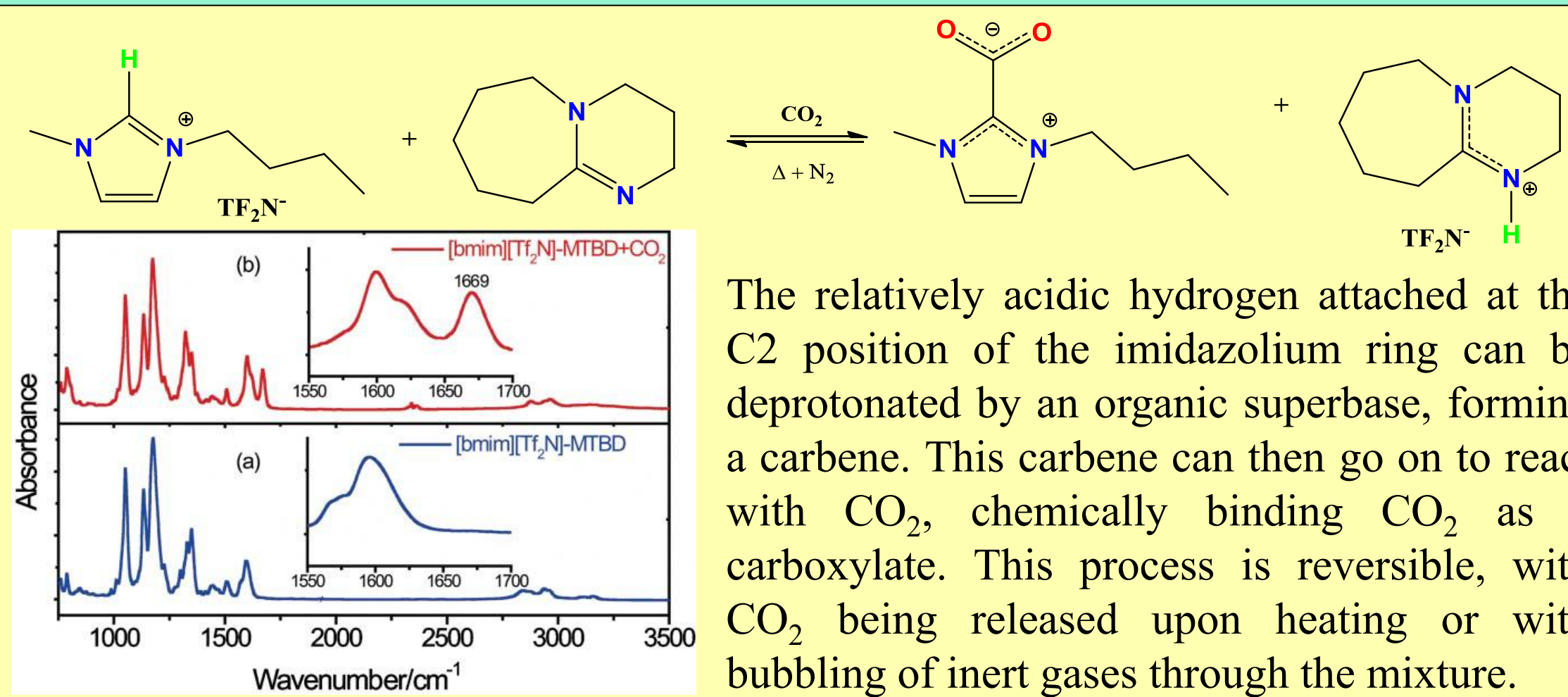


Ionic Liquids as Versatile Media for Post-Combustion Carbon Capture

Patrick C. Hillesheim, Pasquale F. Fulvio, Shannon M. Mahurin, Joseph Singh, Joshua S. Yeary and Sheng Dai*
Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

