Cl_2	47	35.4	44	Trace ^e
2	(E)-Stilbene	CH ₃ CN	64	48	68	16
		CH_2Cl_2	61	45.9	57	Trace ^e
	(Z)-Stilbene	CH_3CN	61	45.7	$67 \ (cis: trans = 77: 23)$	25 (trans)
		CH_2Cl_2	57	42.9	$54 \ (cis: trans = 60: 40)$	21 (trans)
	Styrene	CH_3CN	57	50.4	61	Trace ^e
		CH_2Cl_2	59	44.4	53	Trace ^e
3	(E)-Stilbene	CH_3CN	79	59.4	74	21
		CH_2Cl_2	66	49.5	62	14
	(Z)-Stilbene	CH_3CN	78	58.5	$72 \ (cis: trans = 90: 10)$	27 (trans)
		CH_2Cl_2	74	55.5	$67 \ (cis: trans = 75: 25)$	22 (trans)
	Styrene	CH_3CN	72	54	69	11
		CH ₂ Cl ₂	67	50.4	65	Trace ^e

^{*a*} Catalyst (0.1 mmol), alkenes (30 mmol), PhIO (30 mmol), and CH₃CN or CH₂Cl₂ (25 mL), are stirred at room temperature for 4 h in air. ^{*b*} TON = moles of substrate converted per mole of catalyst. ^{*c*} Isolated epoxide yield. ^{*d*} Determined by ¹H NMR (300 Hz) in the presence of Eu(hfc). ^{*e*} Trace = concentration < 5%. ^{*f*} Configuration not determined.



Fig. 3 Main DFT geometrical parameters of the initial halogen Fe(III) complexes. (UB3LYP/6-311+G(d,p) with LANL2DZ pseudopotential for Fe, Cl, Br, and I.) All distances in angstroms.

computationally checked that high spin initial complexes are about 15 kcal mol⁻¹ more stable in Gibbs energy than the corresponding low spin ones (Table S3, ESI[†]).

DFT geometrical parameters essentially match those provided by X-ray except for a slight lengthening of bond distances. Metal ion is bonded through stronger bonds to both O atoms (bond distances of 1.91 Å) than to both N atoms (average bond distances of 2.12 Å), forming average O–Fe–O and N–Fe–N bonds of 100.3° and 77.4°, respectively. The metal is also bonded to a chloride anion at a distance of 2.37 Å and placed slightly over a distorted plane of a square pyramid. Such similar geometries for the three initial complexes indicate that geometry is not a factor determining a different oxidation capability.

As oxidation is mainly and electronic issue, we also checked the NBO charge of some relevant atoms at each initial complex. The charges of the halogens in the aromatic rings become increasingly positive when moving from chlorine to bromine and iodine systems (-0.02 to +0.08 to +0.20, respectively for para halogens), as expected due to their diminishing electronegativity. The electron density that halogens donate makes the negative charge on atoms bonded to Fe(III) slightly higher as the atomic number of the halogen increases. Thus, as an average, O atoms charges go from -0.686 to -0.688 to -0.693, whereas those of N atoms vary from -0.521 to -0.522 to -0.525 for chlorine, bromine, and iodine systems, respectively. However, the slightly more negative charges of atoms bonded to Fe(III) do not make the metal more negatively charged since it lets the charge flow to chloride ligand (Fe charges goes from 1.219 to 1.220 and to 1.222 whereas that of chloride goes from -0.502 to -0.505 and to -0.511).

Geometry and charge distribution of the oxidized Fe(v) complexes. Assuming that the metal complexes become oxidized by iodosylbenzene, PhIO, during the epoxidation of



Fig. 4 Main DFT geometrical parameters of the final oxidized Fe(v) complexes. (UB3LYP/6-311+G(d,p) with LANL2DZ pseudopotential for Fe, Cl, Br, and I.) All distances in angstroms.

