

Supplementary Information for

Double Emulsion Microencapsulation of Ionic Liquids for Carbon Capture

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Experimental

Materials

LUDOX® TMA SiO₂ (34 wt% suspension in H₂O), sodium dodecyl sulfate, Span® 85, pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) (>95%), cyclohexane (≥99%), dichloromethane (≥99.5%), and acetone were obtained from MilliporeSigma. Trimethoxy(propyl)silane (98%), bis(triphenylphosphine)iminium trifluoroacetate (PPNTFA) (98%), mesitylene (99%), toluene (≥99.5%), n-pentane (98%), and acetonitrile (>99%) were obtained from Fischer Scientific. 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) (99%), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) (99%), and 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) (99%) were obtained from Iolitec. Ammonium hydroxide (28-30% solution in H₂O) was obtained from Oakwood Chemical, 2,2-dimethoxy-2-phenylacetophenone (DMPA) (>98%) was obtained from TCI, and dimethyl sulfoxide-d₆ was obtained from Cambridge Isotope. 4-vinyl cyclohexene oxide (VCHO) (98% mixture of isomers) was obtained from Alfa Aesar and dried over CaH₂ under reduced pressure prior to use. Catalyst salen Co(III)TFA was synthesized as previously reported.¹ Solvents for polymer synthesis were dried using the MBraun Manual Solvent purification system packed with Alcoa F200 activated alumina desiccant. All other reagents/solvents were used as received.

Instrumentation

Probe emulsification was completed with a QSonica Q55 Sonicator. Bath sonication was accomplished with a Fisherbrand CPX3800 Ultrasonic Bath 5.7 L. Vortex mixing was done with a Fisherbrand vortex mixer. Centrifugation was completed with a Thermo Scientific Sorvall ST 8 centrifuge. Fourier transform infrared spectroscopy (FTIR) was collected in ATR (bulk ILs, microcapsules, hollow shells) or transmission mode (silica particles). For ATR mode, a JASCO FT/IR-4600 with a ZnSe/diamond prism was used with 64 scans per sample. For transmission mode, a Thermo Nicolet 6700 FTIR equipped with a liquid-nitrogen-cooled MCT A (HgCdTe) detector was used with 64 scans per sample at a resolution of 1 cm⁻¹. Approximately 5 mg of sample was added to 100 mg of KBr in a mortar, ground into a uniform powder with a pestle, then pressed into a pellet using a Specac 15 Ton Hydraulic KBr Press. Nuclear magnetic resonance (¹H NMR) spectroscopy was carried out using a Bruker Avance NEO 400 MHz NMR spectrometer. Thermogravimetric analysis (TGA) was carried out under N₂ using a TA Instruments TGA 5500. The procedure used for all bulk IL, microcapsule, and hollow shell experiments was as follows: ramp 20 °C/min to 100 °C, isothermal 5 min, ramp 20 °C/min to 600 °C. The procedure used for all silica particle experiments was as follows: ramp 20 °C/min to 900 °C. Size exclusion chromatography (SEC) was performed with a Tosoh HLC-8320 GPC using a refractive index (RI) detector and equipped with TSKgel Super HZ-M columns; THF was used as the mobile phase (50 °C, 0.1 mL/min flow rate, 2.0 mg/mL concentration). Microcapsule size analysis was completed

on a Horiba Partica LA-960 particle sizer: a small sample (<50 mg) was dispersed in methanol via sonication for 5 min and analysis was accomplished via laser diffraction while the sample was under magnetic stirring. Optical microscopy images were taken using an AmScope 150C-2L microscope equipped with an 18 MP USB 3.0 camera. To prepare emulsions for imaging, one drop of emulsion sample was placed on a glass slide and diluted with one drop of continuous phase. Scanning electron microscopy (SEM) images were taken using a Tescan Vega 3 SEM with an accelerating voltage of 20.0 kV. SEM samples were sputter coated with 10 nm of Au prior to imaging. EDS analysis was performed on the same instrument with an Oxford Instruments EDS system.