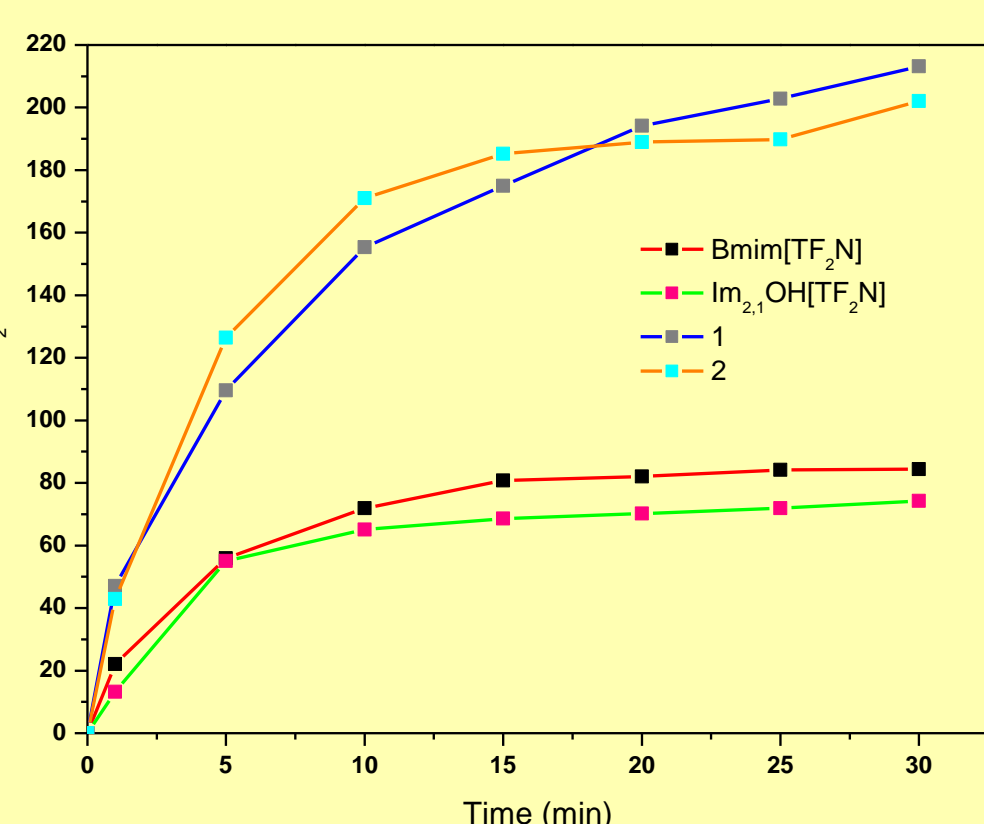
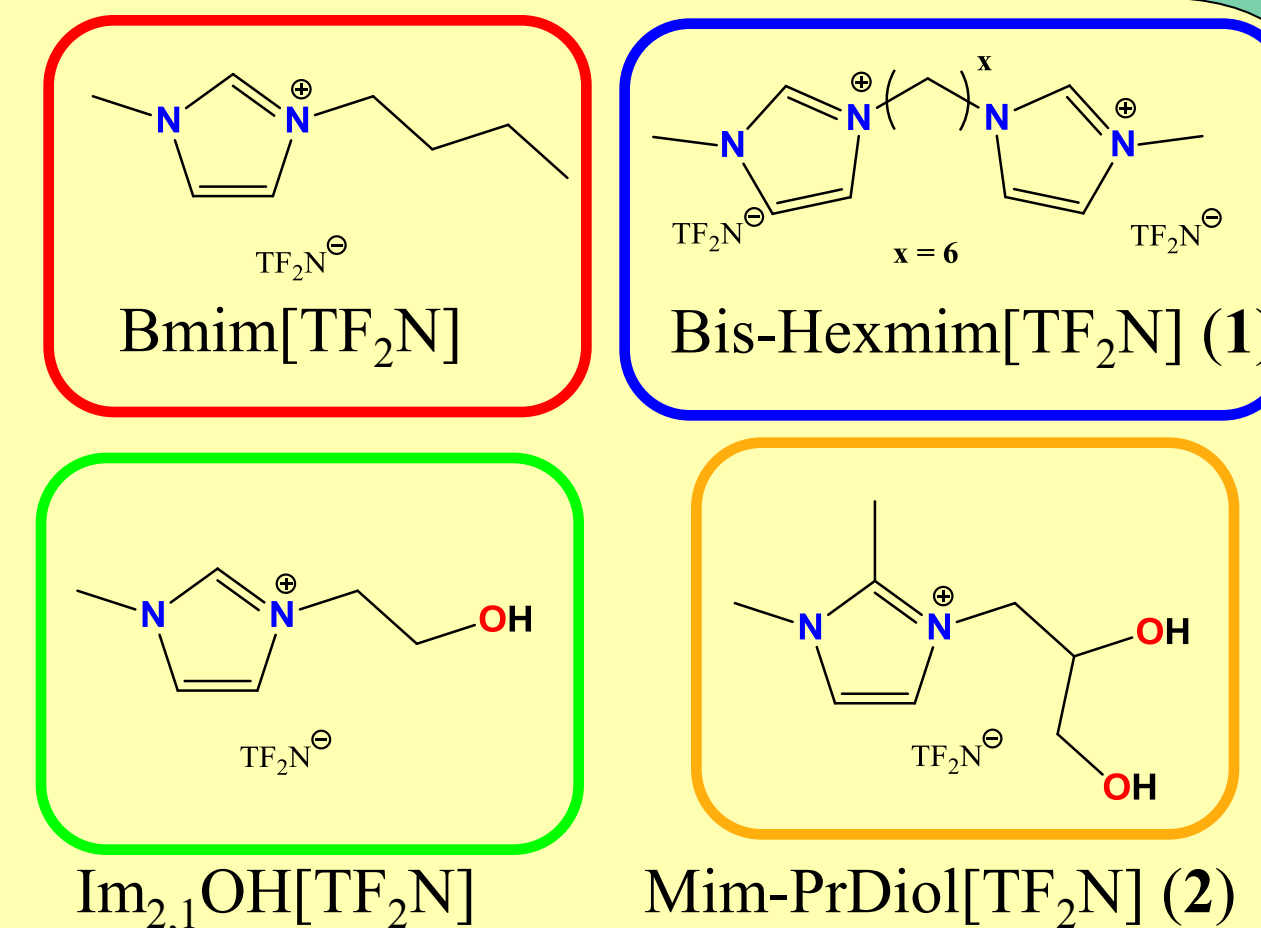
Abstract: The necessity for novel materials with the capability to capture and store CO₂ is an area of research which is receiving significant attention. Ionic liquids possess numerous qualities which make them ideal candidates for use in post-combustion carbon capture. With their diverse reactivity and unique properties, ionic liquids are viable materials for the separation and storage of CO₂. Herein we present three methods in which ionic liquids have been applied to the mitigation of carbon emission.

