CHAPTER-III

Experimental
3. Experimental

3.1 Materials

1,2-diaminopropane (99%, Sigma-Aldrich), 1,3-dibromopropane (99%, SRL Pvt. Ltd), 3-Aminopropyltriethoxy silane (98%, Sigma-Aldrich), 8-hydroxy quinoline (98%, Sigma-Aldrich), Cetyl trimethyl ammonium bromide (99%, Loba Chemie), Copper (II) acetate (99% SRL Pvt. Ltd), Copper(II) carbonate (95%, SRL Pvt. Ltd), Copper(II) chloride (97%, Sigma-Aldrich), Crystalviolet (96%, Loba Chemie), Diethylenetriamine (97%, SRL Pvt. Ltd), Diidomethane (99% Merck Pvt.Ltd), Ethylenediamine (99%, Sigma-Aldrich), Formaldehyde (37%, Loba Chemie), Fluorescein (Sigma-Aldrich), Fumed silica (Sigma-Aldrich), Hydrogen peroxide (30%, Merck Pvt.Ltd), Isonicotinyl hydrazide (99%, Sigma-Aldrich), Methyl Orange (SRL Pvt.Ltd), Methyl phenylamine (98% Spectrochem), Methylene blue (96%, Loba Chemie), Nickel(II) acetate, Nickel(II) carbonate (Loba Chemie), Perchloric acid (60%, Loba Chemie), Phenol red (Spectrochem Pvt.Ltd), Potassium carbonate, Reactive Red-198 (Alpha chemical Pvt.Ltd), Rhodamine-B (98%, Sigma-Aldrich), Selenium dioxide (98%, Sigma-Aldrich), Sodium carbonate (96%, Loba Chemie), Sodium sulphate (SRL Pvt. Ltd), Sodium chloride (99.9% Merck Pvt.Ltd), Sodium hydroxide (Merck Pvt.Ltd), Tetraethoxyorthosilicate (98%, Sigma-Aldrich) and Na-Y (Sigma-Aldrich) were used without further purification.

The commercial grade methanol and ethanol were refluxed for six hours with lime and distilled. The middle fraction was collected and used. Acetone was refluxed over alkaline potassium permanganate for 5 h and then distilled.
1,4-Dioxane, Dimethylformamide, Dimethyl sulphoxide, Acetonitrile, Chloroform, Dichloromethane, n-Hexane, Ethyl acetate, Toluene and other analar grade chemicals were used without further purification. Millipore water was used throughout the work.

3.2 Characterization techniques

**Fourier-Transform Infrared spectroscopy (FTIR)**

FTIR spectra of the ligands and their grafted complexes were recorded in the region 400 to 4000 cm\(^{-1}\) by using KBr pellets on a Perkin-Elmer 8300 FTIR spectrometer.

**Diffuse reflectance UV-visible spectroscopy (DRS)**

DRS-UV is a very effective technique for getting information about d-d transitions and charge transfer transitions in metal complexes encapsulated in solid supports from which, coordination geometries of the encapsulated complexes can be obtained. Diffuse reflectance spectra of the solid state catalyst (SSC) and zeolite encapsulated metal complexes (ZEMC) were recorded at room temperature in the wavelength range 200 to 800nm on a Perkin-Elmer lambda 650 double beam spectrophotometer. The UV-Visible spectra of liquid samples were recorded on a Perkin-Elmer Lambda-35 spectrophotometer. The spectra were recorded directly in absorbance mode.

**X-ray Diffraction studies (XRD)**

XRD is one of the most widely used techniques in heterogeneous catalysis. Powder X-ray diffraction patterns of Na-Y and MCM-41, the NaY/MCM41 grafted
complexes were compared to find out any change in the crystalline structure. The crystalline nature of all compounds were studied by powder X-ray diffraction using Bruker D8 Advance X-ray diffractometer with monochromatic Cu-Kα1 radiation (λ = 1.5418 Å), The sample was recorded over the diffraction angles (2θ) range between 2° and 80°.

**X-ray Photoelectron spectroscopy (XPS)**

The XPS surface speciation analyses of the compounds were carried out by Omicron nanotechnology, ESCA-14. 1000XM-Monochromator, Al Kα radiation with 1486.7 eV. The instrument was operated at 300 W. The compounds were made as pellets and used for XPS analysis. The XPS data were calibrated to C 1s core peak.