UV Photoreactor

All microcapsule preparation experiments were completed using a UV photoreactor. A 500 cm strip of 12 volt black LEDs purchased from YAYIT (model no. YYT-DT06-UV-USA) was wrapped around the inside of a 1000 mL Pyrex beaker with a diameter of 12.2 cm (**Figure S1**). The outside of the beaker was wrapped in aluminum foil.

Methods

Preparation of SiO₂-C3. LUDOX® TMA colloidal silica was functionalized as reported previously.² Silica suspension (50 mL), ethanol (50 mL), and sodium dodecyl sulfate (50 mg) were charged to a 250 mL round-bottom flask with a large stir bar. Under vigorous stirring, the pH of the mixture was raised from approximately 7.5 to 9.0 via dropwise addition of aqueous ammonium hydroxide. Excess trimethoxy(propyl)silane (0.02 mol) was added dropwise and the dispersion was stirred for 24 h under ambient conditions to overcome any gelation that occurred overnight. The temperature was then increased to 80 °C and the mixture was heated/stirred for approximately 2 h. Modified particles were isolated via centrifugation (4500 rpm, 30 min), washed thrice with acetone, and dried in vacuo overnight.

Synthesis of poly(VCHO). Catalyst salen Co(III)TFA (0.01 mmol), cocatalyst PPNTFA (0.01 mmol), epoxide monomer VCHO (1 mL), toluene (0.2 mL), and DCM (0.2 mL) were added to an oven dried stainless steel reactor in an argon glovebox. The reactor was sealed, pressurized with 2 MPa dry CO₂, and allowed to stir for 72 h at 45 °C. Crude polymer was dissolved in a minimal amount of DCM and precipitated into acidic methanol. This work-up was repeated three times total and the purified polymer was dried under reduced pressure for 24 h.

Single Emulsion Preparation. The primary continuous phase was prepared by dispersing SiO₂-C3 (0.2127 g) in a mixture of toluene (4 mL) and acetonitrile (1 mL) via bath sonication for at least 30 min, yielding a 5 wt% silica suspension. To generate an IL-in-oil emulsion, 1 mL of IL was

added to the 5 mL suspension and the resulting biphasic mixture was emulsified via probe sonication for three cycles of 20 s on, 5 s off at 50% amplitude.

Double Emulsion Preparation. The secondary continuous phase was prepared by mixing Span® 85 (0.5 g), toluene (1.0 g), and cyclohexane (8.5 g) in a 10 dram vial. To generate an [IL-in-oil₁]-in-oil₂ emulsion, single emulsion (3 mL) was gently added to the secondary continuous phase under low shear (600 rpm) via micropipette and stirred for 15 min.

Microcapsule Synthesis. IL-in-oil single emulsion (3 mL) was added to a 1 dram vial containing DMPA photoinitiator (5 mg). Poly(VCHO) (96 mg) dispersed in toluene (1 mL) was added, followed by PETMP crosslinker (200 µL) and the system was vortex mixed for 30 s. This volume was then added to the secondary continuous phase under low shear (600 rpm) to generate the [IL-in-oil₁]-in-oil₂ emulsion, stirred for 15 min, and irradiated in the UV photoreactor under stirring for 20 min. Thiol-ene crosslinking in the interphase of the double emulsion was confirmed by the optical shift of the secondary continuous phase from translucent (pre-irradiation) to opaque (post-irradiation). The reaction vessel was capped with pentane, vortex mixed for 30 s, and IL microcapsules gravity settled at the bottom. The supernatant was decanted and this wash procedure was repeated three additional times with approximately 40 mL of pentane to remove excess surfactant and unreacted components. Isolated microcapsules were dried under reduced pressure for 24 h.

Hollow Shell Preparation. Approximately 100 mg of microcapsules was dispersed in 15 mL of acetone via vortex mixing which dissolved the IL. Shells were isolated via centrifugation (4500 rpm, 15 min) and the procedure was repeated two additional times to ensure complete IL extraction. The product was dried at room temperature in vacuo for 24 h.

