IONIC LIQUIDS

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OVERVIEW

- Introduction
- Historical Review
- Experimental
- Discussion
- Conclusion
- References

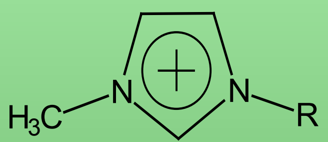
WHAT ARE IONIC LIQUIDS ?

- Organic salts composed of cations and anions that are liquid at conditions around room temperature

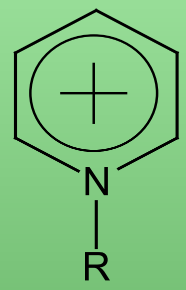
- No effective vapor pressure, thermal stability, wide range of liquid, and large electrochemical window

STRUCTURES OF IONIC LIQUIDS

CATIONS

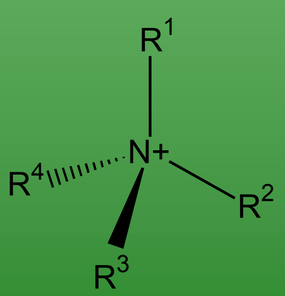


imidazolium

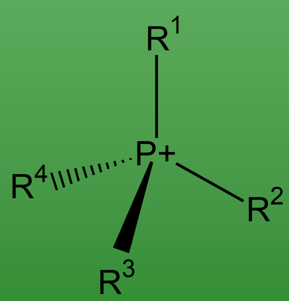


pyridinium

R = $-C_2H_5$, $-C_4H_9$, $-C_8H_{17}$



tetra alkylammonium



tetra alkylphosphonium

ANIONS

Cl^- / $[AlCl_3]$ — Reactive to water

Cl^-, Br^-, I^-

$[NO_3]$, $[SO_4]^{2-}$

$[CF_3COO]^-$, $[CF_3SO_2]^-$