**Surface area measurements**

The N₂ adsorption and desorption isotherms and Brunauer–Emmett–Teller (BET) specific surface area measurements were carried out at -196 °C on a Micrometrics ASAP (Model 2020) surface area analyzer using nitrogen and helium gases with a purity of 99.999%. The SSC/ZEMC was taken in a standard sample tube with filler rod, which is closed with seal frit and covered with isothermal jacket to maintain constant temperature during analysis. The analyzer is equipped with two independent vacuum systems, one for sample preparation and the other for sample analysis. In the first step, the sample tube containing solid materials was evacuated to 50 μm Hg for two hours at 150 °C. In the second step, sample tube was cooled in liquid nitrogen and then is exposed to nitrogen gas at a series of precisely controlled
pressures. With each incremental pressure increase, the number of nitrogen gas molecules adsorbed on the solid compounds surface increases. The isotherm was obtained by plotting a graph of quantity of nitrogen gas adsorbed versus $P/P_0$ values. The analysis of the isotherm yields the surface area of the samples. The surface area of SiMCM41 and Na-Y was found to be 900 m$^2$/g and 600 m$^2$/g respectively.

**Nitrogen adsorption: Physical adsorption isotherms**

To measure total surface area the non-specific physical adsorption is required, but even with physical adsorption the isotherm varies with the nature of the adsorbent (the solid). Most physical adsorption isotherms may be grouped into five categories, which are frequently referred to as the Brunauer–Emmett–Teller (BET) classification (Figure 3.1). In all cases the amount of vapor adsorbed gradually increases as its partial pressure is increased, becoming at some point equivalent to a monolayer, but then increasing to a multilayer, which eventually merges into a condensed phase.

Type-I is frequently known as the Langmuir type. The asymptotic value was originally ascribed to a monolayer, as derived from the Langmuir equation. However, this isotherm is seldom encountered in nonporous materials. It is fairly common with certain activated carbons, silica gels, and Na-Y that contain only very fine pores, and it is now generally believed that in these cases the asymptotic value represents the complete filling of micropores at a relative pressure substantially less than unity, rather than monolayer adsorption. This type of isotherm would also be expected for reversible chemisorption.
Type-II, sometimes termed the sigmoid or S-shaped isotherm, is commonly encountered in nonporous structures. Point B occurs at a “knee” and is the stage at which monolayer coverage is complete.

Type-III, isotherm is convex over the entire range and does not exhibit the point B. It is relatively rare and is typical of a system where the forces of adsorption are relatively weak, as when the adsorbate is not wetted by the surface, e.g., water vapor on graphite.

Type-IV is encountered with porous materials. At low values of $P/P_0$ the isotherm is similar to type II, but then adsorption increases markedly at higher values of $P/P_0$ where pore (capillary) condensation takes place. A hysteresis effect associated with this pore condensation is frequently, but not always, observed. Isotherms of this type are often encountered with industrial catalysts, and the capillary condensation curve may be used to determine a pore size distribution.

Type-V is similar to type III, but with pore condensation taking place at higher values of $P/P_0$. It is also relatively rare. The Brunauer-Emmett-Teller (BET) method was widely used for the evaluation of the surface area from physisorption isotherm data. It is now generally agreed that the BET method is based on an over simplified model of physisorption and that it is necessary to ensure that certain conditions are fulfilled before any BET area is accepted as the true surface area.

Most of the computational procedures in current use are related to the BJH method, proposed by Barrett, Joyner, and Halenda. These procedures are based on the notional emptying of the pores by a step-wise reduction of $P/P_0$, allowance being
made for the thinning of the multilayer in those pores already emptied of condensate.

The derived mesopore size distribution is usually expressed in the graphical form dV/dr_p (or dA/dr_p) versus r_p (or d_p). dV/dr_p reveals the porosity volume distribution in terms of cubic centimetres over the pore range. The dA/dr_p reveals the adsorption-desorption surface area contribution to the total surface area by individual pore sizes. The mesoporous material would appear as a straight line, the greater the numbers of a certain pore size, the greater the contribution to the total volume and total surface area.

Figure 3.1: The five types of adsorption isotherms as classified by Brunauer et al. 1938.
In adopting this approach (BJH), it must necessarily be assumed that:

(i). The Kelvin equation is applicable over the mesopore range

(ii).The meniscus curvature is controlled by pore size and shape

(iii). The pores are rigid and of uniform shape

(iv). The distribution is confined to the mesopore range

(v). There are no pore-blocking effects

(vi). Adsorption on the pore walls conforms to the standard isotherm.