Determination of IL Weight Percent of Microcapsules via ¹H NMR. Per a previously reported procedure,³ approximately 20 mg of IL microcapsules was added to a vial containing a 0.050 M solution of mesitylene (internal standard) in DMSO-d₆. The mixture was then sonicated/vortex mixed to extract all IL from the microcapsules. Next, the solution was passed through a poly(tetrafluoroethylene) syringe filter (0.45 µm cutoff) to remove the solid shell and the eluent was analyzed by ¹H NMR spectroscopy. The weight percent contribution from the encapsulated IL was determined by comparing the relative integration of the methyl peak from mesitylene (2.22 ppm) to the methyl peak of the IL cation (3.85 ppm) (**Figure S2**). This procedure was replicated thrice and the average determined.

CO₂ Uptake Measurements. Gravimetric CO₂ uptake and release measurements were performed using the TGA described previously to measure the weight gain/loss during cycling coupled with a TA Blending Gas Delivery Module (GDM) to switch between CO₂ and N₂. The samples were loaded in the TGA pan, enough to cover the surface of the pan (around 15 mg). Ambient pressure

(1 bar) of pure gases was maintained throughout the experiment. The mass flow rate was set to 25 mL/min for both gases and the temperature ramp rate was set to 10 °C/min. Initially, each sample was heated to 65 °C under N₂ for 1 h to remove any volatile components or dissolved CO₂. The samples were then cooled to 30 °C (the ambient temperature of the lab), and the gas switched from pure N₂ to pure CO₂ for 30 min (enough to reach a stable mass). Afterwards, the gas was switched back to N₂ and the temperature was raised to 65 °C again for 10 min, until all the dissolved CO₂ is removed. The procedure was repeated for 3 cycles and maintained constant for all the samples.

CO₂ isotherms of the prepared microcapsules were collected using a Micromeritics TriStar II sorption analyzer in a pressure range of 0–1 bar at a constant temperature of 30 °C, respectively. Approximately 400 mg of sample was used for each analysis. Prior to each measurement, samples were degassed at 65 °C under continuous N₂ flow for 6 h to remove any unwanted gas molecules or dissolved gases. Results were reproducible within an experimental error range of ± 15%.

Table S1. Average IL microcapsule diameter.

Sample	Method	Average Diameter (μm)
[BMIM][BF ₄] Microcapsule	Laser Diffraction	15.0 ± 7.3
[BMIM][PF ₆] Microcapsule		31.2 ± 13.0
[EMIM][BF ₄] Microcapsule		29.9 ± 24.0

Table S2. Calculation of IL weight percent contribution from the core.

Sample	[BMIM][BF ₄]	[BMIM][PF ₆]	[EMIM][BF ₄]
Microcapsule mass (mg)	21.3	21.2	21.3
Mesitylene amount (M)	0.0505	0.0503	0.0501
Relative integration of methyl peak from mesitylene (2.22 ppm) to methyl peak from IL cation (3.85 ppm)	0.38	0.32	0.44
Calculated content of IL (M)	0.0591	0.0468	0.0662
Calculated mass of IL (mg)	13.4	13.3	13.1
Average percent core (%)	62.0 ± 0.5	62.8 ± 0.6	61.3 ± 0.3

Table S3. Comparative literature results for CO₂ capture using encapsulated ILs.