$[BF_4]^-$

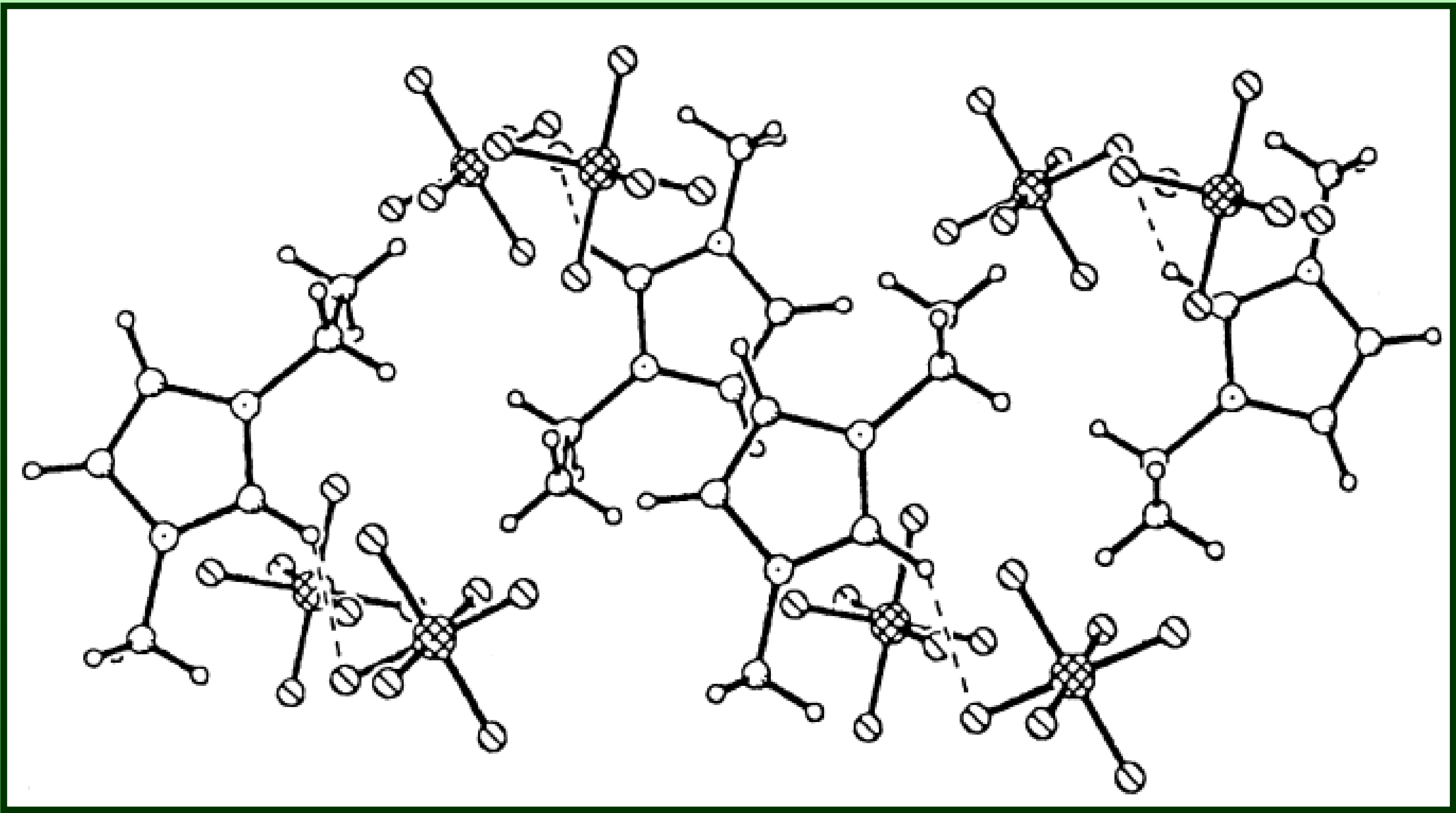
$[PF_6]^-$

$[(CF_3SO_2)_2N]^-$

Air and water stable

Decreasing coordinating ability

Increasing hydrophobicity



Crystal structure of
1-ethyl-3-methylimidazolium hexafluoro phosphate

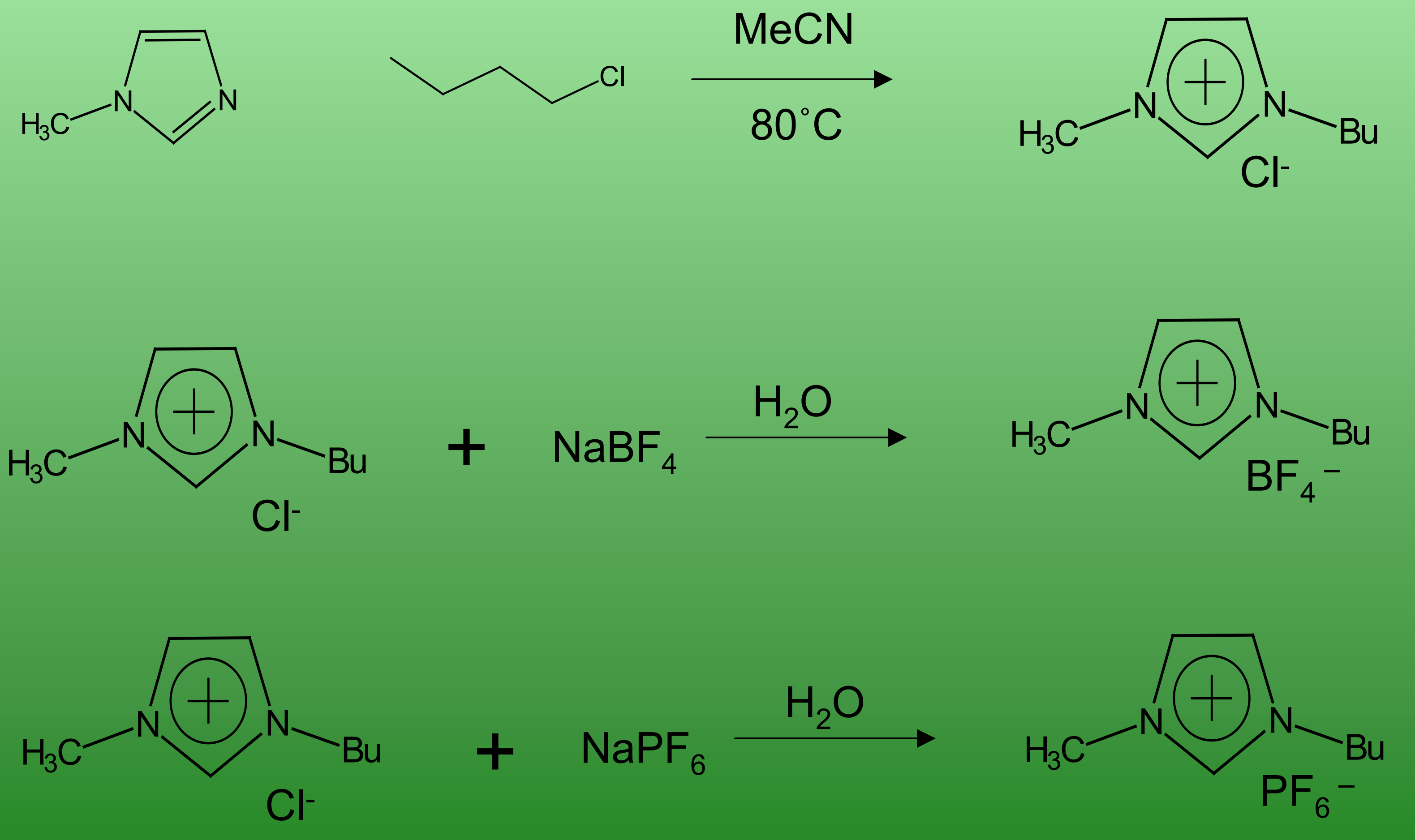
Historical Review

- First discovery of the room temperature ionic liquid
  - N-ethylpyridinium bromide-aluminium chloride melt(Hurley et al., 1951)
- Development of air- and water-stable imidazolium based ILs by Wilkes et al.(1992)
- The range of available anions and cations has expanded enormously in the past decades.
- Application of Chemical synthesis, catalysis, and electrolytes (Holbrey et al., 1999)
- Extraction of organic solutes using ILs and supercritical CO_2 (Blanchard et al., *Nature*, 1999)

WHY IONIC LIQUIDS ?