**Thermo Gravimetric Analysis (TGA)**

In thermogravimetric analysis, the samples to be analysed are subjected to a controlled heating to high temperature at a specified heating rate. The weight loss of the sample on heating is being recorded as a function of temperature. The weight loss was due to the rupture or formation of physical or chemical bonds at elevated temperatures. This technique has widespread application in determining the phase composition, percentage weight loss, stability limits of a complex, drying range, dehydration and decomposition temperature.

TGA/DTG experiments were performed with Versa Therm Cahn thermo balance TG-151 attached to an analytical thermal system. The experiments were conducted in the temperature range of 27 -900°C.

**Field Emission Scanning Electron Microscopy (FESEM)**

Surface morphology of solid state catalysts was investigated using a HITACHI-S3890 Scanning Electron Microscope. The powder sample was directly used for the analysis.
High Resolution Transmission Electron Microscopy (HRTEM)

The morphological studies analysis was carried out by using a FEI TECNAI G2 (T-30) transmission electron microscope (HRTEM) with an accelerating voltage of 250 KV.

Electron Paramagnetic Resonance (EPR) studies

EPR spectra of neat complexes were recorded in appropriate solvents with Varian E-112 spectrometer at liquid nitrogen temperature (77 K). For encapsulated systems the spectra were taken in solid mode by taking 50 mg of the sample in a quartz tube. The X-band EPR spectra of the Cu(II) complexes were recorded in DMSO, CH$_3$CN at liquid nitrogen temperature using Varian E-112,X-band spectrometer. The EPR spectra of the Na-Y encapsulated Cu(II)complexes were also recorded. The g values were determined relative to the standard tetracyanoethylene (TCNE, g = 2.0027). The axial symmetry parameter (G) was calculated by the standard procedures.

Nuclear Magnetic Resonance (NMR)

The $^1$H NMR spectra were recorded on a Bruker Avance 400MHz NMR spectrometer and $^{13}$C-NMR spectra were recorded on a Bruker Avance 100MHz NMR spectrometer

ESI-MS data

The ESI mass spectral data were obtained using ESI-MS Thermo Finnigan LCQ model advantage MAX 6000ESI spectrometer. Sample solutions were introduced to the mass spectrometer via a loop injection or directly infused by a syringe pump.
Catalytic studies by UV-Visible spectrophotometry

The photocatalytic ability of the synthesized materials was determined by spectrophotometric method. In dye degradation experiments the spectral changes monitored at $\lambda_{max}$ values for rhodamine-B, reactive red-198, methyl orange, methylene blue, phenol red, crystal violet and fluorescein are 554, 519, 464, 665, 437, 583, 476 nm respectively. The spectral changes were recorded on a Perkin Elmer Lambda 35 spectrophotometer operating in the range 200-800 nm at the given $\lambda_{max}$. The spectrophotometric technique was used for the determination of percentage of conversion and catalytic efficiency for the synthesized materials. The percentage conversion in the photo oxidation process is determined by the following equation:

$$\%\text{Conversion} = \frac{A_0 - A_t}{A_0} \times 100$$  \hspace{1cm} (3.1)

Here $A_0$= Initial absorbance, $A_t$ = Absorbance at time (t).

3.3 Synthesis of metal hydrazone Schiff base complexes

3.3.1 Synthesis of the bis salicylaldehyde derivative (SAL)

Salicylaldehyde (0.53 mL, 5 mmol) was dissolved in 20 mL of DMF, and potassium carbonate (1.73 g, 12.5 mmol) was added. The mixture was stirred at room temperature, and then 1,3-dibromopropane (0.51 g, 2.5 mmol) was added dropwise. Then, the reaction mixture was stirred under reflux for 6 h. The resulting mixture was partitioned between water and ethylacetate. The ethyl acetate layer was collected, concentrated under reduced pressure and was then subjected to silica gel (100-200 mesh) column chromatography using hexane-ethylacetate (1:9) as eluent.
to afford the product (1.07 g, 75%) in pure form. The purified SAL was characterized by spectral studies and the results were compared with those of earlier reports.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$: 2.43 (2H, p, OCH$_2$CH$_2$CH$_2$O), 4.33 (4H, t, $J = 7.6$ Hz, OCH$_2$CH$_2$CH$_2$O), 7.03 (4H, m, Ar-H), 7.55 (2H, t, $J = 7.7$ Hz, Ar-H), 7.83 (2H, d, $J = 7.7$ Hz, Ar-H), 10.49 (2H, s, Aldehyde-H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 29.2, 64.7, 112.5, 121.0, 124.9, 128.8, 136.2, 161.0, 189.6.