Reference	Core	Shell	Conditions	CO ₂ Capacity (mol/kg)
Starvaggi et al. (This work)	[BMIM][BF ₄]	Polycarbonate	1 bar, 30 °C	0.053
	[BMIM][PF ₆]	Polycarbonate	1 bar, 30 °C	0.029
	[EMIM][BF ₄]	Polycarbonate	1 bar, 30 °C	0.047
Wang et al. ⁴	[BMIM][PF ₆]	Polystyrene	1 bar, 25 °C	0.45
	[BMIM][PF ₆]	SiO ₂	1 bar, 25 °C	0.61
Huang et al. ⁵	[HMIM][TFSI]	Polyurea	1 bar, 20 °C	0.068
Kaviani et al. ⁶	[EMIM][TFSI]	PVDF-HFP	5 bar, 23 °C	0.465
	[HMIM][TFSI]	PVDF-HFP	5 bar, 23 °C	0.565
Guar et al. ³	[BMIM][PF ₆]	Polyurea	1 bar, 20 °C	0.025-0.065 (different shells)
Bernard et al. ⁷	[EMIM][TFSI]	Polysulfone	1 bar, 25 °C	0.90
	[BMIM][TFSI]	Polysulfone	1 bar, 25 °C	0.84
	[HMIM][TFSI]	Polysulfone	1 bar, 25 °C	0.79
Nisar et al. ⁸	[BMIM][TFSI] + Fe ₂ O ₃	Polysulfone	4 bar, 45 °C	1.3
Santiago et al. ⁹	[BMIM][PRO]	Porous carbon	1 bar, 30 °C	0.705
	[BMIM][MET]	Porous carbon	1 bar, 30 °C	0.455
	[BMIM][GLY]	Porous carbon	1 bar, 30 °C	0.864
Polesso et al. ¹⁰	[EMIM][TFSI]	Polysulfone	4.3 bar, 45 °C	1.22
Santiago et al. ¹¹	[EMIM][TCN]	Carbon	1 bar, 28 °C	0.086
	[BMIM][TCN]	Carbon	1 bar, 28 °C	0.084
	[BMIM][DCN]	Carbon	1 bar, 28 °C	0.07
	[BMIM][OcSO ₄]	Carbon	1 bar, 28 °C	0.07
Moya et al. ¹²	[BMIM][OAc]	Carbon	1 bar, 30 °C	1.82

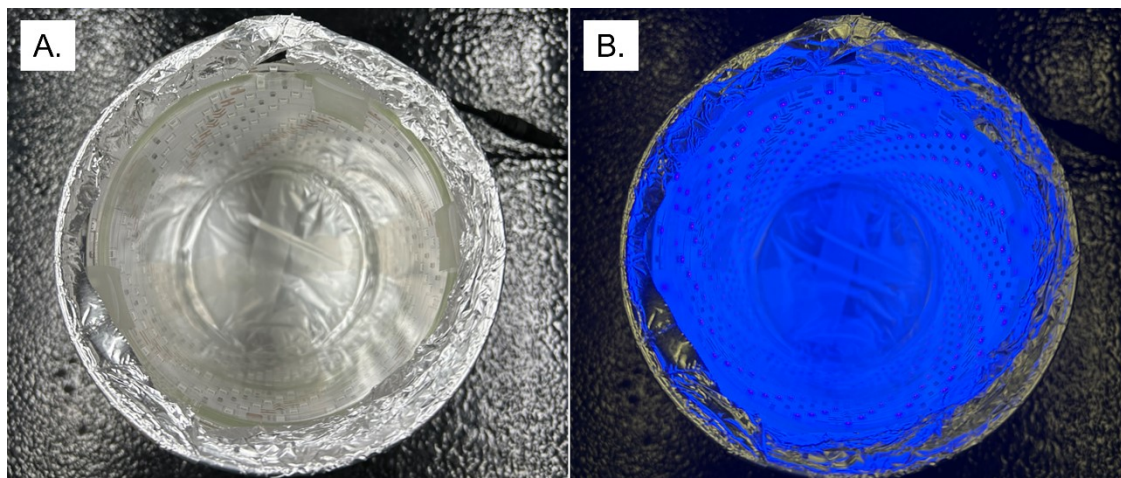


Figure S1. Top view of UV photoreactor with (A) light off and (B) light on.