- **Traditional process (using organic solvents)**
  - ⇨ volatile, toxic, flammable
  - ⇨ cross-contamination
  - ⇨ violate environmental regulations
- **Alternative Solvent**
  - ⇨ Ionic liquids
    - ☞ strong solvent that is liquid under ambient conditions
    - ☞ lack of appreciable vapor pressure
  - ⇨ Supercritical Carbon dioxide
    - ☞ unusual properties near the critical point
    - ☞ gas like to liquid like properties

SYNTHESIS



Huddlestone et al

PHYSICAL PROPERTIES

- **Melting point (-96°C ~)**

  Melting point is lowered with increasing length of alkyl chain in cations

  - Packing inefficiency

    Eg. N,N'-dialkylimidazolium salts are liquids at RT

  - Methylation of C-2 position increases m.pt.

- **Density**

  1.1 ~ 1.6 g/cm^3 at ambient temperature (291~303K)

- **Viscosity**

  - Several tens to hundred times that of water at room temperature
    - Longer alkyl chains of cation makes the liquid more viscous.
    - Structure and basicity of anion affects the viscosity.

Polarity

- Aki et al.(*Chem. Commun.*, 2001)

[BMIM][PF6], [C8mim][PF6], [BMIM][NO3], and [N-bupy][BF4] are more polar than acetonitrile and less polar than methanol.

These ionic liquids are expected to be at least partially miscible with water

RECOVERY OF ORGANIC PRODUCTS FROM IONIC LIQUIDS USING SUPERCRITICAL CO_2 - Blanchard et al.

Recent studies showed that non-volatile organic compounds can be quantitatively extracted from ILs using supercritical CO_2.

E.g.. Organic Solute = Naphthalene

IL = 1-n-butyl-3-methylimidazolium hexafluorophosphate {[bmim][PF_6]}

Why supercritical CO_2 ?

In-expensive

Non-flammable

Non-toxic

➯ CO_2 is a GREEN SOLVENT

Lack of cross-contamination

CO_2 is dissolved in IL, but IL is not dissolved in CO_2

The solute can be separated by simple depressurization

Experimental

Solubility measurement:

Ionic Liquid : 1-n-butyl-3-methylimidazolium hexafluorophosphate {[bmim][PF6]}
{[bmim][PF6]} should be dried and degassed
Existence of water affects the solubilty of CO_2 in IL

Measurement Methods:

UV-Vis spectroscopy (To determine the conc. of organic-saturated [bmim][PF6] phase using Beer's Law)

Gravimetry (For UV-Vis inactive organics)

Organic solutes employed: benzene and its substitutes (aromatics)
hexane and its substitutes (aliphatics)

Extraction experiments:
Each solute below the solubility limits dissolve in ILs
Measurement of the recovery of organic in solution
Measurement of the recovery ratio with the amount of CO_2

Results

Solubility Measurement

- Solubility is affected by strong intermolecular interaction
- Large dipole moment ⇨ Miscibility or large degree of solubility
- Benzene family are completely miscible
- Hexane family are generally immiscible
- Solubilities of solid solute are considerably less than those of the liquid organics

Extraction

All organic solutes exhibit a greater than 95% recovery
(Several organic solutes accomplish greater than 98% recovery)

Solid solutes at room temperature require the largest CO_2 for 95% solute recovery

solute[a]	solubility (solute mole fraction)	dipole moment (Debye)	analysis method (wavelength (nm))	T_m (°C)	T_b (°C)
benzene	0.66	0	UV–vis (255, 261)	5.5	80
chlorobenzene (s) (halogen)	0.58	1.69	UV–vis (258, 271)	−45	132
phenol (alcohol)	0.69	1.45	UV–vis (273)	40	182
anisole (ether)	miscible	1.38	UV–vis (271, 278)	−37	154
aniline (amine)	miscible	1.53	UV–vis (236, 286)	−6	184
acetophenone (ketone)	miscible	3.02	UV–vis (241)	19	202
benzoic acid (s) (carboxylic acid)	0.07	1.00	UV–vis (231)	121	249
methyl benzoate (ester)	miscible	2.55	UV–vis (273)	−12	198
benzamide (s) (amide)	0.04	3.60	UV–vis (225)	128	288
benzaldehyde (aldehyde)	miscible	2.80	UV–vis (245)	−26	178
hexane	miscible	0	gravimetric	−95	69
1-chlorohexane (halogen)	0.25	1.99	gravimetric	−94	133
1-hexanol (alcohol)	0.26	1.65	gravimetric	−52	156
butyl ethyl ether (ether)	0.06	1.22	gravimetric	−124	91
cyclohexane	0.21	0	gravimetric	6.5	81
2-hexanone (ketone)	miscible	2.68	UV–vis (278)	−57	127
hexanoic acid (carboxylic acid)	0.13	1.57	UV–vis (219)	−3	202
methyl pentanoate (ester)	0.59		UV–vis (209)		128
hexanamide (s) (amide)	0.06	3.90	UV–vis (203)	100	225
1,4-butanediol	0.51	2.58	gravimetric	16	230

[a] Solids are indicated by (s).