Molten Salts as Liquid Sorbents



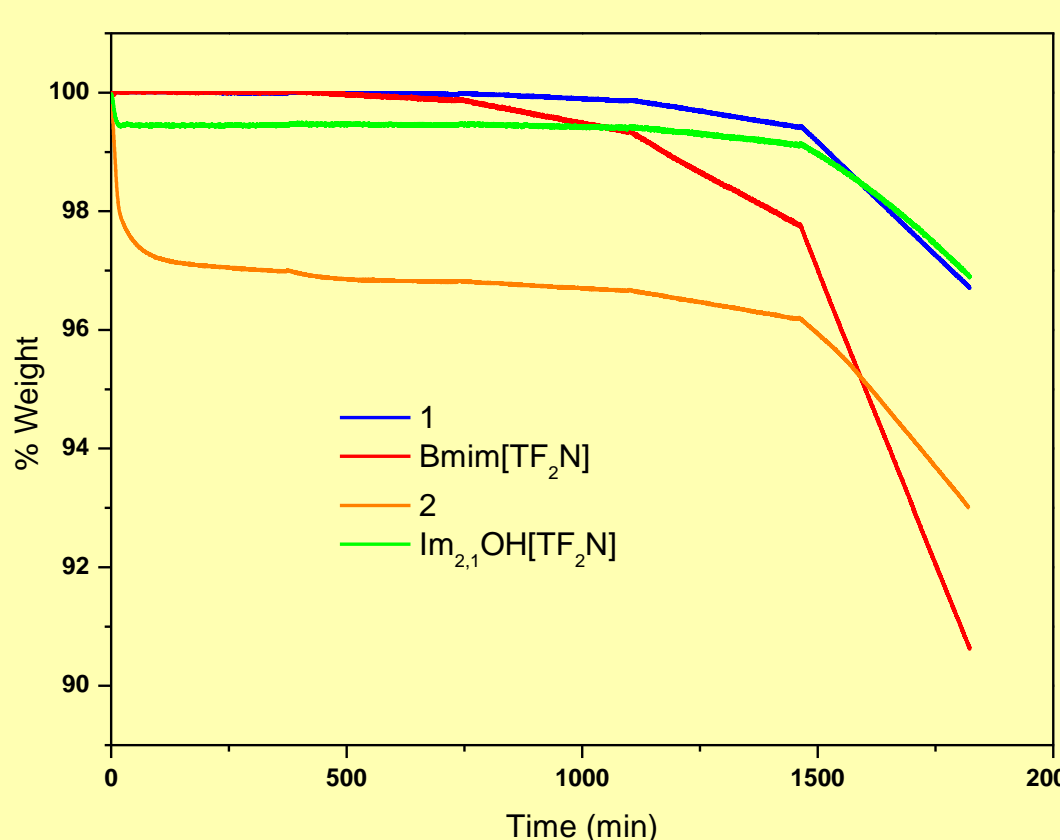
Optimizing The Liquid Media Capture Process

A series of task-specific ionic liquids were synthesized (right) in an effort to improve on the overall capture process described above. One major drawback of ionic liquids is their inherent viscosity. To overcome this issue, multiple potential binding sites for CO₂ were incorporated into the new ionic liquids, offer the potential of increased binding kinetics via the statistical increase in active sites.