alkenes, it is interesting to characterize the oxidized metal complexes through DFT calculations. The three oxidized complexes, complex 1-oxo, complex 2-oxo, and complex 3-oxo, have been optimized including the released chloride anion in such a way that the whole system is electrically neutral (Fig. 4). It is interesting to note that the presence of the oxygen atom at the apical position of the complex yields less distorted square pyramid geometries for the Fe(v) than that observed for Fe(III). N–Fe bonds (1.930 Å in average) are now stronger and closer in length to O-Fe bonds (1.917 Å in average), whereas O-Fe-O and N-Fe-N angels are both of about 85°. Concerning NBO charges, the same trend described for the initial complexes is found for the oxidized ones: heavier halogens more easily donate electron charge that goes by through O and N atoms bonded to Fe(v) and from the metal to the apical oxygen (oxygen charge evolves from -0.350 to -0.372 and to -0.385 when going from chlorine to bromine and iodine oxidized complexes).

Reaction energy for the intermediate oxidation of the catalyst by PhIO

As already said, initial Fe(III) complexes are assumed to be oxidized by PhIO ((a) in Fig. 5) to render the oxidized complexes just described and PhI ((b) at Fig. 5), being this oxidation an



Fig. 5 Main DFT geometrical parameter of the oxidized ((a), PhIO) and reduced ((b), PhI) iodobenzine molecule. (UB3LYP/6-311+G(d,p) with LANL2DZ pseudopotential for I.) Distance in angstroms.

Table 2Reaction electronic and Gibbs energy in acetonitrile solutioncalculated at B3LYP/6-31+G(d,p) with LANL2DZ psudopotential for Fe,Cl, Br, and I. Left values at each column for the reaction between themost stable spin-states of reactants and products; right values for thereaction in the doublet state (see text)

Complex	$\Delta E_{\rm e} ({\rm kcal} {\rm mol}^{-1})$	$\Delta G_{ m sol} (m kcal mol^{-1})$		
1	6.6	9.1		
2	3.7	6.2		
3	-0.6	2.1		

intermediate step in the epoxidation of alkenes. The oxidation of the catalyst is schematically represented by eqn (1).

$$Complex + PhIO \Leftrightarrow complex-oxo + PhI$$
(1)

Theoretical results show that the high-spin initial complexes are about 15 kcal mol⁻¹ more stable in Gibbs energy than lowspin ones, whereas oxidized complexes present similar energies for both spin states (Table S3, ESI†). With these data at hand and to fulfill the required spin-conservation along the reaction displayed in eqn (1), two situations are possible. On the one hand, an ancillary reaction involving a spin transition from a quartet to a sextet could happen associated to the oxidation of the catalyst to allow its spin crossover, or, on the other hand, the oxidation of the catalyst could take place in the doublet state. Few examples of spin flip during catalysis are already reported.³⁷⁻³⁹ The second assumption involves an energy supply from the environment to excite Fe(m) complexes from the most stable sextet to the doublet one.

Table 2 collects the electronic and Gibbs energy of the catalyst oxidation step (calculated as the summation of the energy of the corresponding products menus summation of the energy of the corresponding reactants in eqn (1)) for both hypotheses. For the first one, considering the electronic energy, only the products of oxidized complex 3 are more stable than the corresponding initial reactants. In terms of Gibbs energy in acetonitrile solution, all the oxidized products are less stable than the initial ones. However, both electronic and Gibbs energies agree to show that the yield of oxidized complexes is expected to increase from chlorine to bromine and iodine complexes. The second hypotheses, renders the same trend, now predicting exothermic processes in all the cases. As a consequence, what is most important for this study is that theoretical calculations based on any of the possible assumptions agree to point the iodine catalyst as the most effective one.

Preparation and characterization of Fe₃O₄@dopa@FeL³Cl

A schematic diagram of Fe_3O_4 @dopa@FeL³Cl formation is presented in Scheme 4. Firstly, the preparation of magnetic nanoparticles Fe_3O_4 and then their surface modification has been done following the procedure earlier reported by R. S. Varma *et al.* in 2009.⁴⁰ For the preparation of Fe_3O_4 @ dopa@FeL³Cl, 1 g of FeL³Cl is added in the dispersed acetonitrile solution of amine-functionalized nano-Fe₃O₄ (500 mg). The mixture is stirred for 12 h at room temperature. The product is allowed to settle, washed several times with acetonitrile, and dried under vacuum at 60 °C for 2 h. Newly prepared Fe_3O_4 @ dopa@FeL³Cl has been characterized by the following process.