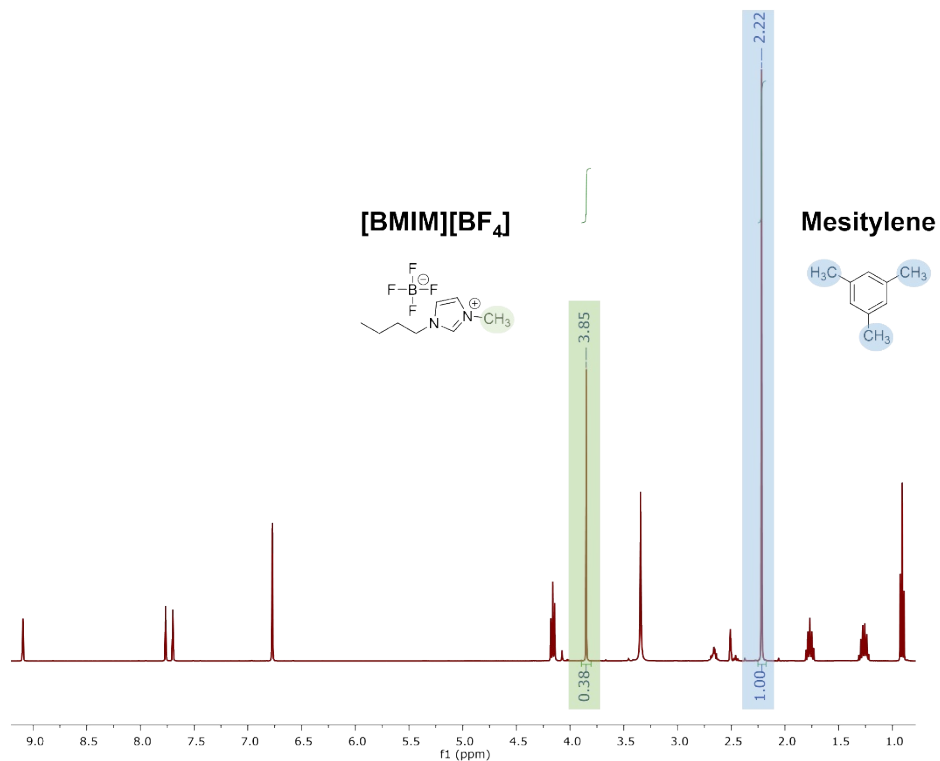


Figure S2. Representative ¹H NMR spectrum of extracted [BMIM][BF₄] in deuterated dimethyl sulfoxide with mesitylene as an internal standard. The relative integration of peaks shaded in green and blue was used to determine weight percent contribution of the core.

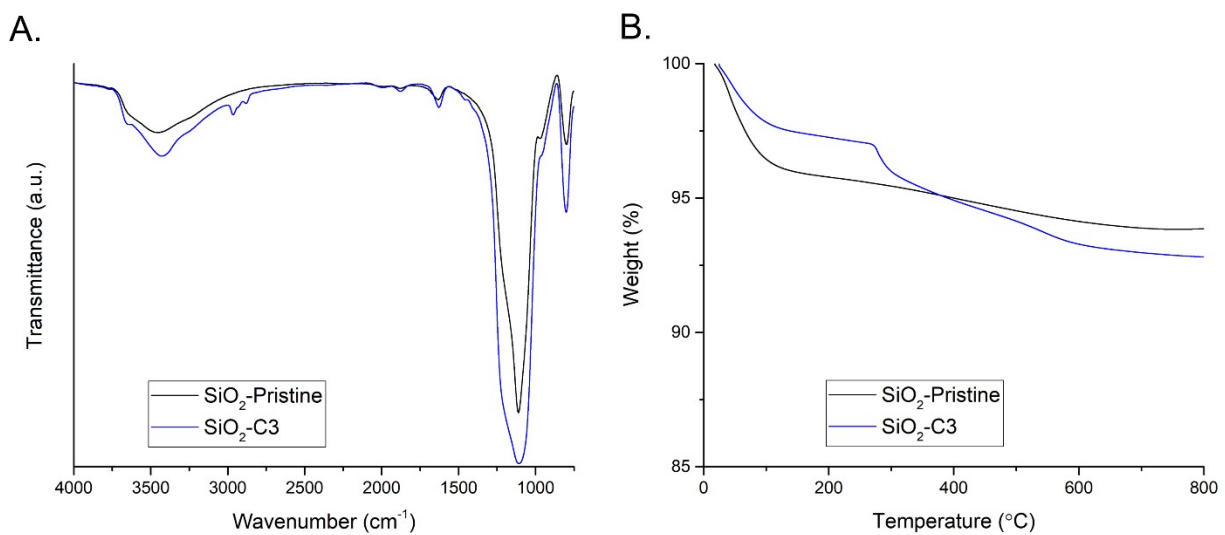


Figure S3. Normalized FTIR spectra (A) and TGA weight loss profiles (B) for SiO₂-Pristine and SiO₂-C3.