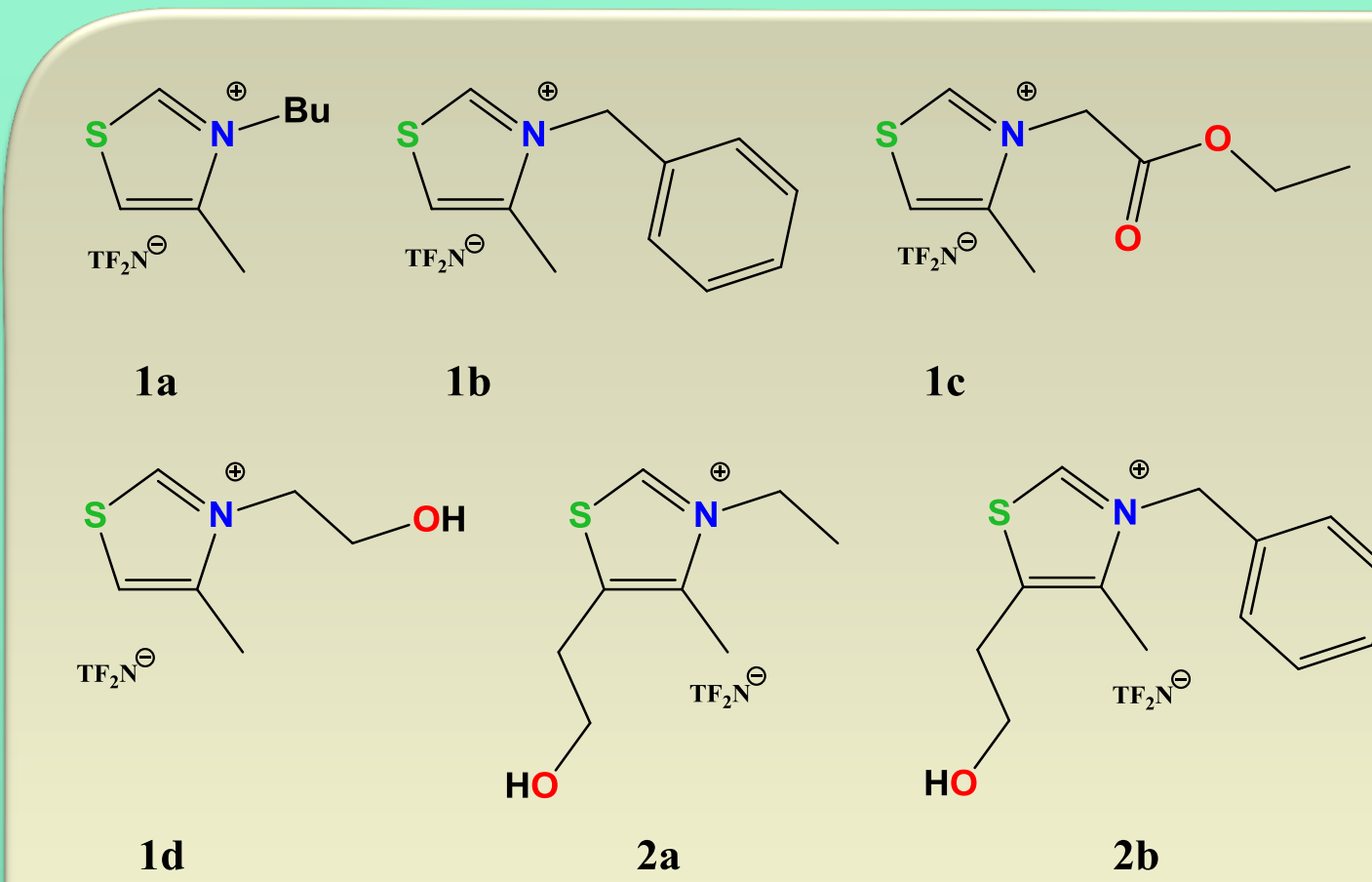


As can be seen in the absorption graph (left), compounds 1 and 2 showed nearly double the rate at which 1 eq of CO₂ was captured. Bmim[TF₂N] and Im_{2,1}OH[TF₂N] captured 1 eq of CO₂ in approximately 10 minutes, while both compounds 1 and 2 captured over 1 eq of CO₂ in 5 minutes. Maximum capacity for 1 and 2 (2eqs of CO₂) which was achieved in approximately 20 minutes. This slower rate of max absorption, as compared with Bmim[TF₂N] and Im_{2,1}OH[TF₂N], is related to the higher initial viscosity of these compounds.

Another important aspect of post-combustion CO₂ capture systems is their long-term thermal stability. Absorbent material would ideally be thermally regenerated, necessitating thermally stable materials. Long-term thermal experiments were conducted on the four ionic liquids (right). The ionic liquids were held at elevated temperatures for six hour increments. At temperatures > 200° C, Compound 1 displayed higher thermal stability than Bmim[TF₂N] while compound 2 displayed stabilities comparable to Im_{2,1}OH[TF₂N].