3.3.2 Synthesis of the O, O'-trimethylene bis (salicylidene isonicotinoyl hydrazine) ($H_2L$)

The O, O'-trimethyl bis (salicylidene isonicotinyl hydrazone) was prepared by refluxing the aliquot of the SAL (0.6 g, 2.2 mmol), isonicotinyl hydrazide (0.6 g, 4.4 mmol), two drops of glacial acetic acid in absolute EtOH (40 mL) for 2 h, the resulting white solid was washed with the water, EtOH, chloroform, diethyl ether and dried under vacuum, Yield: 0.94 g (80%). M.p. 248-250 °C. ESI-mass: m/z 545.27 (M+Na). $^1$HNMR (DMSO-d$_6$, 400 MHz) ppm: 12.02 (s, 2H, amide NH), 9.01-8.42 (m, 6H, Ar-H and imine CH), 8.07-7.53 (m, 6H, Ar-H), 7.37 (s, 2H, Ar-H), 7.11 (s, 2H, Ar-H), 6.98 (s, 2H, Ar-H), 4.27 (s, 4H, OCH$_2$) and 2.26 (s, 2H, OCH$_2$CH$_2$CH$_2$O); $^{13}$C NMR (DMSO-d$_6$, 100 MHz) ppm: 162.08, 157.57, 150.77, 149.99, 144.91, 141.02, 132.37, 126.27, 123.60, 122.68, 122.03, 121.41, 113.26, 65.30 and 29.26.

3.3.3 Synthesis of Ni(II)L.$(ClO_4)_2$

To the DMF solution (5 mL) of the ligand ($H_2L$) (0.52 g, 1 mmol), 30 mL ethanolic solution of nickel(II) perchlorate hexahydrate (0.38 g, 0.5 mmol) was
added and then heated at 80°C for 3 h. The resulting lemon yellow solid was washed with hot water, MeOH, diethyl ether and dried under vacuum, Yield: 0.6 g (72%), m.p. and decomposition > 270 °C; ESI-mass m/z 579.2.

3.3.4 Synthesis of Cu(II)L(ClO4)2

To the DMF solution (5 mL) of the ligand H2L (1.1 g, 0.5 mmol), 30 mL ethanolic solution of copper(II) perchlorate hexahydrate (0.36 g, 0.5 mmol) was added and heated at 80 °C for 3 h. The resulting olive green solid was washed with hot water, MeOH, and diethyl ether and dried under vacuum, Yield: 0.7 g (80 %) m.p. and decomposition >240 °C; MS: m/z 585.

3.3.5 Synthesis of metal exchanged Na-Y, (M(II)-Y [M=Ni(II) and Cu(II)])

The metal perchlorate (M(ClO4)2.6H2O, 0.1 mmol) was added to the 50 mL aqueous solution of 1 g of Na-Y and it was stirred for 8 h at 95 °C The products was filtered, washed with 100 mL of hot distilled water and dried under vacuum for 10 h at 80 °C.

3.3.6 Synthesis of the metal hydrazone Schiff base complexes in the Na-Y (M(II)L-Y) via FLM

The preparation of Schiff base aryl hydrazone metal complexes in the cavities of Na-Y was achieved by heating at 333 K in DMF/methanolic solution of H2L with M(II)-Y for 8 h. The resulting solid was washed with hot DMSO (10 mL), water and dried at 60 °C for 12 h. The product was Soxhlet extracted with EtOH and acetonitrile/DMF 6 and 24 h respectively to remove excess of unreacted starting materials adsorbed onto the external surface of Na-Y crystalline. The resulting solid
was dried at 80 °C under vacuum for 24 h, Yield: 0.3-0.34 g. Color: [Ni(II)L-Y] (pale yellow), [Cu(II)L-Y] (pale green).

3.4 Synthesis of covalently anchored metal complexes by Si-MCM41

3.4.1 Synthesis of MCM41 by sol-gel process

The Si-MCM41 was synthesized according to the earlier procedure [Ramanjaneya and Balasubramanian. 2015]. A typical synthesis involves 2 g of CTAB in 120 mL of deionised water containing 1 g of NaOH and heated up to 50 °C. To this solution 6 mL of TEOS was added. The mixture was then stirred vigorously at room temperature for 6 h and then aged at 110 °C for 24 h in an autoclave under static air condition. The product was isolated by filtration and washed with deionized water and MeOH. The resulting white powder was dried at 550 °C overnight and was again calcined at 550 °C for 12 h.