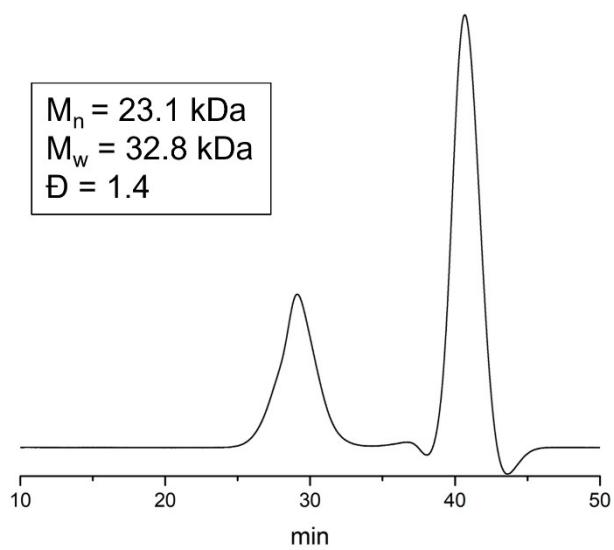


Figure S4. SEC trace of poly(VCHO) utilized for IL microencapsulation.

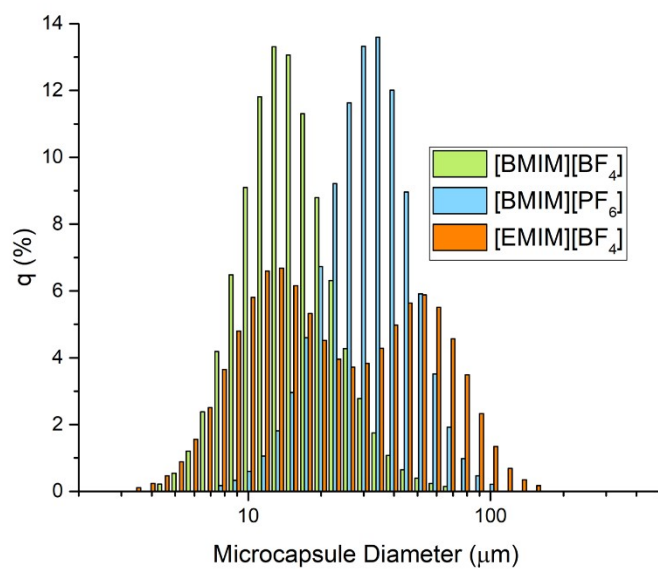


Figure S5. Particle size distribution for [BMIM][BF₄], [BMIM][PF₆], and [EMIM][BF₄] microcapsules.

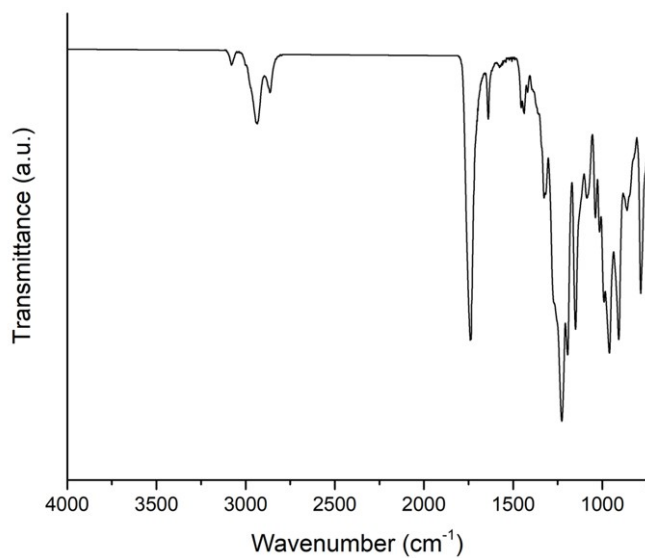


Figure S6. FTIR spectrum of poly(VCHO) utilized for IL microencapsulation.