Fourier-transform infrared spectra (FTIR) of Fe_3O_4 , Fe_3O_4 @dopa and Fe_3O_4 @dopa@FeL³Cl are represented in Fig. 6. The peaks at around 583 cm⁻¹ and 636 cm⁻¹ are the



Scheme 4 Schematic representation of the preparation of Fe₃O₄@dopa@FeL³Cl particles.



Fig. 6 Fourier-transform infrared spectra (FTIR) spectra of Fe_3O_4 NPs, Fe_3O_4 @dopa and Fe_3O_4 @dopa@FeL³Cl.

characteristic absorptions of the Fe–O bond, which confirmed the presence of iron oxide, as previously reported.⁴¹ For Fe₃- O_4 @dopa a peak around 1485 cm⁻¹ arises, which may be due to the vibration of the benzene ring present at dopamine moiety. Several new peaks are generated for Fe₃O₄@dopa@FeL³Cl, along with the characteristic peak of Fe₃O₄. The peak at 1526 cm⁻¹ may be assigned as the skeleton vibration of the complex, the sharp peak at 1624 cm⁻¹ may be due to the C=N vibration



Fig. 7 Power X-ray diffraction (PXRD) spectra of Fe₃O₄ NPs, Fe₃-O₄@dopa and Fe₃O₄@dopa@FeL³Cl.



Fig. 8 Solid state UV spectra of Fe $_3O_4$ NPs, Fe $_3O_4$ @dopa and Fe $_3O_4$ @dopa@FeL $^3Cl.$

of incorporated complex moiety. The FTIR spectra allow to conclude that the desired surface medication of MNPs has been successfully done.

The degree of crystallinity of magnetic Fe₃O₄, Fe₃O₄@dopa and Fe₃O₄@dopa@FeL³Cl are obtained from PXRD measurements (Fig. 7). The PXRD data of the synthesized magnetic nanoparticles show diffraction peaks at $2\theta = 29.69^{\circ}$, 35.19° , 42.61° , 56.5° , 59.5° and 62.36° which can be assigned to the (220), (311), (400), (422), (511) and (440) planes of Fe₃O₄, respectively, indicating that the Fe₃O₄ particles in the nanoparticles are pure Fe₃O₄ with a cubic spinel structure. These match well with the standard Fe₃O₄ sample. The same peaks are observed in both of the Fe₃O₄@dopa and Fe₃O₄@dopa@FeL³Cl in PXRD patterns, indicating that the resultant nanoparticles contain pure Fe₃O₄ with a spinel structure and that the grafting



Fig. 9 Thermogravimetric analysis (TGA) diagrams of Fe $_3O_4$ NPs, Fe $_3O_4$ @dopa and Fe $_3O_4$ @dopa@FeL 3 Cl.



Fig. 10 Scanning electron microscopy (SEM) images of (a) Fe_3O_4 -NPs, (b) Fe_3O_4 @dopa and (c) Fe_3O_4 @dopa@FeL³Cl.

process does not induce any phase change of Fe_3O_4 as previously mentioned by other group previously.⁴²

Solid state UV spectrum of Fe_3O_4 is very similar to a previously reported one.⁴³ The existence of Fe_3O_4 in the Fe_3O_4 @dopa and Fe_3O_4 @dopa@FeL³Cl species has been proved by comparing the solid state UV (Fig. 8). FeL³Cl has a broad shoulder at ~495 nm (Fig. S2, ESI†). Increment of the absorbance at ~500 nm for Fe_3O_4 @dopa@FeL³Cl clearly suggests the conjugation of FeL^3 Cl onto Fe_3O_4 @dopa.