3.4.2 Synthesis of the Schiff base ligand by condensation method (QATES)

3-APTES (1 ml 4.2 mmol) was added to the ethanolic solution of 8-Hydroxyquinoline-2-carboxaldehyde (0.72 g 4.2 mmol) and then refluxed for 8 h. The solution was filtered and the resulting yellowish brown solid was washed with MeOH, chloroform, diethyl ether and dried at 80 °C, Yield: 1.1 g (70%).

3.4.3 Grafting the Schiff base ligand with Si-MCM41 (SiOF)

About 0.4 g of the Si-MCM41 was suspended in 30 mL toluene along with 0.6 g QATES, and sonicated for 15 min. The reaction mixture was then heated for 8 h at 90°C. The resulting dirty white solid was washed with EtOH, toluene and dried for 12 h at 100 °C, Yield 0.62 g.
3.4.4 Synthesis of solid supported Schiff base complex (NiOF)

0.3 mmol of Ni(II) perchlorate salt (0.1 g) were added to the ethanolic solution of 0.2 g of SiOF and was refluxed for 3 h and the resulting solid was dried, and Soxhlet extracted with EtOH for 6 h and dried again at 120 °C, Yield 0.18 g.

3.4.5 Synthesis of solid supported Schiff base complex (CuOF)

0.3 mmol of Cu(II) perchlorate (0.11 g) was added to the ethanolic solution of 0.2 g of SiOF and was refluxed for 3 h and the resulting solid was dried, and Soxhlet extracted with EtOH for 6 h and dried again at 120 °C, Yield 0.23 g.

3.5 Synthesis of the covalently anchored N₂O₂ Schiff base metal complexes with Si-MCM41

3.5.1 Synthesis of O,Oˈ-mono methylene bis(salicylidene) (SL)

Salicylaldehyde (0.53 mL, 5 mmol) was dissolved in 20 mL of DMF to which potassium carbonate (1.73 g, 12.5 mmol) was added and the mixture was stirred at room temperature. To this mixture 1,1-diiodomethane (0.21 mL, 2.5 mmol) was added and then stirred under reflux for 6 h. The resulting mixture was partitioned between water and ethylacetate. The ethyl acetate layer was collected, concentrated under reduced pressure and was then subjected to silica gel (100-200 mesh) column chromatography using hexane-ethylacetate (1:9) as eluent to afford the product, Yield: 1.1 g (90%) in pure form. The purified SL was characterized by spectral studies and the results were compared with those of earlier reports. ¹H NMR (CDCl₃, 400 MHz): δ: 2.4 (2H, p, CH₂O), 4.33 (4H, t, J = 7.6 Hz, OCH₂O), 7.03 (4H, m, Ar-H), 7.55 (2H, t, J = 7.7 Hz, Ar-H), 7.83 (2H, d, J = 7.7 Hz, Ar-H), 10.49
(2H, s, aldehyde-H); $^{13}$C NMR (CDCl$_3$, 100 MHz):  δ 29.2, 64.7, 112.5, 121.0, 124.9, 128.8, 136.2, 161.0, 189.6.

### 3.5.2 Synthesis of Schiff base ligand with 3-APTES (SLTES)

The O,O·-mono methylene bis(salicylidene) (SL) (0.5 g, 2 mmol) was dissolved in 50 mL of EtOH and to this 3-APTES (1 ml, 4.2 mmol) was added. The solution was refluxed for 6 h and the resulting dirty white solid was washed with hot EtOH, acetone and diethyl ether, dried under vacuum for 6 h. Yield: 1 g (80%).

### 3.5.3 Grafting Schiff base ligand with Si-MCM41 (SOF)

About 0.1 g of the Si-MCM41 was suspended in 30 mL toluene along with 0.2 g SLTES, and then sonicated for 15 min. The reaction mixture was then heated for 8 h at 90 °C. The resulting dirty white solid was washed with EtOH, toluene and dried for 12 h at 100 °C. Yield: 0.25 g.

### 3.5.4 Synthesis of solid supported Schiff base complexes (NOF&COF)

0.5 mmol of M(II)[M(II):Ni(II)&Cu(II)] chloride salt (0.18 g) was added to the ethanolic solution of 100 mg of SOF and was refluxed for 3 h and the resulting solid was dried, and Soxhlet extracted with EtOH for 6 h and dried again at 120°C.