Separations Using Ionic Liquids

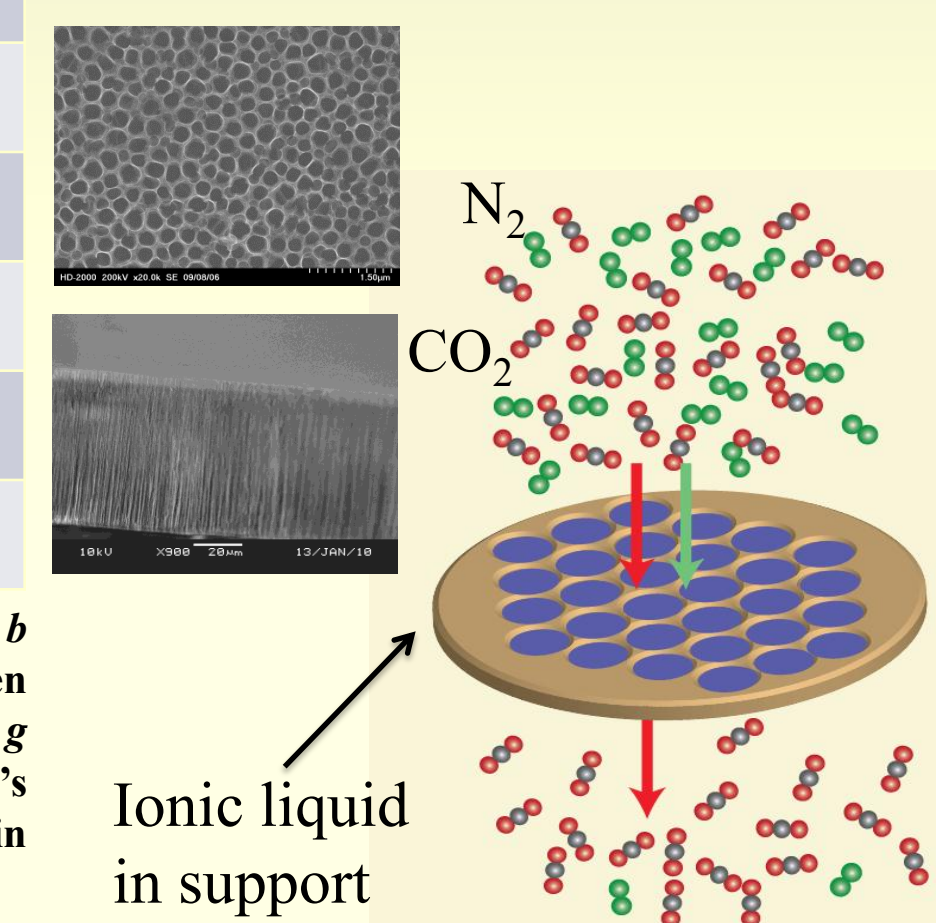


Ionic liquids (ILs) are receiving a great deal of interest in the field of separations of complex mixtures of gases, with much interest in arising from membrane based systems incorporating ILs. These supported ionic liquid membrane (SILM) systems take advantage of the high solubility of sour gases in ILs, allowing for facile separation of mixed gases. There are numerous properties which are thought to affect the both the solubility and permeability of gases in ILs. Herein, we selected to examine a series of thiazolium-based ILs. Various cation structures

