

Table of Contents

Contents	Page No.
Abstract	i
Keywords	viii
Declaration by Student	ix
Certificate from the supervisor	x
Certificate of the External Examiner and ODEC	xi
List of Figures	xii
List of Schemes	xviii
List of Tables	xxi
List of Abbreviations	xxiv
List of Symbols	xxvi

Chapter 1: General Introduction and Review of Literature **Page No.**

1.1	Introduction	1.1
1.1.1	Task-specific ionic liquids	1.3
1.1.2	Halometallate ionic liquids	1.4
1.2	Physicochemical and electrochemical properties of acidic ionic liquids	1.5
1.2.1	Conductivity of ILs	1.6
1.2.2	Thermal stability of ILs	1.10
1.2.3	Electrochemical stability of the ILs	1.12
1.2.4	Acidity of the ILs	1.15
1.2.5	Viscosity of ILs	1.18
1.2.6	Density of ILs	1.19
1.2.7	Surface tension of ILs	1.21
1.2.8	Surfactant-like properties of the ILs	1.23
1.3	Application of ionic liquids in catalysis and nanoparticle synthesis	1.27
1.3.1	Catalytic application of ILs	1.28
1.3.1.1	Claisen-Schmidt condensation	1.28

1.3.1.2 Michael addition	1.33
1.3.1.3 Multicomponent synthesis of 2-amino-3-cyanopyridines	1.36
1.3.2 Application of ILs in nanoparticle synthesis	1.40
Bibliography	1.42

Chapter 2: Objectives and Methodology	Page No.
2.1 Objectives of the present work	2.1
2.1.1 Objectives	2.3
2.2 Methodology	2.4
2.2.1 Required Materials	2.5
2.2.2 Analytical methods	2.5
2.2.2.1 Fourier Transform Infrared (FT-IR) spectroscopy	2.5
2.2.2.2 Nuclear Magnetic Resonance spectroscopy (NMR)	2.5
2.2.2.3 Thermogravimetric analysis (TGA)	2.6
2.2.2.4 CHN Elemental analysis	2.6
2.2.2.5 UV-Visible spectroscopy	2.6
2.2.2.6 Raman spectroscopy	2.7
2.2.2.7 Mass spectrometry	2.7
2.2.2.8 Powder-X-ray Diffraction (PXRD) analysis	2.7
2.2.2.9 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis	2.7
2.2.2.10 Transmission Electron Microscopy (TEM) analysis	2.8
2.2.2.11 UV-Visible Diffuse Reflectance Spectroscopy	2.8
2.2.2.12 The Brunauer - Emmett – Teller (BET) analysis	2.8
2.2.2.13 Fluorescence measurements	2.8
2.2.2.14 Conductivity measurements	2.9

2.2.2.15 Cyclic Voltammetry technique	2.9
2.2.2.16 Melting point measurements	2.9
2.2.2.17 X-ray photoelectron spectroscopy (XPS)	2.9
Bibliography	2.10

***Chapter 3: Investigation of the Physical and Electrochemical Page No.
Behaviour of Direct N-SO₃H Functionalized 1, 3-Disulfo-2-
alkyl-imidazolium Trifluoroacetate Ionic Liquids in
Molecular Solvents***

3.1 Introduction	3.1
3.2 Results and Discussion	3.4
3.2.1 Characterization of the N-SO ₃ H functionalized Brønsted acidic ionic liquids (BAILs)	3.4
3.2.1.1 FT-IR analysis	3.4
3.2.1.2 NMR analysis	3.6
3.2.2 Investigation of the physicochemical properties of the BAILs	3.6
3.2.2.1 Thermogravimetric analysis (TGA)	3.6
3.2.2.2 Hammett acidity	3.7
3.2.2.3 Density of the BAILs	3.9
3.2.2.4 Conductivity study of BAILs in molecular solvents	3.10
3.2.2.5 Electrochemical stability of ionic liquids in molecular solvents	3.21
3.3 Summary	3.24
3.4 Experimental section	3.24
3.4.1 Synthesis of the N-SO ₃ H functionalized Brønsted acidic ionic liquids (BAILs)	3.24
3.4.2 Spectral data of the N-SO ₃ H functionalized BAILS	3.25
3.4.3 NMR spectra of the [EDSIM][TFA] & [BDSIM][TFA] ionic liquids	3.28
Bibliography	3.30

