

LIST OF FIGURES

Figures in Chapter 1		Page no.
Figure 1.1	Pictorial representations of 2D and 3D porous polymeric networks.....	2
Figure 1.2	Synthesis of first two COFs (COF-1 and COF-5) by condensation of 1,4-diboronic acid	4
Figure 1.3	Different type of covalent linkages (in red) associated in the reversible reactions between building units during COF synthesis ...	5
Figure 1.4	3D COF-320 constructed on the surface of functionalized ceramic α -Al ₂ O ₃ (a) and the interpenetration of the diamondoid net (b) of COF synthesized	6
Figure 1.5	Single crystals of three covalent nitroso polymer networks obtained by polymerization of tetrakis(4-nitrosophenyl)methane (a), tetrakis(4-nitrosophenyl)silane (b) and 1,3,5,7-tetrakis(4-nitrosophenyl)adamantane (c) building units and the corresponding crystal structures (d, e, f)	6
Figure 1.6	Synthesis of first CTF with the hexagonal columnar pores	7
Figure 1.7	Representation of anion template PAF with tuned pore sizes.....	9
Figure 1.8	Various types of linkages and/or building units used in the preparation of MOPs	10
Figure 1.9	Synthesis of different CMPs via Buchwald-Hartwig (BH) C–N coupling reaction	11
Figure 1.10	Schematic representation of COF synthesized using mechanochemical grinding techniques	13
Figure 1.11	Synthesis of COF-5 on the surface of graphene sheet employing solvothermal technique	14
Figure 1.12	FT-IR spectra of building units and synthesized COF (a), ¹³ C	15

	ssNMR spectrum of monomeric unit (b) and the high resolution TEM images (c to f) of COF synthesized mechanochemically	
Figure 1.13	Single crystal structure of the molecular unit in COF-320 (a) and the diamondoid network with columnar rectangular channel in it (b) obtained by employing RED technique	17
Figure 1.14	(a) Nitrogen adsorption-desorption isotherm, type-I and (b) argon adsorption desorption isotherm (type-I and type-IV) exhibited by COFs	17
Figure 1.15	Schematic representation of benzobisoxazole (BBO) that exhibits excellent activity toward CO ₂ absorption	19
Figure 1.16	Selective adsorption of ethylene over ethane by PAF through π -complexation between ethylene and the framework	20
Figure 1.17	Schematic representation of TPE-Ph COF having dual pore frame (a) and its fluorescence image (b) that acts as robust sensor for NH ₃ detection	20
Figure 1.18	Inclusion of comonomer dopant to tune the photophysical properties of CMPs acting as fluorescence sensor for volatile organic compounds	21
Figure 1.19	Displaying electropolymerization of poly(3,4-ethylenedioxythiophene), (PEDOT) into the pores of 2D COF 2,6-diaminoanthraquinone-2,4,6-triformylphloroglucinol (DAAQ-TFP)	22
Figure 1.20	Sulfonic acid functionalized POP exhibiting proton conduction better than that exhibited by Nafion	23
Figure 1.21	Micrographs of MCOP under irradiation with an 808 nm laser at constant time interval (a); Photothermal images of the whole mice after intratumoral injection of MCOP (b); Monitoring of temperature (c) and Representative photostability test (d) of MCOP; Photographs of tumors (e) and mice (f) under different treatment conditions	24
Figure 1.22	Schematic representation of Pd loaded 2D COF (Pd/COF-LZU1)	26