Organic solute solubilities in [bmim][PF_6] at T= 22 ^{0} C , along with solute dipole moments , melting temperatures and Normal boiling temperatures.

Discussion

- Solubility
  - The compounds most similar to [bmim][PF_6] will have the highest solubility
  - Benzene-based compounds are several times greater than those of their hexane-based counterparts
    - Compounds with larger dipole moments, excluding the solid compounds, are completely miscible in [bmim][PF_6]
  - The solubility of the solids in the IL are lower than those of the organic liquids

CONCLUSION

CO_2 can completely extract a wide array of organic solutes from an ionic liquid.

Using hexane, benzene roots and their substitute, a correlation relating dipole moment to the amount of CO_2 necessary for solute recovery has been established.

Intermolecular interaction between the organics and $[bmim][PF_6]$ do not limit the degree to which a solute can be separated from the IL.

Overall, ionic liquids and $SCCO_2$ offer not only a new avenue for reactions and separations but have the additional asset of environmental sustainability

APPLICATIONS

Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids

- Improving the ability of crown ethers to remove metal ions from aqueous solutions.
- The highest distribution coefficient value is over four orders of magnitude greater than those of the conventional extraction systems.

$$D^a = \frac{[\text{Molten Salt } Sr^{2+}]}{[\text{aqueous } Sr^{2+}]}$$

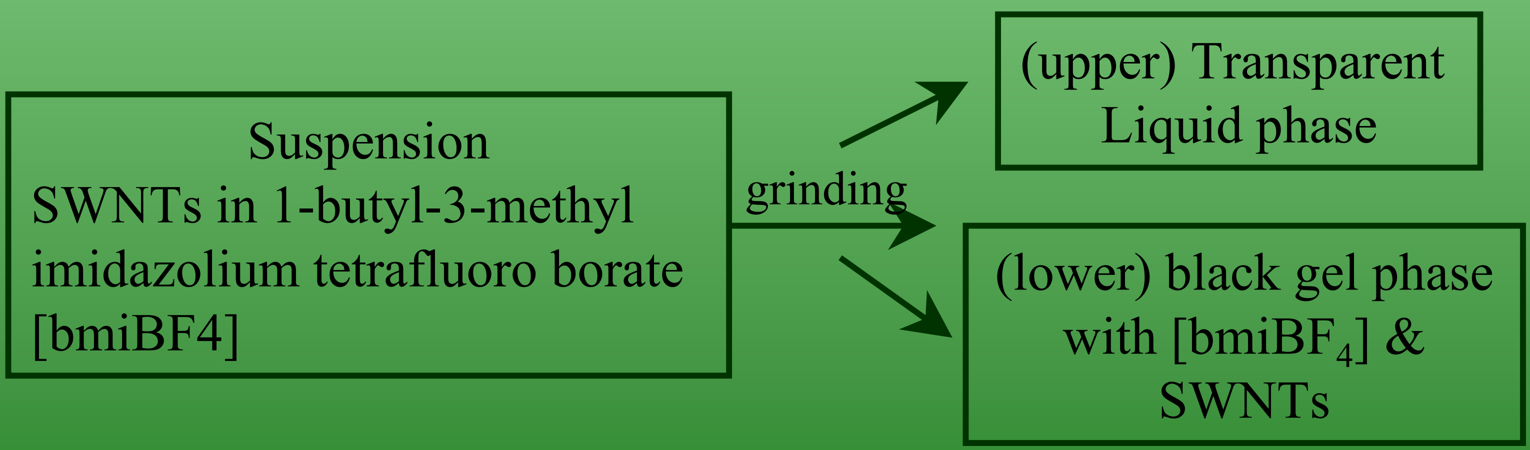
Extract phase	D^a(with crown ether)	D(without crown ether)
$BuMe_2ImPF_6$	4.2	0.67
$BuMeImPF_6$	2.4×10^{1}	0.89
$EtMe_2ImTf_2N$	4.5×10^{3}	0.81
$EtMeIMTf_2N$	1.1×10^{4}	0.64
$PrMe_2ImTf_2N$	1.8×10^{3}	0.47
$PrMeImTf_2N$	5.4×10^{3}	0.35
Toluene	7.6×10^{-1}	Not measurable
Chloroform	7.7×10^{-1}	Not measurable

Molecular ordering of organic molten salts Triggered by single walled carbon nanotubes[SWNT]

