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Literature review

**Mark Young
Dr Juan José Villora-Picó
Clare Rice
Emma McCrea
Sanskrita Madhukailya**

QUILL meeting 25th -26th March



Gas Separations

How Do Deep Eutectic Solvents Form Porous Liquids?

The Example of Methyltriphenylphosphonium Bromide: Glycerol and ZIF-8

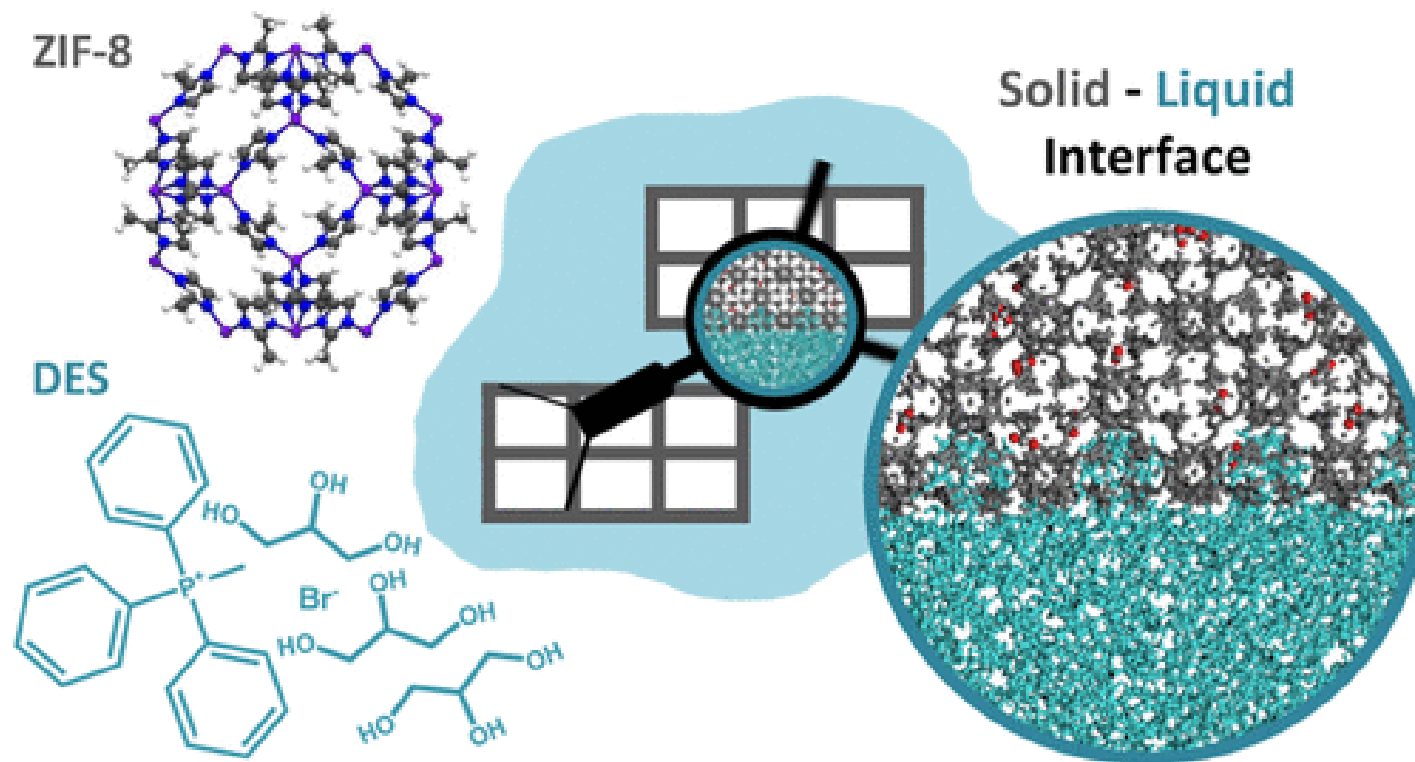


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C. Corsini, C. M. Correa, N. Scaglione, M. Costa Gomes,* Agilio Padua* *J. Phys. Chem. B*, 2024, **128**, 10, 2481–2489