For confirmation of the successful surface modification of magnetic Fe₃O₄ and further FeL³Cl grafting on the surface of Fe₃O₄@dopa, thermogravimetric analysis (TGA) is carried out. As shown in Fig. 9, the trace amount of weight loss within the range of 100-200 °C is caused by the trace amount of water vapor adsorbed by magnetic Fe₃O₄. 7% weight loss occurred in the range of 30-800 °C for Fe₃O₄-NPs. Weight loss within the same range for Fe₃O₄@dopa and Fe₃O₄@dopa@FeL³Cl are 19% and 27.6%, respectively. TGA results clearly suggest that the enhancing weight loss is due to the increasing amount of attached organic moiety from Fe₃O₄(a)dopa to Fe₃O₄(a) dopa@FeL³Cl. Similar results have been described by other groups.44 Raman spectrum of FeL3Cl and Fe3O4@dopa@FeL3Cl are depicted in Fig. S5 (ESI[†]). FeL³Cl has peaks at 500, 594, 776, 876, 967, 1312, 1442, 1516, 1590 cm⁻¹. FT Raman spectra for Fe₃O₄(a)dopa(a)FeL³Cl resemble the unbound FeL³Cl demonstrating that the catalyst moiety remains intact during the process of encapsulation as earlier reported.20c,45

SEM images of Fe_3O_4 , Fe_3O_4 @dopa and Fe_3O_4 @ dopa@FeL³Cl are presented in Fig. 10. Fig. 10(a) suggests Fe_3O_4 NPs have square shaped morphology with 20–30 nm size. The morphologies of Fe_3O_4 @dopa (Fig. 10(b)) and Fe_3O_4 @ dopa@FeL³Cl (Fig. 10(c)) are quite different from that Fe_3O_4 @ NPs. Both Fe_3O_4 @dopa and Fe_3O_4 @dopa@FeL³Cl contained agglomerated particle having larger sized particle in the case of Fe_3O_4 @dopa@FeL³Cl. Alteration in morphology from Fig. 10(a) and (b) confirmed the surface modification process.

TEM images of Fe₃O₄-NPs, Fe₃O₄@dopa and Fe₃O₄@ dopa@FeL³Cl are shown in Fig. 11(a)-(c), respectively. A close examination of the TEM image in Fig. 11(a) reveals that the magnetic nanoparticles are quasi-spherical with the average diameter of 10-15 nm. The measurement of the hydrodynamic size of Fe₃O₄-NPs by dynamic light scattering (DLS) shows stable non-aggregated particles with a mean diameter of 30 nm (Fig. S6, ESI[†]). The NPs show good stability in water. The observed sizes of the NPs from TEM images are approximately smaller than the hydrodynamic diameter obtained from the DLS experiment. Transmission electron microscopy measure the size in the dried state of the sample, whereas DLS measure the size in the hydrated state of the sample, so the size measured by DLS is a hydrodynamic diameter and is larger. The nanoparticles, depicted in Fig. 11(b) after dopamine encapsulation step, have a discrete core-shell structure, and Fe₃O₄ is surrounded by 3-5 nm thick dopamine shell as previously reported.⁴¹ Fig. 11(c) illustrates the grafting of FeL³Cl on to the surface of Fe₃O₄@dopa. Energy-dispersive X-ray spectroscopy (EDX) spectrum of Fe_3O_4 (adopa FeL³Cl is depicted in Fig. 12. Fe and O signals come from the Fe₃O₄ nanoparticles and carbon (C) from dopamine. Signals of I and Cl are responsible for the presence of those elements in FeL³Cl. The gold (Au) signals come from the coating material of the instrument.



Fig. 11 Transmission electron microscopy (TEM) images of (a) $Fe_{\tau}O_4$ -NPs, (b) $Fe_{\tau}O_4$ @dopa and (c) $Fe_{\tau}O_4$ @dopa@FeL³Cl.