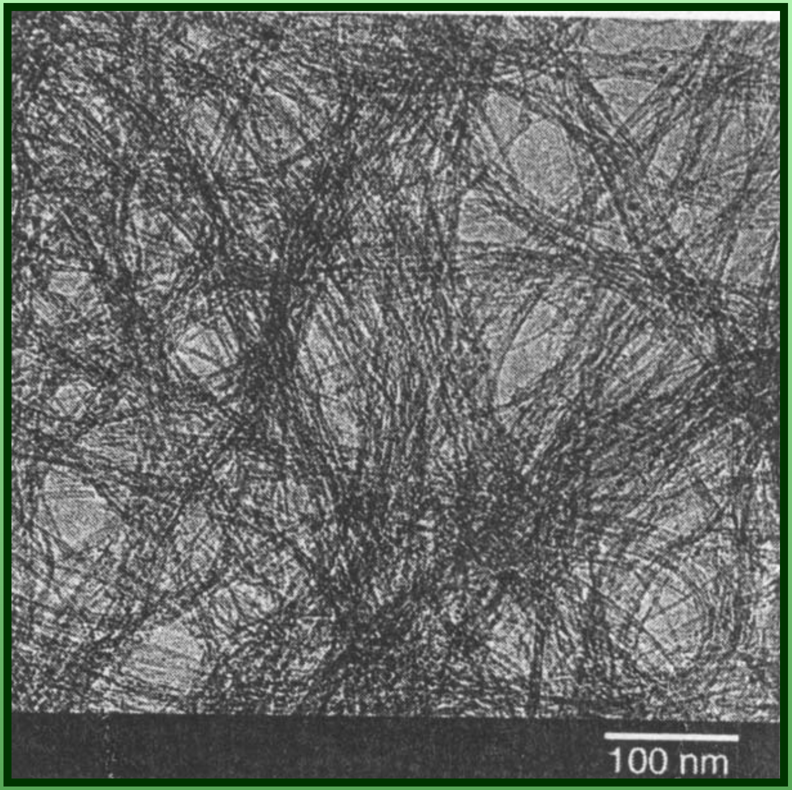
– Fukushima et al

Room temperature ionic liquids of imidazolium ions upon being ground with single walled nanotubes form physical gels