- Porous liquids formed from dispersions of solids in liquids
- Generally formed from sterically hindered liquids and ionic liquids
- Glycerol “should” penetrate the pores but does not



Porous Ionic Liquids Go Green

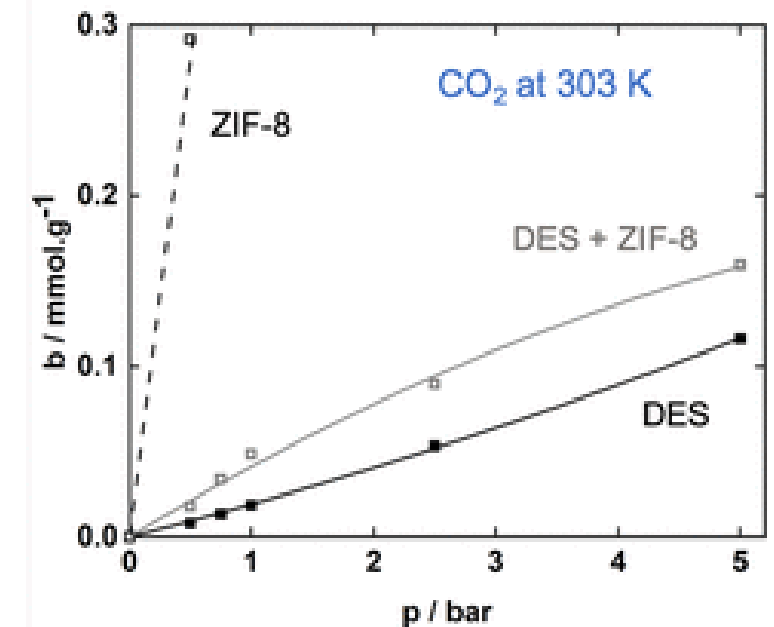
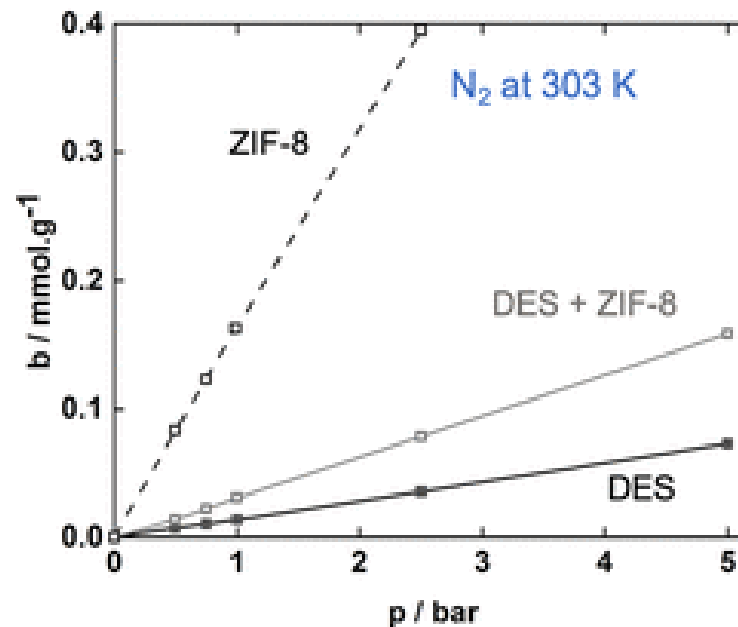
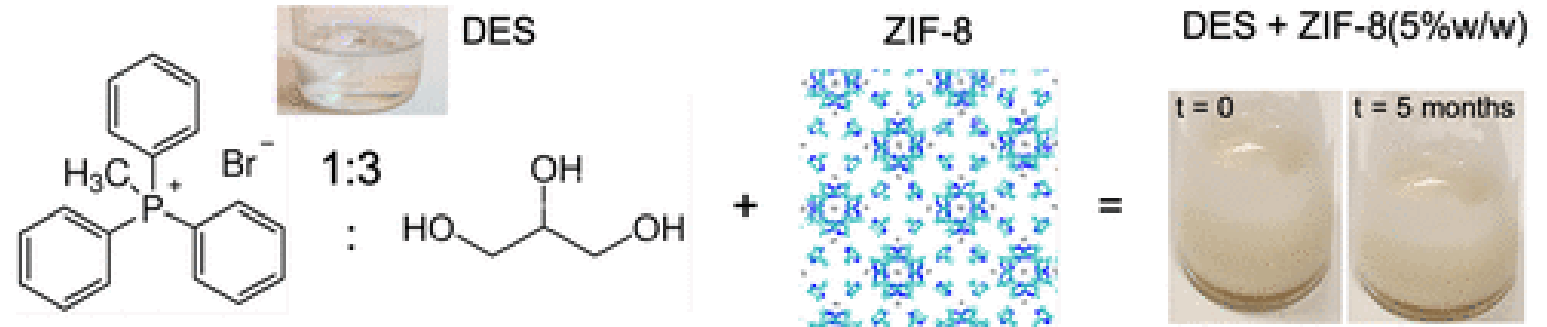