Chapter 4: Comparative Study on the Physicochemical Properties of N-SO₃H Functionalized Ammonium and Imidazolium Based Brønsted Acidic Ionic Liquids

4.1	Introduction	4.1
4.2	Results and Discussion	4.3
4.2.1	Characterization of the N-SO ₃ H functionalized Brønsted acidic ionic liquids (BAILS)	4.3
4.2.1.1	FT-IR analysis	4.4
4.2.1.2	NMR analysis	4.6
4.2.2	Investigation of the physicochemical properties of the BAILS	4.6
4.2.2.1	Thermogravimetric analysis (TGA)	4.6
4.2.2.2	Hammett acidity of the BAILS	4.12
4.2.2.3	Electrochemical stability of the BAILS in molecular solvents	4.15
4.2.2.4	Conductivity of the BAILS in molecular solvents	4.25
4.2.2.5	Polarity study of the BAILS with Fluorescence probe	4.27
4.2.2.6	Density of the ILs	4.29
4.3	Summary	4.29
4.4	Experimental Section	4.30
4.4.1	Synthesis of the N-SO ₃ H functionalized imidazolium and ammonium based ionic liquids	4.30
4.4.2	Spectral data of the ILs	4.32
4.4.3	NMR spectra of the [EDSIM][BF ₄] & [DBDSA][TFA] ionic liquids	4.36
	Bibliography	4.39

Chapter 5A: N-SO₃H functionalized Imidazolium Ionic Liquids Catalysed Sequential Michael-like Addition of Indole with Chalcones via Claisen-Schmidt Condensation Page No.

5A.1	Introduction	5A.1
5A.2	Results and Discussion	5A.2
5A.2.1	Characterization of the N-SO ₃ H functionalized Brønsted acidic ionic liquids	5A.2
5A.2.1.1	FT-IR analysis	5A.3
5A.2.1.2	NMR analysis	5A.4
5A.2.1.3	Hammett acidity of the BAILS	5A.5
5A.2.1.4	Thermogravimetric analysis	5A.7
5A.2.2	Catalytic Study	5A.9
5A.2.2.1	Selective formation of chalcones	5A.9
5A.2.2.2	Sequential synthesis of 3-substituted indoles	5A.11
5A.2.2.3	Plausible mechanism	5A.13
5A.2.2.4	Catalyst recyclability	5A.14
5A.3	Summary	5A.14
5A.4	Experimental Section	5A.15
5A.4.1	Synthesis of the N-SO ₃ H functionalized Brønsted acidic ionic liquids (BAILS)	5A.15
5A.4.2	General procedure for preparation of chalcone derivatives	5A.16
5A.4.3	General procedure for one-pot synthesis of 3-substituted indole derivatives	5A.16
5A.4.4	Spectral data of the ILs	5A.17
5A.4.5	Spectral data of the chalcones	5A.20
5A.4.6	Spectral data of Michael addition products	5A.23
5A.4.7	NMR spectra of [MDSIM][TFA] ionic liquid	5A.28
5A.4.8	NMR spectra of 3a	5A.29
5A.4.9	NMR spectra of 4c	5A.30
	Bibliography	5A.31

**Chapter 5B: N-SO₃H Functionalised Ionic Liquid Catalysed Page No.
Sequential One-Pot Multicomponent Synthesis of 2-Amino-3-
cyanopyridines**