with differing N-alkyl/aryl substitutions were evaluated for their viability in SILM systems.

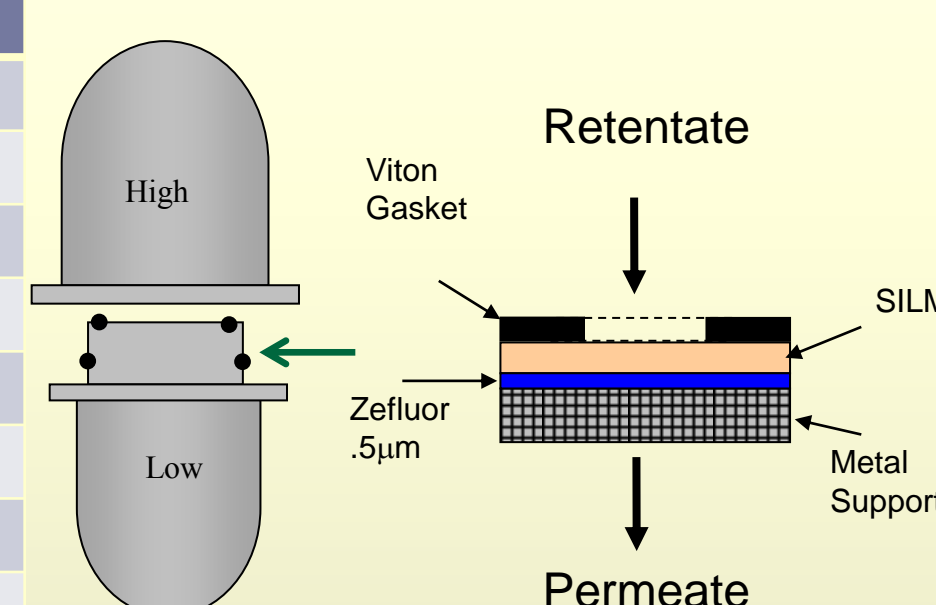
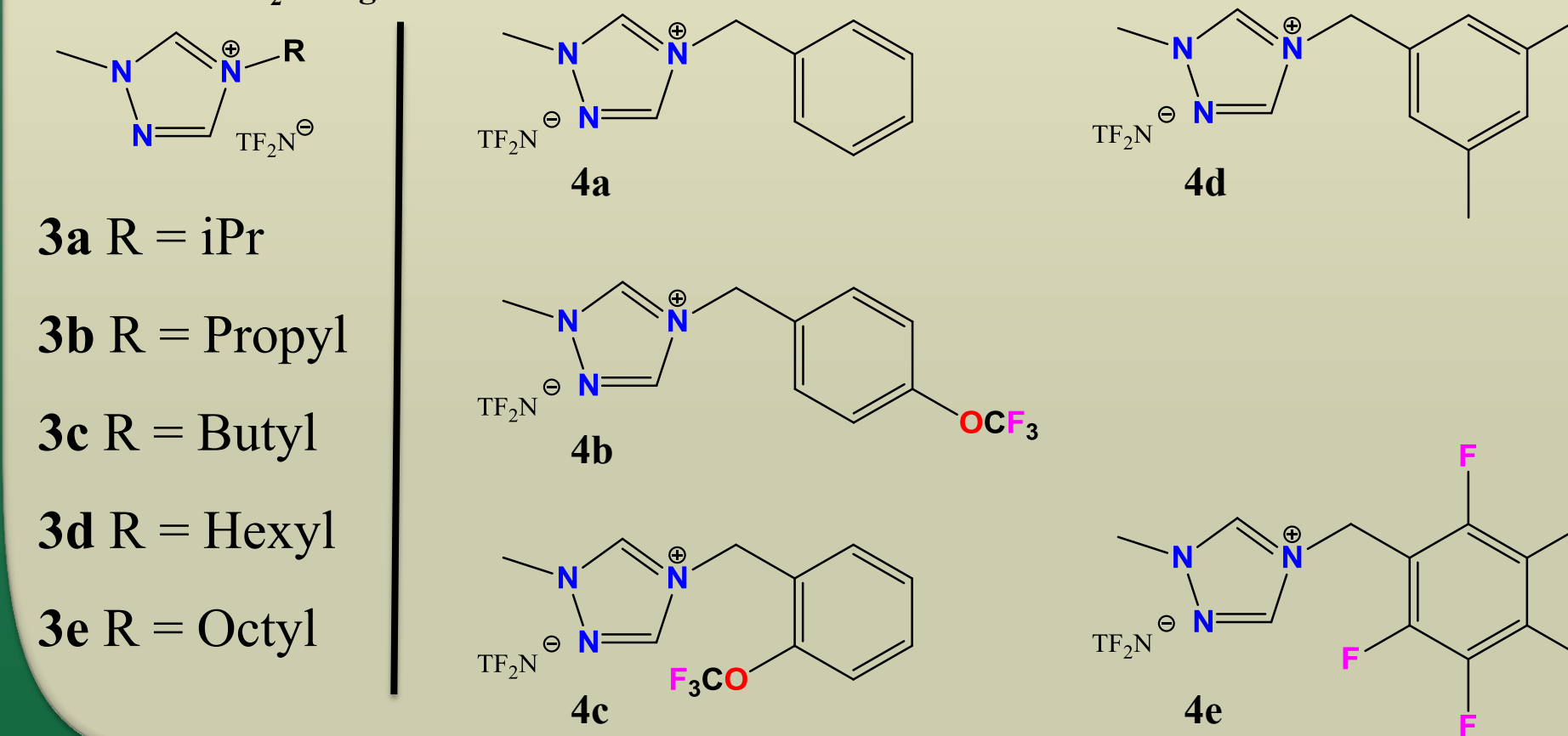
Compound	^b D (g/cm ³)	^c T _g (°C)	^d T _{dec} (°C)	^e η (cP)	^f Perm _{CO2} (barrer)	^g Sel _{CO2/N2}	^h Sol _{CO2} (mol/L·atm)	ⁱ K _{H,px} (atm)
1a	1.505	-68.1	354.5	129 ± 2	362 ± 17	28 ± 4	0.0964	37
1b	1.548	-46.5	271.0	443 ± 5	235 ± 6	21 ± 2	0.0869	41
1c	1.562	-46.9	309.6	613 ± 9	248 ± 5	18 ± 3	0.0986	35
1d	1.626	-64.4	344.8	216 ± 6	284 ± 12	25 ± 2	0.0902	44
2a	1.540	-40.9	364.5	212 ± 3	435 ± 20	36 ± 4	0.0858	40
2b	1.504	-62.8	296.2	1292 ± 10	96 ± 5	12 ± 3	0.0720	45