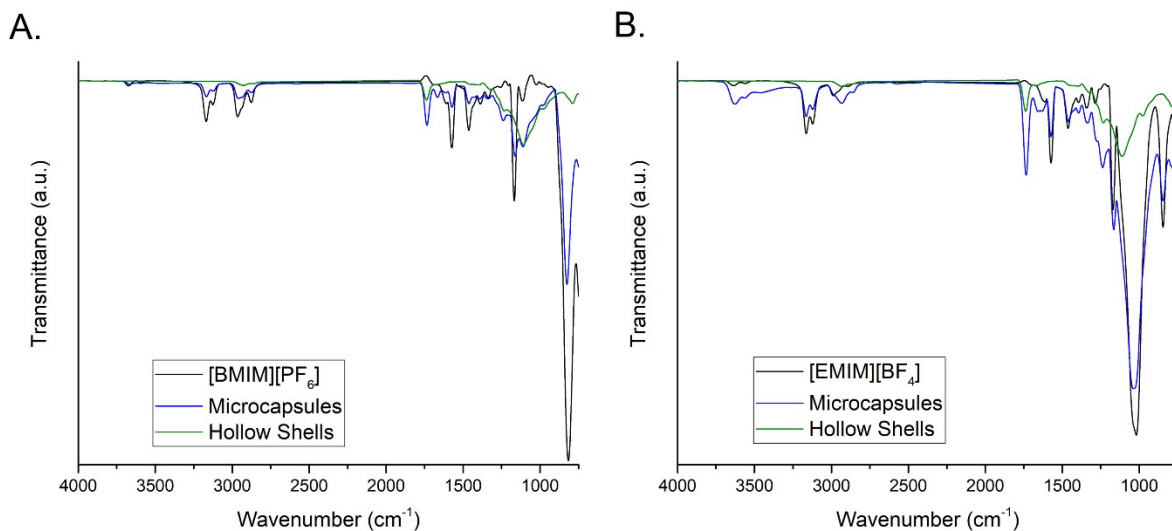


Figure S7. FTIR spectra for (A) bulk [BMIM][PF₆], [BMIM][PF₆] microcapsules, and hollow shells and (B) bulk [EMIM][BF₄], [EMIM][BF₄] microcapsules, and hollow shells.

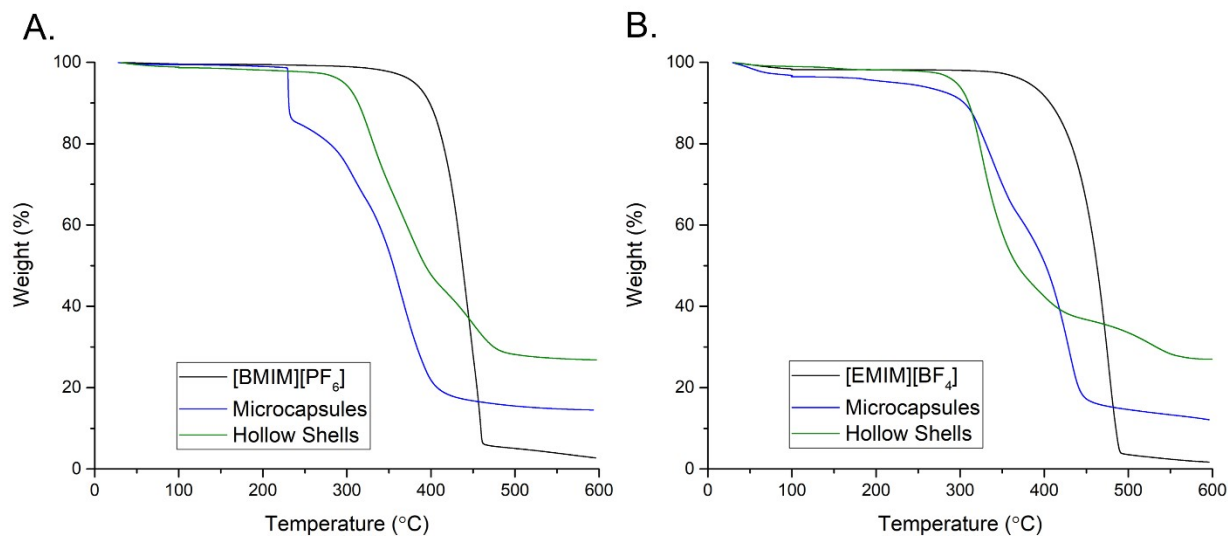


Figure S8. TGA weight loss profiles for (A) bulk [BMIM][PF₆], [BMIM][PF₆] microcapsules, and hollow shells and (B) bulk [EMIM][BF₄], [EMIM][BF₄] microcapsules, and hollow shells.