Epoxidation property of Fe₃O₄@dopa@FeL³Cl

We also evaluated the optimum reaction conditions to achieve the maximum epoxide yield with the heterogeneous catalyst as already done for the homogeneous system (Table S4, ESI[†]). For this purpose the weight of Fe_3O_4 @dopa@FeL³Cl is varied between 50 and 200 mg per 3 mmol of (*E*)-stilbene. Enhancement in the yield of epoxide is observed when the amount of catalyst is increased from 50 to 100 mg but the yield remain same with further increment of catalyst amount up to 200 mg. The reaction has also been studied with varying the amounts of terminal oxidant, PhIO and the time. The results show that using 3 mmol PhIO and 6 h stirring the best epoxidation yield is obtained. At the end of the reaction, the catalyst has been magnetically separated out and reuse for further epoxidation. Here it is noteworthy that we did not find any leaching of catalysts during the epoxidation reaction.

Again, here we have studied Fe_3O_4 @dopa@FeL³Cl catalyzed epoxidation of three different alkenes [(*E*)-stilbene, (*Z*)-stilbene, or styrene] in CH₃CN or CH₂Cl₂ with PhIO and the results are presented in Table 3.

Magnetization behavior of the (a) Fe_3O_4 -NPs, (b) Fe_3O_4 (a) dopa and (c) Fe_3O_4 (a) dopa (a) $Fe_3^3C_1$ nanoparticles under the applied magnetic field is depicted in Fig. 13. The curves exhibit an extremely interesting phenomenon showing a decrease in the values of the saturation magnetization (M_s) from the Fe_3O_4 nanoparticles (58.06 emu g⁻¹) to Fe_3O_4 (a) dopa (39.24 emu g⁻¹) to the final Fe_3O_4 (a) dopa (a) FeL^3C_1 nanocatalyst (26.39 emu g⁻¹) which can be attributed to the gradual increment of

Fig. 13 Magnetic curves of Fe₃O₄ NPs, Fe₃O₄@dopa and Fe₃O₄@ dopa@FeL³Cl; and inset: image of the efficiency of the magnetic separation of the catalyst.

diamagnetic organic materials from Fe₃O₄ to Fe₃O₄^(a) dopa@FeL³Cl. Furthermore, in comparison with the bulk magnetite nanomaterials that typically show a saturation magnetization value of 92 emu g⁻¹, the M_s value of the Fe₃O₄ nanoparticles is found to be much lower. Since the magnetization of a particle in an external field is a function of its size, it is normal that small nanoparticles show in the M_s value.⁴⁶ However, the net magnetism exhibited by the final nanocatalyst is sufficiently good for an effective separation from the solution medium through the application of an external magnetic force.

Characterization and reusability Fe₃O₄@dopa@FeL³Cl

We have studied the recycling efficiency of the magnetically separable heterogeneous catalyst Fe_3O_4 @dopa@FeL³Cl, *i.e.*, whether the catalyst can be reused further for several cycles. (*E*)-Stilbene has been chosen as a representative case for recycling experiments. After each reaction cycle the catalysts are recovered by magnetic separation, washed thoroughly with acetonitrile and dried at 100 °C for 2 h. The used catalyst has been further characterized by FTIR, UV-Vis in solid state and scanning electron microscopy (Fig. 14). Comparing all the experimental results of the used catalyst with virgin one it is easy to

Table 3Epoxidation of alkenes catalyzed by $Fe_3O_4@dopa@FeL^3Cl$ in CH_3CN and CH_2Cl_2 with PhIO							
Catalyst ^a	Substrate	Solvent	Conversion (%)	TON^b	Yield ^c (%)	$ee^{d,f}(\%)$	
Fe ₃ O ₄ @dopa @FeL ³ Cl	(E)-Stilbene	CH ₃ CN	79	40.5	62	Trace ^e	
-		CH_2Cl_2	66	33.8	57	18	
	(Z)-Stilbene	CH ₃ CN	78	40.0	$67 \ (cis: trans = 80: 20)$	29 (trans)	
		CH_2Cl_2	74	37.9	62 (cis: trans = 75: 25)	21 (trans)	
	Styrene	CH ₃ CN	72	36.9	63	17	
		CH_2Cl_2	67	34.3	55	Trace ^e	

^{*a*} Catalyst (100 mg), alkenes (3 mmol), PhIO (3 mmol), and CH_3CN or CH_2Cl_2 (25 mL), were stirred at room temperature for 6 h in air. ^{*b*} TON = moles of substrate converted per mole of catalyst per hour. ^{*c*} Isolated epoxide yield. ^{*d*} Determined by ¹H NMR (300 Hz) in the presence of Eu(hfc). ^{*e*} Trace = concentration < 5%. ^{*f*} Configuration not determined.