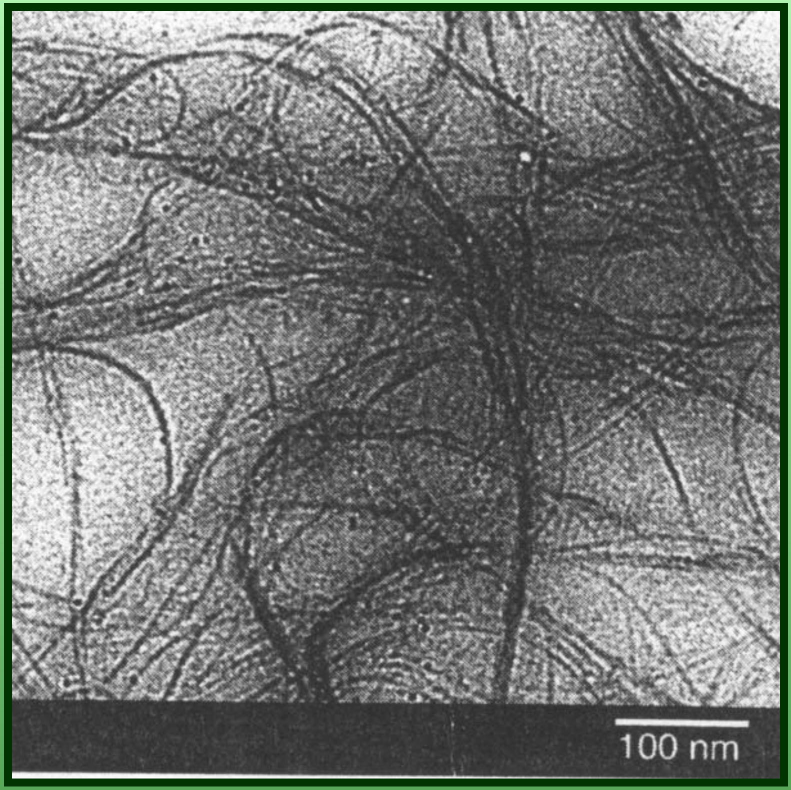
PREPARATION OF BUCKY GELS OF ILs



TEM Pictures

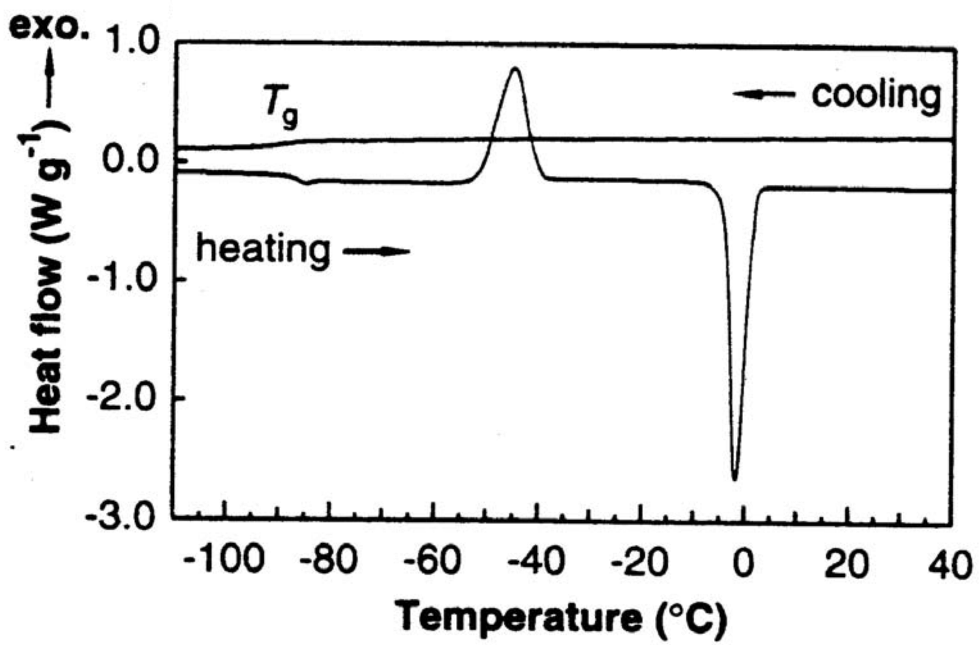


TEM image of as received SWNTs as reference, after sonication in ethanol

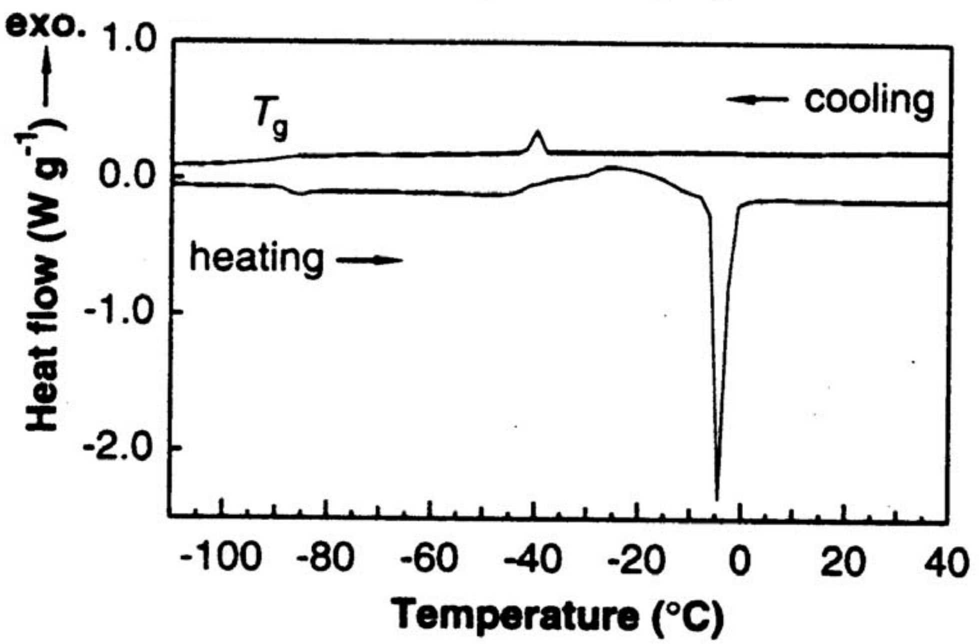


TEM image of SWNTs obtained by dispersing a bucky gel of [bmiBF_4] in deionized water