5B.1	Introduction	5B.1
5B.2	Results and Discussion	5B.3
	5B.2.1 Characterization of the N-SO ₃ H functionalized Brønsted acidic ionic liquids	5B.3
	5B.2.1.1 FT-IR analysis	5B.4
	5B.2.1.2 NMR analysis	5B.5
	5B.2.1.3 Hammett acidity of the BAILS	5B.6
	5B.2.1.4 Thermogravimetric analysis	5B.7
	5B.2.2 Catalytic Study	5B.7
	5B.2.2.1 Synthesis of chalcones via Claisen-Schmidt condensation	5B.7
	5B.2.2.2 Synthesis of 2-amino-3-cyanopyridine derivatives	5B.10
	5B.2.2.3 Substrate Scope Study for 2-amino-3-cyanopyridines derivatives	5B.13
	5B.2.2.4 Recycling of the catalyst [TSPi][Cl] ₂	5B.13
	5B.2.2.5 Plausible mechanism	5B.15
5B.3	Summary	5B.17
5B.4	Experimental section	5B.17
	5B.4.1 Synthesis of the N-SO ₃ H functionalized Brønsted acidic ionic liquids (BAILS)	5B.17
	5B.4.2 Synthesis of 2-amino-3-cyanopyridine derivatives through one-pot sequential reaction	5B.18
	5B.4.3 Spectral data of the ILs	5B.18
	5B.4.4 Spectral data of chalcones	5B.20
	5B.4.5 Spectral data of 2-amino-3-cyanopyridine	5B.24
	5B.4.6 NMR spectra of [TSPi][Cl] ₂ ionic liquid	5B.28
	5B.4.7 NMR spectra of 3d	5B.29
	5B.4.8 NMR spectra of 4a	5B.30
	Bibliography	5B.31

Chapter 6: Investigation of Photocatalytic Activities of Nickel Sulphide Nanosheets Synthesized using Imidazolium Based Chloronickellate Ionic Liquids as Precursor/Template for Photocatalytic Degradation of Organic Dyes

6.1	Introduction	6.1
6.2	Results and Discussion	6.2
6.2.1	Characterization of N-SO ₃ H functionalized imidazolium based chloronickellates	6.2
6.2.1.1	FT-IR analysis	6.3
6.2.1.2	NMR analysis	6.4
6.2.1.3	ESI-Mass spectrometry analysis	6.6
6.2.2	Characterization of the nickel sulphide nanoparticles	6.6
6.2.2.1	Powder X-ray diffraction (PXRD) analysis	6.7
6.2.2.2	TEM analysis	6.8
6.2.2.3	EDX and SEM analysis	6.10
6.2.2.4	FT-IR analysis	6.12
6.2.2.5	Raman analysis	6.13
6.2.2.6	X-ray Photoelectron spectroscopy study	6.14
6.2.2.7	Optical analysis	6.15
6.2.2.8	BET surface area analysis	6.16
6.2.3	Catalytic study	6.16
6.2.3.1	Active species for the degradation of dyes	6.23
6.2.3.2	Evidence for degradation of dyes	6.25
6.2.3.3	Recyclability of the catalyst	6.27
6.3	Summary	6.28
6.4	Experimental section	6.28
6.4.1	Synthesis of the N-SO ₃ H functionalized imidazolium based chloronickellates	6.28
6.4.2.	Synthesis of nickel sulphide nanoparticles using N-SO ₃ H functionalized imidazolium based chloronickellates as precursor and template.	6.29
6.4.3.	General procedure for degradation of organic dyes using nickel sulphide nanoparticles	6.29
6.4.4	Spectral data of the ILs	6.30
6.4.5	NMR spectra of imidazolium chloronickellate 1b	6.31
6.4.6	ESI-mass spectra of imidazolium chloronickellates	6.32

Chapter 7: Conclusion and Future Scope **Page No.**

7.1	Conclusion	7.1
7.2	Future Scope	7.6

List of Academic Publications, Conferences and Symposiums attended xxvii