Fig. 14 (A) Fourier-transform infrared spectra (FTIR), (B) solid state UV and (C) scanning electron microscopy (SEM) images of used $Fe_3O_4@$ dopa@FeL³Cl. (D) Recyclability and reusability test of $Fe_3O_4@$ dopa@FeL³Cl for the epoxidation of (*E*)-stilbene.

conclude that no significant change in the catalyst after epoxidation reaction. That implies no structural deformation has taken place in the active site of catalyst which is probably the key factor for its reusability. The catalytic reactions have been carried out following the same experimental procedure as that with the original catalysts, and for all cases, the yields are not significantly different through first to fifth use (Fig. 14).

Experimental

Materials and methods

All chemicals were obtained from commercial sources and used as received. Solvents were dried according to standard procedure and distilled prior to use. 3,5-Dichloro salicylaldehyde; 3,5dibromo salicylaldehyde; 3,5-diiodo salicylaldehyde; (R)-1,2diaminopropane, styrene, (E)-stilbene and (Z)-stilbene were purchased from Aldrich and used in epoxidation experiments without further purification. Iron(m) chloride was purchased from Merck.

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer. Infrared spectra (4000–500 cm⁻¹) were recorded at 27 °C using a Perkin-Elmer RXI FT-IR spectrophotometer with KBr pellets. Electronic spectra (800–200 nm) were obtained at 27 °C using a Shimadzu UV-3101PC with methanol as solvent and reference. Thermal analyses (TG-DTA) were carried out on a Mettler Toledo (TGA/SDTA851) thermal analyzer in flowing dinitrogen (flow rate: 30 cm³ min⁻¹). Field Emission Scanning Electron Microscope (FE-SEM) measurement was carried out with JEOL JSM-6700F field-emission microscope. X-ray powder diffraction (PXRD) was performed on a XPERT-PRO Diffractometer monochromated Cu-Ka radiation (40.0 kV, 30.0 mA) at room temperature. Raman spectra (Horiba Jobin Yvon, T64000 model) were recorded in solution via 90° scattering by exciting the sample with an Ar⁺ ion laser source of 48 mW power at the sample. The spectra of the samples were recorded at room temperature in solid phase. The light irradiation dependent study was done after different irradiation times with a white light source compiled with a <420 nm cut off filter. Conductance of the methanolic solution of complexes was measured using a SYSTRONICS 306 conductivity meter. A vibrating sample magnetometer (EV-9, Microsense, ADE) was utilized for obtaining the magnetization curves. The CD spectra were measured with a Jobin Ivon CD 6 spectrophotometer. All the spectra were recorded in acetonitrile.

Syntheses of catalysts

Synthesis of [FeL¹Cl] (1). 10 mL of ethanolic solution of (*R*)-1,2-diaminopropane (0.74 g, 1 mmol) was added slowly to the 20 mL ethanolic solution of 3,5-dichlorosalicylaldehyde (0.382 g, 2 mmol). Immediate precipitation of H_2L^1 took place. 10 mL ethanolic solution of ferric chloride hexahydrate (0.135 g, 0.5 mmol) was added to suspension of H_2L^1 . Yellow precipitate of H_2L^1 was disappearing readily and the solution was turned deep reddish brown. The solution was allowed to stir for 1 h. Brown colored micro crystals of 1 were formed. Anal. calcd for 1: C, 40.11; H, 2.35; N, 5.50. Found: C, 40.08; H, 2.30; N, 5.41. IR (KBr): ν (C=N) 1638 cm⁻¹; ν (skeletated vibration) 1526 cm⁻¹. UV λ_{max} (ACN)/nm 267, 308, 482sh (ε /dm³ mol⁻¹ cm⁻¹ 24 806, 15 253, 5816).