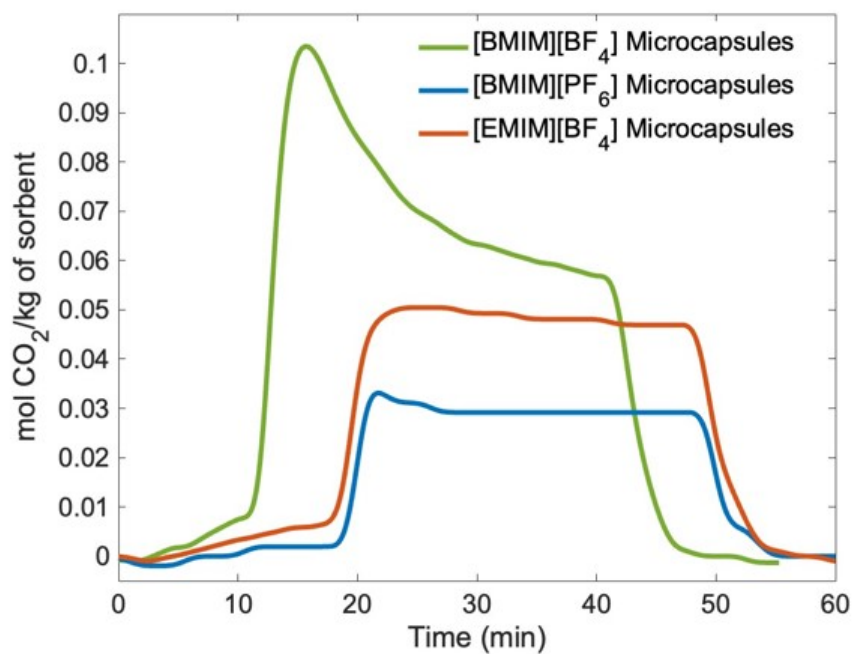


Figure S9. Initial sorption-desorption cycle to condition IL microcapsules prior to gravimetric analysis measurements.

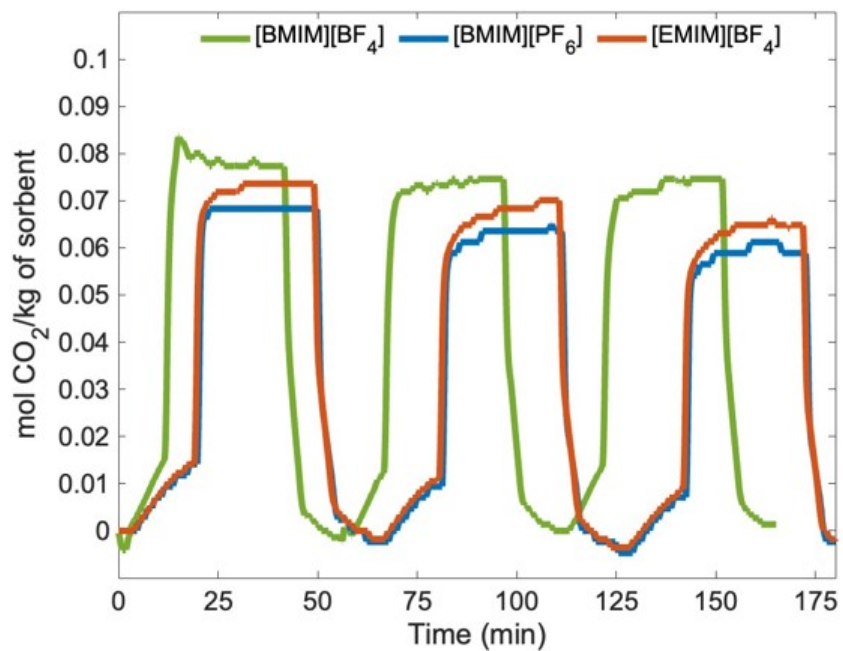


Figure S10. CO₂ uptake capacity for hollow shells of all three IL microcapsules.

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