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J. Avila, C. Corsini, C. M. Correa, M. Rosenthal, A. Padua, and M. Costa Gomes* *ACS Nano*, 2023, **17**, 20, 19508–19513

- Stable dispersions of ZIF-8 formed
- Increased CO₂ and N₂ capacity of PL
- Various other application including electrochemistry and biocompatibility



Solvation Environments in Porous Ionic Liquids

Determine Selectivity in CO₂ Conversion to Cyclic Carbonates

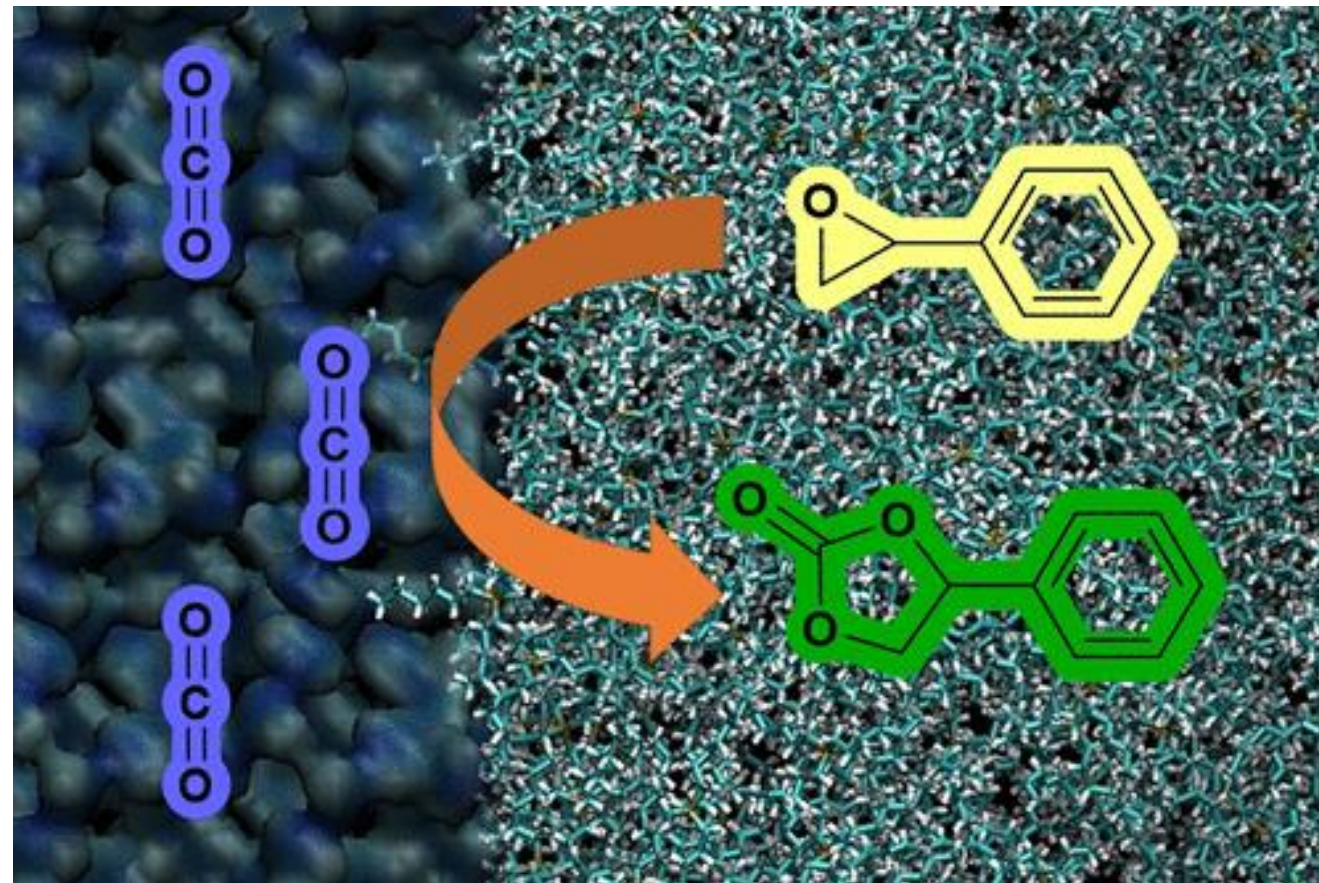