Synthesis of [FeL²Cl] (2). Complex 2 was synthesized following the same procedure as mentioned for 1. Here 3,5-dibromosalicylaldehyde (0.56 g, 2 mmol) was used in place of 3,5-dichlorosalicylaldehyde. The solution was allowed to stir for 1 h. Brown colored micro crystals of 2 were formed. Micro-crystals were dissolved in DMF and kept the solution in dark. X-ray suitable single crystals of 2 were obtained from the solution. Anal. calcd for 2: C, 29.71; H, 1.74; N, 4.07. Found: C, 29.68; H, 1.70; N, 4.01. IR (KBr): ν (C=N) 1631 cm⁻¹; ν (skeletated vibration) 1511 cm⁻¹. UV λ_{max} (ACN)/nm 265, 309, 484sh (ε /dm³ mol⁻¹ cm⁻¹ 27 214, 15 712, 5816).

Synthesis of [FeL³Cl] (3). Complex 3 was prepared by adopting the same procedure as that for 1 using 3,5-diiodosalicylaldehyde (0.748 g, 2 mmol) in place of 3,5-dichlorosalicylaldehyde. Anal. calcd for 3: C, 23.32; H, 1.37; N, 3.20. Found: C, 23.28; H, 1.32; N, 3.18. IR (KBr): ν (C=N) 1609 cm⁻¹; ν (skeletated vibration) 1498 cm⁻¹. UV λ_{max} (ACN)/nm 266, 317, 495sh (ε /dm³ mol⁻¹ cm⁻¹ 21 414, 12 026, 4423).

Synthesis of Fe_3O_4 NPs. Preparation of magnetic nanoparticles Fe_3O_4 have been done following the same procedure as reported earlier by R. S. Varma *et al.* at 2009.⁴⁰

Synthesis of Fe₃O₄@dopa. Fe₃O₄@dopa has been prepared by following the similar method as mentioned previously.⁴⁰

Synthesis of Fe₃O₄@dopa@FeL³Cl. Fe₃O₄@dopa@FeL³Cl has been synthesized by following similar procedure^{20c,45} but with some modification where 1 g of FeL³Cl is added in the dispersed acetonitrilic solution of Fe₃O₄@dopa (500 mg). The mixture is stirred for 12 h in room temperature. The product is allowed to settle, washed several times with acetonitrile, and dried under vacuum at 60 °C for 2 h. IR (KBr): ν (C=N) 1624 cm⁻¹; ν (skeletated vibration) 1526, 1485 cm⁻¹; ν (Fe₃O₄) 583 cm⁻¹. UV λ_{max} (solid)/nm ~502sh, ~279.

X-ray data collection and structure determination

Diffraction data for complex 2 was collected at room temperature (293 K) on a Bruker Smart CCD diffractometer equipped with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Cell refinement, indexing and scaling of the data set were carried out using Bruker SMART APEX and Bruker SAINT package.⁴⁷ The structure was solved by direct methods and subsequent Fourier analyses⁴⁸ and refined by the full-matrix least-squares method based on F^2 with all observed reflections using SIR-92 and SHELX-97,⁴⁹ software. For the complex, all non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were fixed at their respective positions riding on their carrier atoms and refined anisotropically. All the calculations were performed using the WinGX System, Ver 1.80.05,⁵⁰ PLATON99,⁵¹ ORTEP3 (ref. 52) programs. Selected crystallographic data and refinement details are displayed in Table 4.

Preparation of iodosylbenzene

It was prepared by hydrolysis of the corresponding diacetate with aqueous sodium hydroxide according to literature method.⁵³ In every epoxidation experiment freshly prepared PhIO was used.

Epoxidation study of catalysts

Epoxidation of alkenes catalyzed by complexes (1–3). To a solution of alkene (30 mmol) in acetonitrile or dichloromethane (25 mL), 0.1 mmol of complex was added and then PhIO (30 mmol) was added portion wise to that solution and then the resultant mixture was stirred at room temperature for 4 h in air. The reaction progress was monitored by TLC. After removal of solvent, the crude product was purified by flash chromatography. Identification of the epoxide was performed by ¹H NMR spectroscopy.