### 3.6 Synthesis and encapsulation of the saturated macrocyclic complexes (THA) by template method

#### 3.6.1 Synthesis of NTHA macro cyclic complex

To a stirred methanolic solution of (50 ml) of nickel(II) acetate (0.9 g, 3.9 mmol) were added diethylenetriamine (0.84 mL, 7.8 mmol) and 36% formaldehyde (0.47 mL, 0.016 M). The reaction mixture was heated at reflux for 3 h. An excess of
sodium perchlorate was added to the reaction mixture and the solution was stirred at room temperature until yellow precipitate was formed. The product was filtered out, washed with methanol, diethyl ether and recrystallized from water, Yield: 1.65 g (80%).

3.6.2 Synthesis of CTHA macro cyclic complex

To a stirred methanolic solution of (50 ml) of copper(II) acetate (3.5 mmol, 0.7 g) were added diethylenetriamine (7.1 mmol, 0.82 mL) and 36% formaldehyde (0.014 M, 0.42 mL). The reaction mixture was heated at reflux for 6 h. An excess of sodium perchlorate was added to the reaction mixture and the solution was stirred at room temperature until blue precipitate was formed. The product was filtered out, washed with methanol, diethyl ether and recrystallized from water, Yield: 1.1 g (65%). The MTHA complexes are soluble in water, acetone, acetonitrile and DMSO but insoluble in alcohol.

3.6.3 Encapsulation hexaazamacrocyclic complexes of Ni(II) and Cu(II) in the cavity of Na-Y

3.6.3.1 Synthesis of bis(deta)M(II)-Y

The precursor complex in methanol was synthesized from stoichiometric amounts of diethylenetriamine and the corresponding metal perchlorate. A solution containing 0.01 M of M(II)ClO₄ and 0.02 M diethylenetriamine was stirred for 12 h. The reaction mixture was isolated on cooling and the resulting precursor complexes were recrystallized from methanol. 0.1 M of the precursor complexes were added to methanolic suspensions of 2 g of the Na-Y zeolite. The reaction mixture was
refluxed under inert atmosphere and then the product was washed with hot water and ethanol. The resulting ion exchanged zeolite was extracted in a Soxhlet apparatus with 1:1 ratio of methanol and chloroform for 12 h to remove excess of the unreacted amine and metal species adsorbed onto the external surface of zeolite. The resulting solid was dried at 90 °C under vacuum for 24 h, Yield: 1.7 g.

3.6.3.2 Synthesis of MTHAY

To a stirred methanolic suspension (50 mL) of [bis(deta)M(II)]-NaY (0.5g) excess formaldehyde was slowly added under N₂ atmosphere. The reaction mixture was refluxed until a pale yellow suspension resulted in the case of NTHAY and pale blue in case of CTHAY. The solution was filtered and the resulting solid was Soxhlet extracted with chloroform, ethanol and acetonitrile for 4 h, 6 h and 8 h respectively, to remove excess of unreacted traces during condensation process and any amine and metal species adsorbed onto the external surface of zeolite. The resulting solid was dried at 90 °C under vacuum for 24 h. Then it was suspended in 0.1 M NaClO₄ solution and filtered. The product was dried at 80 °C under vacuum for 24 h, Yield: 0.46-0.51g.

3.7 Synthesis of hexaazamacrotricyclic complexes by template method

3.7.1 Synthesis of free complexes(FC)

The hexaaza macrocyclic complexes [M(CHA)(ClO₄)₂ [M = Ni(II) and Cu(II)] were synthesized by the simple template condensation of en, trien and formaldehyde in the presence of metal perchlorate salts. Both Ni(II) and Cu(II) complexes are soluble in water, acetone, acetonitrile and DMSO but insoluble in alcohol, Yield 1.1g (55%)
3.7.2 Synthesis of [trien, en]Ni(II)-Na\(Y\)

Typically a 2 g calcined sample of Na-Y was mixed with 0.2 g of (trien, en)Ni(II).2ClO\(_4\) and the reaction mixture was suspended in 70 mL of MeOH and then refluxed for 15 h under N\(_2\) atm. The resulting solid consists of [Ni(trien, en)]\(^{+2}\) exchanged with Na\(^{+}\) ion, which is present in NaY and the product denoted as [trien, en]Ni(II)-Na\(Y\), was collected by filtration and dried. The resulting [trien, en]Ni (II)]-Na\(Y\) was purified by Soxhlet-extraction with a mixture of MeOH (30 mL) and chloroform (50 mL) for 10 h to remove excess of unreacted amine and any Ni(II) complex adsorbed onto the external surface of Na-Y. The resulting solid was dried at 80 °C under vacuum for 24 h. Yield: 1.6 g.