Physicochemical parameters for the thiazolium based ionic liquids and calculated gas absorption data. ^b - calculated density; ^c - glass transition temperature from DSC; ^d - decomposition temperature taken from the maximum of the first peak on the DTG curves; ^e - viscosity; ^f - carbon dioxide permeability; ^g - CO₂ selectivity calculated from the permeability ratios of CO₂ to N₂; ^h - CO₂ solubility; ⁱ - Henry's Law constant calculated according to $K_{H,px} = p/x$, where p is the pressure and x the mol fraction of CO₂ in a given IL.



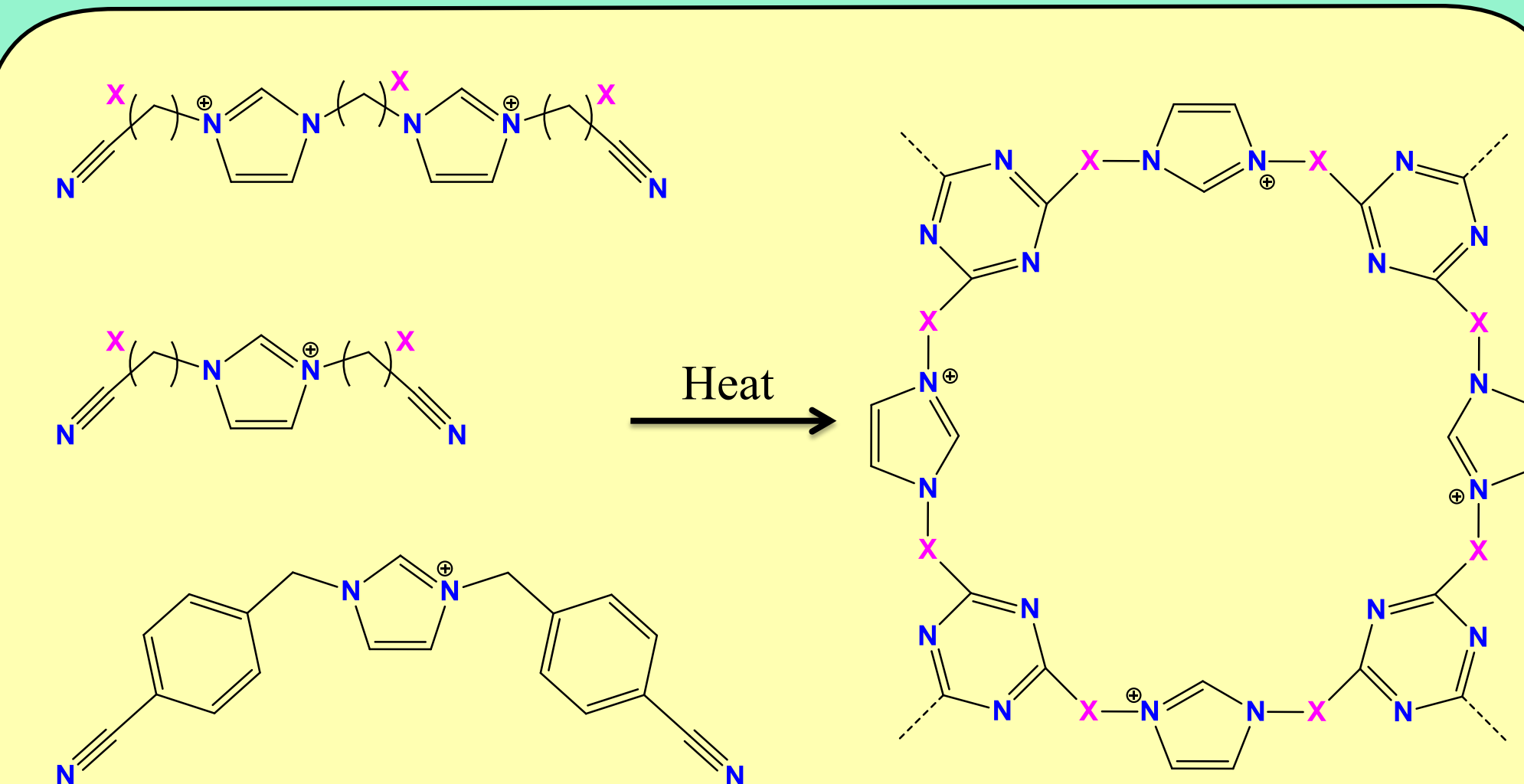
Compound	^a D (g/cm ³)	^b T _g (°C)	^c T _{dec, N2} (°C)	^d η (cP)	^e Perm _{CO2} (barrer)	^f Sel _{CO2/N2}	^g Sol _{CO2} (mol/L·atm)	^h K _{H,px} (atm)
3a	1.484	-68.06	289.71	107 ± 1	641 ± 11	24 ± 2	0.0778	45.0
3b	1.485	-71.11	351.21	102 ± 1	786 ± 14	28 ± 1	0.0813	41.9
3c	1.489	-65.15	342.73	246 ± 3	483 ± 15	22 ± 1	0.0713	45.4
3d	1.372	-70.61	346.83	130 ± 3	804 ± 18	22 ± 1	0.0766	37.8
3e	1.314	-71.24	337.57	154 ± 5	859 ± 9	17 ± 1	0.0755	35.5
4a	1.488	-46.02	271.11	317 ± 10	304 ± 10	21 ± 3	0.0679	44.4
4b	1.590	-44.57	287.53	530 ± 33	407 ± 10	22 ± 1	0.0819	34.1
4c	1.598	-45.70	294.38	573 ± 23	277 ± 11	19 ± 3	0.0689	38.8
4d	1.420	-37.29	253.36	839 ± 34	223 ± 19	19 ± 2	0.0647	43.4
4e	1.626	-34.35	289.51	2048 ± 51	108 ± 7	12 ± 3	0.0492	52.8

Physicochemical parameters for the 1,2,4-triazolium based ionic liquids and calculated gas absorption data. ^a - calculated density; ^b - glass transition temperature from DSC; ^c - decomposition temperature taken from the maximum of the first peak on the DTG curves; ^d - viscosity; ^e - carbon dioxide permeability; ^f - CO₂ selectivity calculated from the permeability ratios of CO₂ to N₂; ^g - CO₂ solubility; ^h - Henry's Law constant calculated according to $K_{H,px} = p/x$, where p is the pressure and x the mol fraction of CO₂ in a given IL.



A series of 1,2,4-triazolium based ILs were analyzed for use in SILM systems. Sequential substitution of N-alkyl and aryl groups allowed for tailoring of physical properties in an effort to maximize the ideal qualities desired for application to separations. Addition of electronegative fluorines and oxygens increase the affinity towards CO₂. Locational substitutions of functional groups affected both selectivity and solubility of CO₂, improving the ILs viability as separation media.