DSC THERMOGRAMS

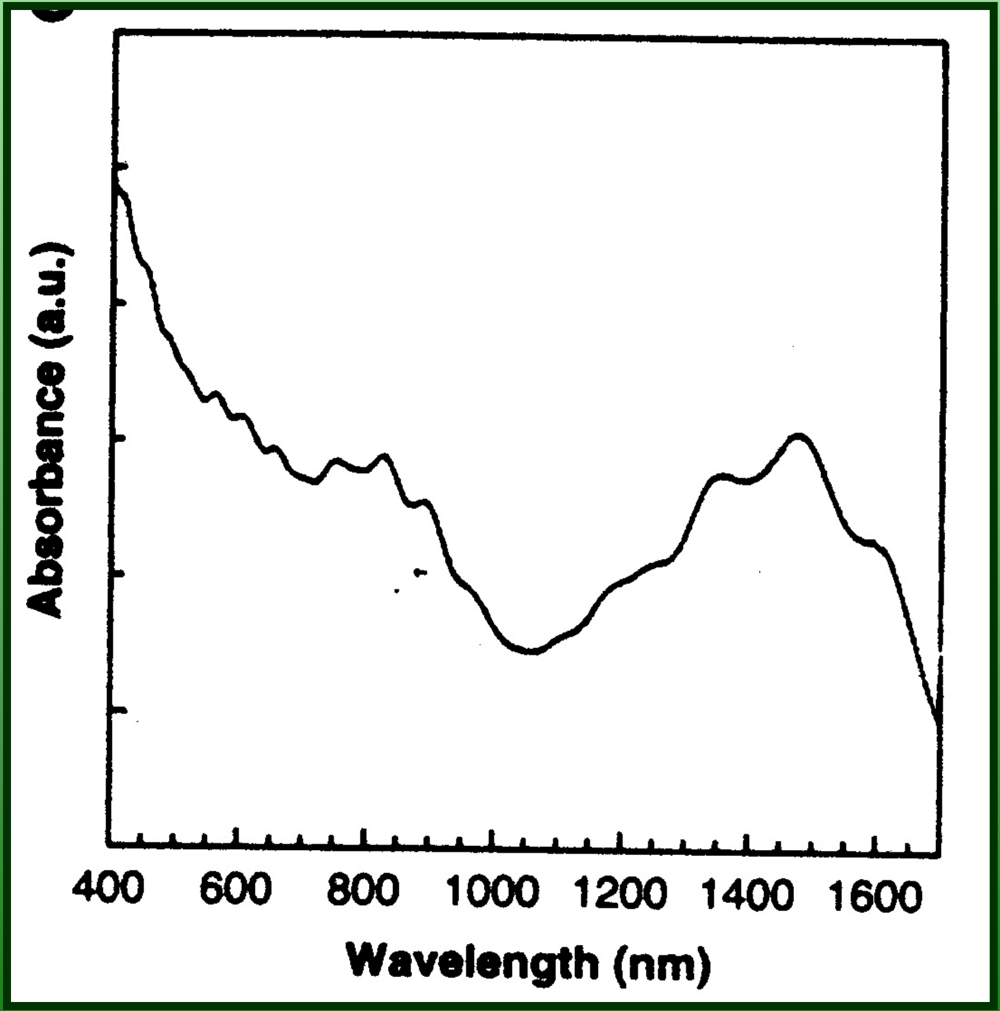


Bucky gel of $BMITf_2N$ containing 0.5 wt % of SWNTs



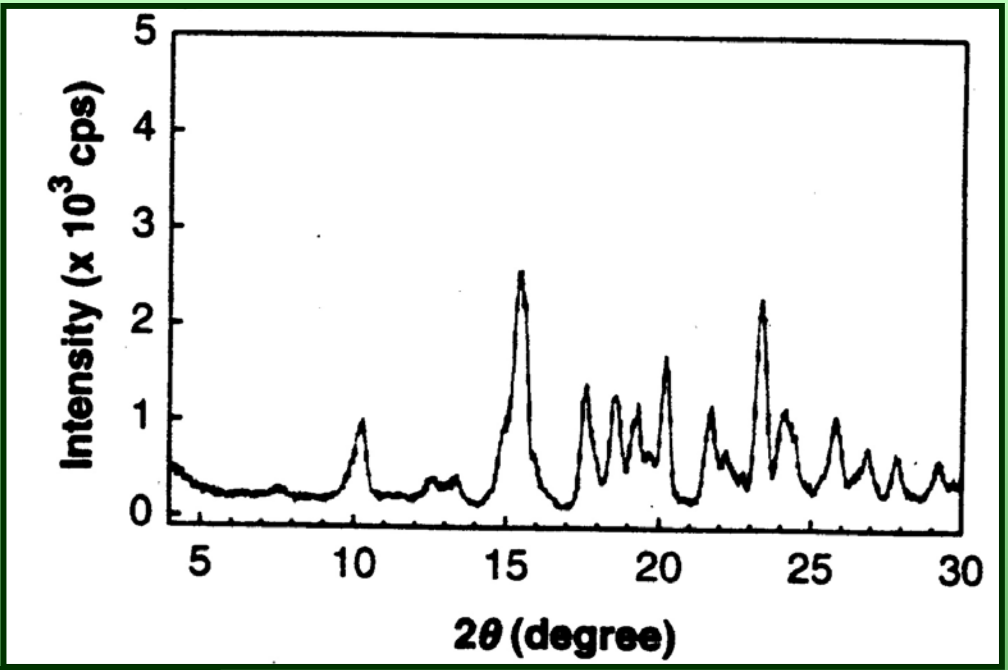
$BMITf_2N$ as reference

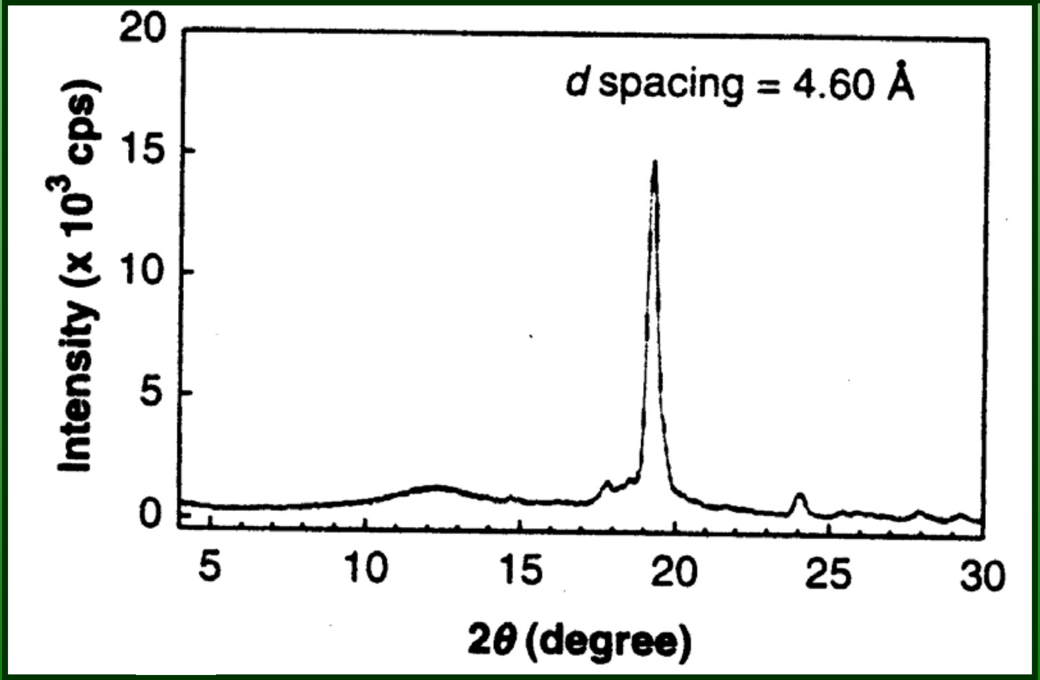
Electron absorption spectrum of bucky gel of [bmiBF_4]