	as catalyst for Suzuki-Miyaura coupling	
Figure 1.23	Visible light promoted photocatalytic selective bromination of electron rich aromatic compounds using MOPs	26
Figure 1.24	Schematic presentation of composite material from graphene and pyrimidine based POP as host for encapsulation of hemoglobin (red) and its catalytic activity toward reduction of oxygen	26
Figures in Chapter 2		
Figure 2.1	Comparison of FT-IR spectra of building units and the synthesized POP-Am reveals the formation of carboxamide (amide C=O in circle) linkage in POP-Am (a) and PXRD pattern evidencing microcrystalline nature of POP-Am having an ordered layered structure (b)	41
Figure 2.2	TGA plot displaying the stability of POP-Am at various conditions (a) and FT-IR spectra displaying the stability of POP-Am at various environments (b)	42
Figure 2.3	The cross polarization magic angle spinning (CP-MAS) ¹³ C-NMR spectrum rendering the chemical environment of POP-Am	42
Figure 2.4	Nitrogen adsorption-desorption isotherm at 77 K displaying the type-II adsorption isotherm of POP-Am (a) and its BET surface area plot from which the surface is calculated to be 65 m ² g ⁻¹ (b) ...	43
Figure 2.5	Structure optimization of a single ring in POP-Am by fixing the extended networking site of the polymer via hydrogen atom displaying nearly planar shape of POP-Am	44
Figure 2.6	SEM images (a,b) and HR-TEM images (c,b) of POP-Am	44
Figure 2.7	Solid UV-Vis spectra (a) and the difference in energy band gap between (b) POP-Am (blue) and its monomeric unit, <i>N</i> -phenyl benzamide (red)	45
Figure 2.8	Bar diagram representing the yield % of <i>p</i> -methyl benzaldehyde in the catalytic reusability of POP-Am (a) and identical PXRD pattern (b) of POP-Am after 4 th cycle (blue) to that of the as	51

	synthesized pattern (black) displays the stability of POP-Am	
Figure 2.9	Plausible interactions between catalyst, oxidant and reactant molecules during catalytic oxidation process. (A) POP-Am + TBHP, (B) POP-Am + H ₂ O ₂ , (C) POP-Am + H ₂ O ₂ + benzyl alcohol, (D) product formation with the liberation of 2 waters	52
Figure 2.10	Stepwise formation of benzaldehyde from benzyl alcohol in presence of TBHP supported by POP-Am as catalyst	52
Figures in Chapter 3		
Figure 3.1	Comparison of FT-IR spectra of POP-Am1 and the building units signify the occurrence of amide functionality in POP-Am1 (a) and FTIR spectra comparison indicates retention of structural integration of POP-Am1 upon impregnation of Cu(II) to afford Cu@POP-Am1	67
Figure 3.2	¹³ C cross-polarization magic angle spinning (¹³ C CP-MAS) ssNMR spectroscopy shows chemical shift environments of various carbon centers of POP-Am1	68
Figure 3.3	TGA plot of (a) as synthesized POP-Am1 indicates inclusion of guests into the pores and (b) confirms thermal stability of Cu@POP-Am1 up to 400 °C	69
Figure 3.4	(a) Sharp crystalline peak in PXRD pattern of as synthesized POP-Am1 indicates the trapping of triethylammonium chloride salt in the cavities (inset: PXRD pattern of triethylammonium chloride salt retrieved from literature) and (b) PXRD pattern of activated POP-Am1 and Cu@POP-Am1 signifying the intact structure of bare POP-Am1 upon metal impregnation	69
Figure 3.5	The reversible nitrogen adsorption-desorption isotherm recorded at 77 K (a) and the pore size distribution curve displaying microporous nature (b) of POP-Am1	70
Figure 3.6	FE-SEM images (a,b) and HR-TEM images (c,d) of activated POP-Am1	70
Figure 3.7	TEM images of Cu@POP-Am1 collected after immobilization of	72

	copper acetate onto POP-Am1	
Figure 3.8	Elemental mapping showing dispersion of C (a), oxygen (b), nitrogen (c) and homogeneous fine dispersion of Cu (d) in Cu@POP-Am1	72
Figure 3.9	EDS spectrum displaying the presence of Cu in Cu@POP-Am1	73
Figure 3.10	UV-visible absorption spectra depicting the reduction of 4NP to 4AP upon using reduced Cu@POP-Am1 (a) and the concentration change of 4NP and 4AP with respect to time as the reaction progress (b)	74
Figure 3.11	UV-visible spectra of reduction of 4NP with time employing in-situ generated reduced Cu@POP-Am1 using NaBH ₄ displays longer time for completion of 4NP reduction (a), change in concentration of 4NP and 4AP with respect to time during the progress of reaction (b)	75
Figure 3.12	UV-visible spectra screening the reduction of <i>p</i> -NA (a) and <i>m</i> -NA (b) to the corresponding phenylenediamine	76
Figure 3.13	UV-vis spectra of reaction mixture of <i>m</i> -NA displaying no progress in its reduction	76
Figure 3.14	Displaying the conversion % of reduction of 4-nitrophenol to 4-aminophenol at each catalytic cycle	77
Figure 3.15	XPS spectrum of (a) Cu@POP-Am1 and (b) Cu 2p of Cu@POP-Am1 revealing the presence of Cu in +2 oxidation state	78
Figure 3.16	PXRD pattern of reused Cu@POP-Am1 clearly displays the structural integrity degradation of Cu loaded POP-Am1 after 5 th catalytic cycle	78