Epoxidation of alkenes catalyzed by Fe_3O_4 @dopa@FeL³Cl. To a solution of alkene (3 mmol) in acetonitrile or dichloromethane (25 mL), 100 mg of Fe_3O_4 @dopa@FeL³Cl was suspended and then PhIO (3 mmol) was added and the resultant mixture were stirred at room temperature for 6 h in air. Here also we added iodosylbenzene portion wise to the solution. The reaction progress was monitored by TLC. After completion of the reaction, the catalyst was separated with magnet and the solvent was removed by rotary evaporator. The crude product was thus obtained was purified by flash chromatography. Identification of the epoxide was performed by ¹H NMR spectroscopy.

Table 4 Crystal data and details of the structure determination for complex 2

Empirical formula	$C_{17}H_{12}Br_4ClFeN_2O_2, C_3H_7NO$			
Formula mass	760.28			
Crystal system	Monoclinic			
Space group	<i>P</i> 21/ <i>n</i> (no. 14)			
a (Å)	13.314(6)			
$b(\dot{A})$	14.720(6)			
c (Å)	13.228(6)			
α (°)	90			
β (°)	101.192(6)			
γ (°)	90			
$V(\mathbf{A}^3)$	2543.2(19)			
Z	4			
<i>T</i> (K)	293			
$\mu(MoK\alpha) (mm^{-1})$	7.009			
$D_{\rm calc} ({\rm Mg}{\rm m}^{-3})$	1.986			
F(000)	1468			
$\theta_{\rm max}$ (degree)	21.8			
Tot., uniq. data, R _{int}	8389, 2956, 0.071			
Observed $(I > 2\sigma(I))$	1883			
N _{ref} , N _{par}	2956, 292			
R, WR_2, S	0.0484, 0.1247, 1.02			
Residual extrema (e $Å^{-3}$)	-0.53, 0.45			

Computational method

All calculations were carried out with the Gaussian 09 series of programs.54 The implicit Polarizable Continuum Model (PCM) of Tomasi and coworkers55 was used to take into account the effect of acetonitrile as solvent (dielectric constant, $\varepsilon = 35.688$), using atomic radii derived from the standard Universal Force Field (UFF). Full geometry optimization of all reactants and products has been carried out using Density Functional Theory with the UB3LYP⁵⁶ functional and the 6-311+G(d,p) basis set for C, N, O and H atoms as well as with LANL2DZ pseudopotential for Fe, Cl, Br, and I atoms. Geometry optimizations were done with the Schlegel's algorithm.57 The located stationary points were checked to be true minima by the analytical computation of the harmonic vibrational frequencies at the same theory level. Due to the open shell nature of the iron complexes under study, the possible low and high spin states have been calculated for non-oxidized and oxidized complexes. High spin structures were found to be more stable than low spin ones in all cases, and they showed practically no spin contamination at the theory level here used. For interpretation purposes, a natural bond orbital (NBO) analysis was performed on the non-oxidized and oxidized complexes in solution.57-59 Thermodynamic magnitude ΔG was also calculated within the ideal gas, rigid rotor, and harmonic oscillator approximations at a pressure of 1 atm and a temperature of 298.15 K.60

Conclusion

In conclusion, here we have demonstrated that among three asymmetric mononuclear Fe(III) complexes of chloro, bromo and iodo substituted Schiff base ligands, the most efficient catalyst towards alkene epoxidation is iodo substituted Schiff base Fe(III) complex. This efficiency is related to the stability of Fe^V=O intermediate which forms during the catalytic process in presence of PhIO. This factor has been well rationalized by DFT calculations. Then, we have adapted an economically viable and energy efficient catalytic process using the iodo substituted Schiff base Fe(III) complex over magnetically separable nanoparticules for the selective epoxidation of alkenes at room temperature. The simple operation, stability and rigidity of catalyst, the use of inexpensive and gentle magnetic nanoparticles as support, the easy recoverability and reusability of the catalyst, along with the high epoxide yield made the proposed protocol a potential candidate for addressing the challenges of sustainability. We consider that this novel magnetic nano composite system would find applications in several other industrially significant catalytic processes as well as the general synthetic organic transformations.

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