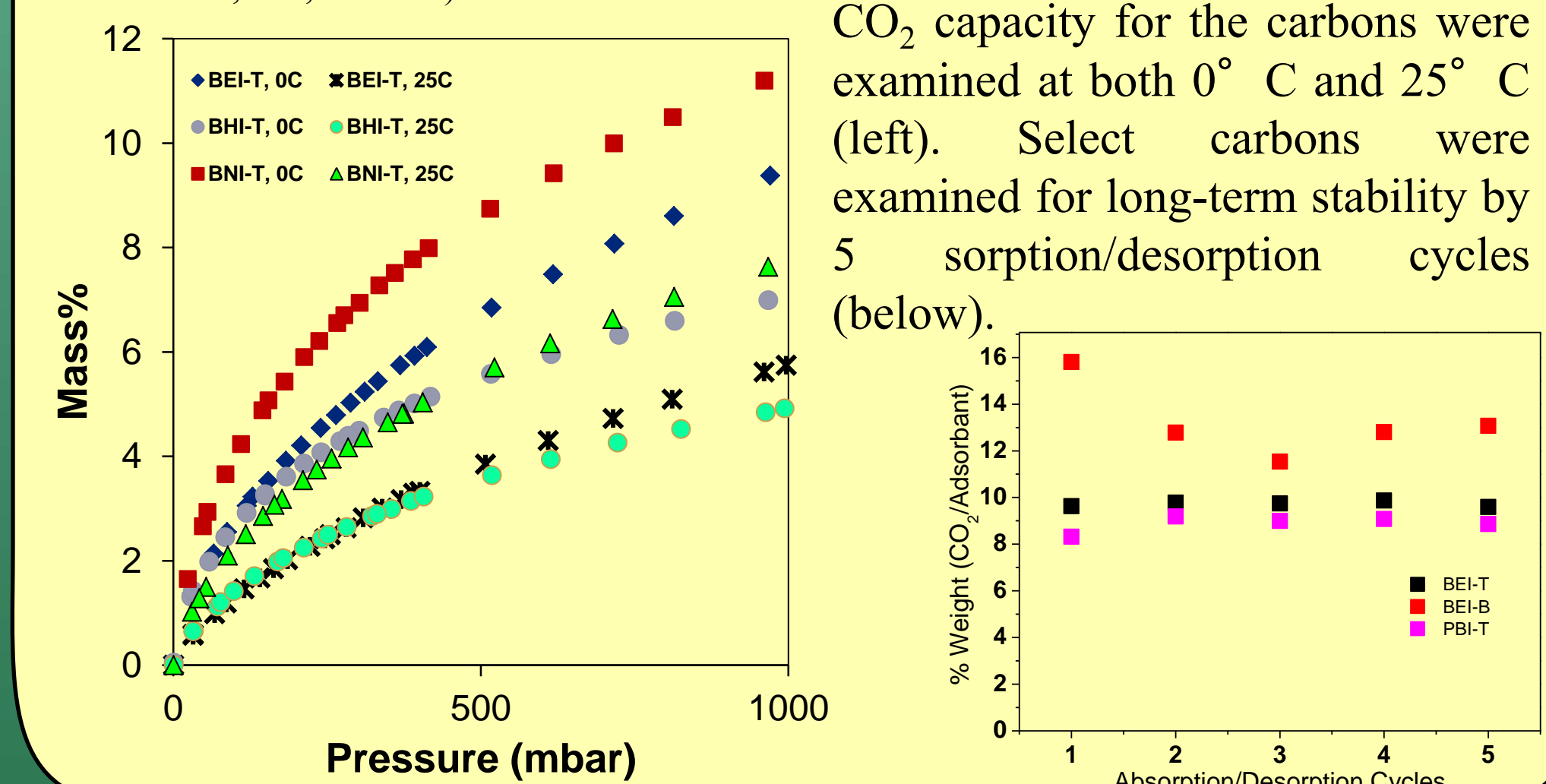
Porous Carbons From Ionic Liquids



A series of ionic liquids bearing nitrile functionalities have been synthesized as starting materials for carbonaceous material for the purpose of reversible CO₂ sequestration. Upon heating of the nitrile-containing ionic liquids, the nitrile groups undergo a cyclization, forming an extended network as depicted above. Through careful design of the ILs, we have been able to tailor the properties of the carbons, allowing for modulation of pore size, structure, and surface area.

Sample	V _{SP} [cm ³ g ⁻¹] (a)	S _{BET} [m ² g ⁻¹] (b)	V _t ^α [cm ³ g ⁻¹] (c)	S _{ext} ^α [m ² g ⁻¹] (d)	V _{mi} ^α [cm ³ g ⁻¹] (e)	S _{mi} ^α [m ² g ⁻¹] (f)
(BEI-T)	0.96	883	0.95	1.74	0.19	457
(BEI-B)	0.86	1013	0.86	3.41	0.32	316
(BHI-T)	0.26	509	0.26	12.8	-	-
(BNI-T)	0.28	500	0.29	14.2	-	-
(PBI-T)	0.35	726	0.35	0.39	-	-

[a] single point pore volume from adsorption isotherms at $p/p_0 \sim 0.98$ [b] specific surface area calculated using the BET equation in the relative pressure range of 0.05-0.20 [c] total pore volume and [d] external surface area calculated in the α_s -plot range of 2.50-9.50 [e] micropore volume and [f] micropore surface area calculated in the α_s -plot range of 0.75-1.00 (*Journal of Colloid and Interface Science* 1997, 192, 250-256)



Acknowledgements

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