XRD PROFILES

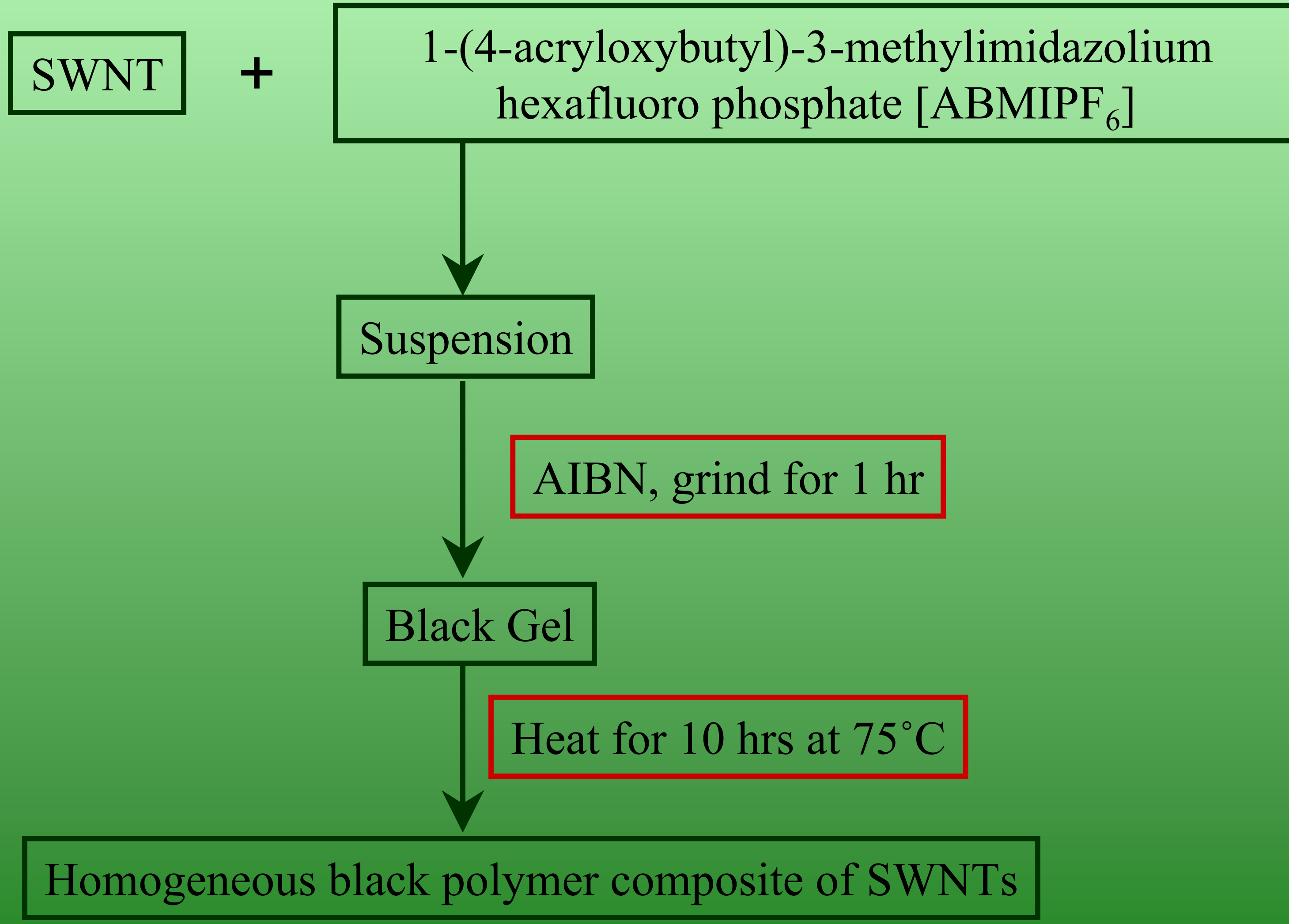
BMITf$_2$N as reference





Bucky gel of BMITf$_2$N containing 0.5 wt % of SWNTs

PREPARATION OF BUCKY GEL POLYMERIZABLE OF ILs



CONCLUSION

Use of polymerizable ionic liquid as the gelling medium allows for the fabrication of a highly electro-conductive polymer/nanotube composite material

↳ Substantial enhancement in the dynamic hardness

APPLICATIONS

- Novel electronic devices
- Coating materials

References

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Thank you