3.7.3 Synthesis of [trien, en]Cu(II)-Na\(Y\)

Typically a 2 g calcined sample of Na-Y was mixed with 0.2 g of (trien, en)Cu(II). 2ClO\(_4\) suspended in 70 mL of MeOH and then refluxed for 15 h under N\(_2\) atm. The solid consists of [Cu(trien, en)]\(^{+2}\) exchanged with Na\(^{+}\) ion, which is present in NaY and the product denoted as [Cu(trien, en)-Y ]\(^{+2}\) is collected by filtration and dried. The Cu(II)(trien, en)-Y was purified by Soxhlet-extraction with the mixture of MeOH (30 mL) and chloroform (50 mL) for 10 h to remove excess of unreacted amine and any Cu(II) complex adsorbed onto the external surface of crystalline Na-Y. The product was dried at 80 °C under vacuum for 24 h, Yield: 3.8 g.

3.7.4 Synthesis of MCHAY

To a stirred methanolic suspension of [[(trien, en)Ni(II)(II)]-Na\(Y\) (1g) excess formaldehyde was slowly added under N\(_2\) atmosphere. The reaction mixture was
refluxed until a colored suspension of MCHAY resulted. The solution was filtered and the product was Soxhlet extracted with chloroform, ethanol and acetonitrile for 5 h, 3 h and 2 h respectively, to remove excess of unreacted traces during condensation process and any amine and metal species adsorbed onto the external surface of zeolite. The product was dried at 90 °C under vacuum for 24 h. The resulting solid was suspended in 0.1 M NaClO₄ solution and filtered. The product was dried at 80 °C under vacuum for 24 h, Yield: 0.8 g

3.8 Synthesis N-substituted hexaazamacrocyclic complex and the corresponding encapsulated complexes

3.8.1 Synthesis of Cu(II)(L).2ClO₄ complex by one-pot template method

To a stirred methanolic (70 mL) solution of Cu(OOCCH₃)₂.H₂O (0.5g, 2.5mmol), 1,2-diamino propane (0.43 mL, 5 mmol) and formaldehyde (0.37 mL, 12.5 mmol), were added. After refluxing the mixture for 4 h, the methanolic solutions of the phenyl ethyl amine (0.5 mL 5mmol) was added slowly and the refluxion was continued for 36 h. The solution was filtered to remove any insoluble material. 2 mL of 60% perchloric acid was added to the filtrate and the solution was stirred at room temperature for 10 h. The solution was allowed to attain room temperature and the resulting pink solid was washed with MeOH and diethyl ether, Yield: 0.8 g (47%). ESI-mass: m/z 600.27 (M+ClO₄). 

3.8.2 Synthesis of [(pn)₂Cu(II)] precursor complex (PC)

The Cu(II).(ClO₄)₂.6H₂O (0.37g, 1 mmol) was added to 50 mL methanolic solution of 1,2-diamino propane (0.17 mL, 2mmol) and stirred for 5 h at room
temperature. The resulting blue solid was washed with ether and recrystallized from MeOH. Yield: 0.3 g(75%).

3.8.3 Synthesis of [bis(pn)Cu(II)]-NaY by impregnation method

Typically a 4 g calcined Na-Y mixed with 0.3 g of PC was suspended in 150 mL of MeOH and then refluxed for 15 h under N₂ atm. The pale blue solid consists of [Cu(N-N)₂]⁺² exchanged with Na⁺ in the NaY, and denoted [Cu(II)(pn)₂-Y] was collected by filtration, and washed with MeOH. The resulting ion exchanged Na-Y was extracted in a Soxhlet apparatus with 1:1 ratio of MeOH and chloroform for 10 h to remove excess of unreacted amine and copper(II) species adsorbed onto the external surface of NaY. The resulting pale blue solid was dried at 60°C under vacuum for 24 h.

3.8.4 Synthesis of [Cu(II)L-Y] by template synthesis

To a stirred methanolic suspension (100 mL) of [bis(pn)Cu(II)-Y] (1 g) excess formaldehyde was slowly added under N₂ atmosphere. The reaction mixture was refluxed until a pale pink suspension resulted. The solution was filtered and the resulting solid was Soxhlet extracted with chloroform, EtOH and acetonitrile for 5 h, 10 h and 3 h respectively, to remove excess of unreacted traces and Cu(II) species adsorbed onto the external surface of Na-Y. The resulting pale pink solid was dried at 60 °C under vacuum for 24 h. The solid was suspended in 0.1 M NaCl solution and filtered. The product was dried at 80 °C under vacuum for 24 h.
3.8.5 Synthesis of Cu(II)L-MCM by occlusion method