Figures in Chapter 4

Figure 4.1	(a) FT-IR spectra comparison of POP-Am2 with its building units, (b) TGA plot displaying the stability and inclusion of guest molecules in the pores of POP-Am2	92
Figure 4.2	¹ H NMR (a) and ¹³ C NMR (b) spectrum of TAPT recorded in DMSO- <i>d</i> ₆	93

Figure 4.3	(a) PXRD pattern of synthesized POP-Am2 displaying the inclusion of triethylammonium chloride salt in its cavities that releases upon thermal activation signifying amorphous nature. (b) ¹³ C ssNMR spectrum and the chemical environments of POP-Am2.....	95
Figure 4.4	Nitrogen adsorption-desorption isotherm (a) and pore size distribution curve (b) of POP-Am2	95
Figure 4.5	FE-SEM (a) and TEM (b) image of POP-Am2	96
Figure 4.6	(a) Catalytic reusability test of POP-Am2 in oxidation of styrene. (b) PXRD pattern of reused POP-Am2 recorded after 4 th cycle and compared to its initial pattern reveals intact structural integrity of POP-Am2 even after catalytic pathways.....	100
Figure 4.7	Optimized geometry of the trimeric unit in POP-Am2 and the incoming oxidant, TBHP displaying the H-bond interaction with π -cloud of the catalyst	101
Figure 4.8	QTAIM analysis attributing the weak interaction between H-atom of TBHP and π -cloud of the central ring of the trimer (a) and NCI calculation revealing the interaction zone between TBHP and the π -cloud of the catalyst (b)	102
Figure 4.9	Generation of the free radicals mediated by the trimer unit of POP-Am2	103
Figure 4.10	Gibbs free energy changes during the radical initiated product formation during styrene oxidation to aldehyde stimulated by POP-Am2	104

Figures in Chapter 5

Figure 5.1	(a) Comparison of IR spectrum of Cu@POP-Am2 and POP-Am2. (b) TGA plot exhibiting the thermal stability of Cu@POP-Am2 up to 400 °C (b)	116
Figure 5.2	(a) PXRD pattern of Cu@POP-Am2 laid over bare POP-Am2 reveals the perseverance of structural integrity of POP-Am2 upon loading with copper. (b) EDS spectrum confirms the existence of	116

	Cu in Cu@POP-Am2	
Figure 5.3	Nitrogen adsorption-desorption isotherm (a) and pore size distribution curve (b) of Cu@POP-Am2	117
Figure 5.4	FE-SEM image of POP-Am2 (a) and SEM image of Cu@POP-Am2 (b)	117
Figure 5.5	XPS spectra of (a) POP-Am2 (black) and Cu@POP-Am2 (red); (b) Cu 2p of Cu@POP-Am2; (c) N 1s and (d) O 1s spectra revealing the presence of Cu(II) and its interaction with N of POP-Am2	118
Figure 5.6	Temperature optimization vs conversion % in oxidation of oluene via sp^3 C-H activation	120
Figure 5.7	Conversion % of toluene vs no. of cycle revealing the reusable efficiency of Cu@POP-Am2	123
Figure 5.8	Stacked IR spectra (a) and PXRD patterns (b) of fresh and reused Cu@POP-Am2 upto 4 th catalytic cycle	123

Figures in Chapter 6

Figure 6.1	POP-Am has been used as metal free catalyst in selective oxidation of benzyl alcohols	134
Figure 6.2	Cu@POP-Am1 used as heterogeneous catalyst in reduction of nitroarenes	135
Figure 6.3	POP-Am2 with enrich π -electrons acting as organic catalyst in performing a peculiar Wacker-type oxidation of olefins accomplishing C=C bond cleavage	136
Figure 6.5	Pictorial representation of the overall thesis	137
Figure 6.6	Representing the future prospects in the synthesis of POPs with tuned properties and their targeted applications in various fields....	138