0.3 g of Cu(II)L.2ClO$_4$ (0.4 mmol) in acetonitrile (10 mL) was slowly added to 0.5 g of MCM41 suspended in toluene. The resulting mixture was heated for 12 h under nitrogen atmosphere. The solid was Soxhlet extracted with 1:1 ratio of the EtOH and acetonitrile mixture for 6 h to remove any unreacted complex, Yield: (0.6 g)

3.9 Photocatalytic experiments

3.9.1 Photocatalytic degradation of RhB under UV and Visible light irradiation by FC and ZEMC

The photocatalytic oxidation reactions were carried out in a glass reactor with the catalyst 0.046 g of Ni(II)L.2ClO$_4$/ 0.047 g of Cu(II)L.2ClO$_4$/ 0.05 g of Ni(II)L-Y/ 0.05 g of Cu(II)L-Y and 0.01 mmol of 100 mL aqueous dye solution. The reaction conditions are optimized in dark at room temperature and the samples were irradiated under UV and visible light. The removal percentage and consequent spectral changes at predetermined time intervals were monitored by UV-Visible absorption spectrum at 554 nm for 3 h. The percentage conversion is calculated by the equation (1).

3.9.2 Photocatalytic removal of crystal violet and FLU under visible light by SOF, NOF and COF

The photocatalytic oxidation reactions were carried out in a glass reactor with the catalyst 0.05 g of SOF/ 0.05 g of NOF/ 0.05 g of COF and 0.01 mmol of 100 mL aqueous CV dye solution. The reaction conditions were optimized in dark at room
temperature and irradiated under visible light (> 360 nm). The removal percentage and consequent spectral changes at predetermined time intervals were monitored by UV-Visible absorption spectrum at 589 nm for 5.5 h at (476 nm for 4.5 h in the case of FLU). The percentage conversion was determined by the equation (1).

3.9.3 Photocatalytic oxidation of MO and RR under UV light by SiOF, NiOF and CuOF

The photocatalytic oxidation reactions were carried out in a glass reactor with the catalyst 0.05 g of SiOF/ 0.05 g of NiOF/ 0.05 g of CuOF and 0.01 mmol of 100 mL aqueous MO dye solution. The reaction conditions were optimized in dark at room temperature and irradiated under UV light (< 360 nm). The removal percentage and consequent spectral changes at predetermined time intervals were monitored by UV-Visible absorption spectrum at 464 nm for 4.5 h (at 519 nm for 7 h in case of RR). The percentage conversion was determined by the equation (1).

3.9.4 Photocatalytic degradation of PR/RR under UV light irradiation by MTHAY and MTHA

The photocatalytic oxidation reactions were carried out in a glass reactor with the catalyst 0.1g of NTHA/ 0.1g of CTHA/ 0.1 g of NTHAY / 0.1 g of CTHAY and 0.01 mmol of 100 mL aqueous dye solution. The reaction conditions are optimized in dark at room temperature and the samples were irradiated under UV light. The removal percentage and consequent spectral changes at predetermined time intervals were monitored by the UV-Visible absorption spectra at 434 nm for 6 h at 521 nm for 9 h in the case of RR).
3.9.5 Photocatalytic oxidation of MB under UV light irradiation MCHAY and MCHA

The photocatalytic oxidation reactions were carried out in a glass reactor with the catalyst (0.1 g of NCHA/ 0.1 g of CCHA/ 0.1 g of NCHAY / 0.1 g of CCHAY) and 0.01 mmol of 100 mL aqueous dye solution. The reaction conditions are optimized in dark at room temperature and the samples were irradiated under UV light. The removal percentage and consequent spectral changes at predetermined time intervals were monitored by UV-Visible absorption spectra at 665 nm for 3 h. The percentage conversion in the MB oxidation process is determined by the equation (1).

3.9.6 Photocatalytic degradation of RhB under UV and Visible light FC and SSC

The photocatalytic oxidation reactions were carried out in a glass reactor with the catalyst (0.042 g of Cu(II)L\_2ClO\_4/ 0.05 g of Cu(II)L-MCM/ 0.05 g of Cu(II)L-Y) and 0.01 mmol of 100 mL aqueous dye solution. The reaction conditions are optimized in dark at room temperature and the samples were irradiated under UV and visible light. The removal percentage and consequent spectral changes at predetermined time intervals were monitored by UV-Visible absorption spectra at 554 nm for 5 h. The percentage conversion is calculated from the equation (3.1).