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R. Clark J. Ávila M. Costa Gomes, A. A. H. Padua,* *J. Phys. Chem. B*, 2023, **127**, 14, 3266–3277

- Uses MOF as a gas reservoir ensuring good CO₂ supply too reaction
- Concept can be applied to many reactions using gas as a reagent
- ZIF-8 increases selectivity and catalyses reaction
- Has large applicability on a large scale



Low-Temperature Molten Salt Electrochemical CO₂ Upcycling for Advanced Energy Materials

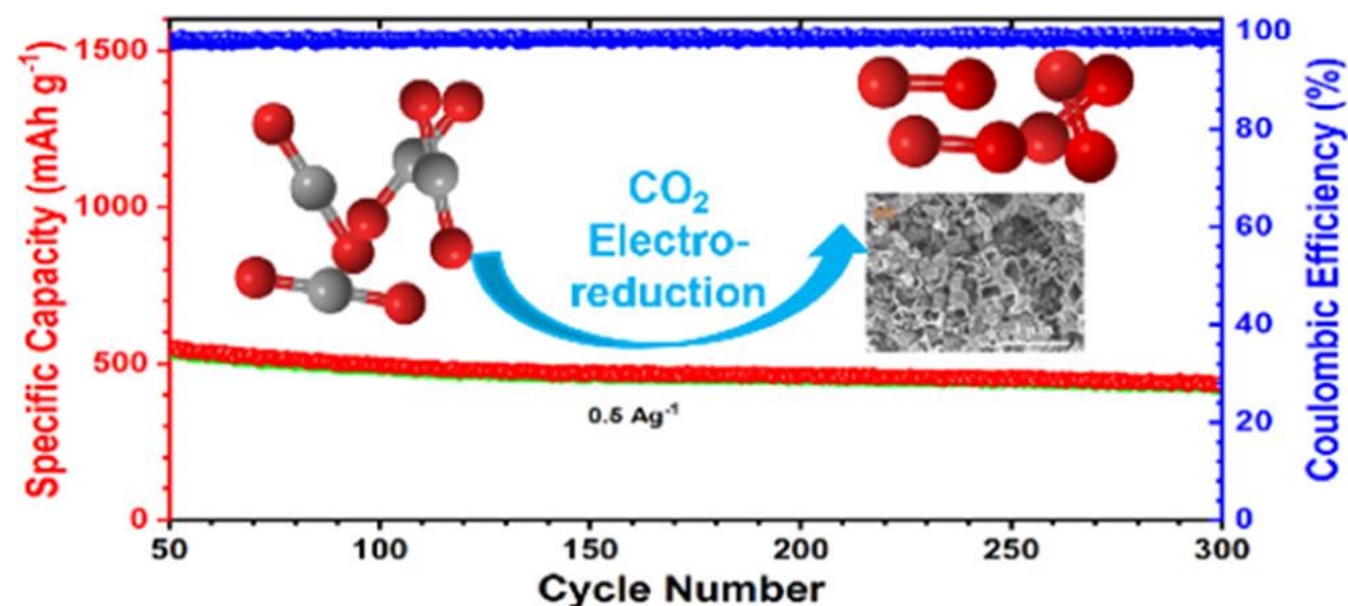


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B. P. Thapaliya*, A. S. Ivanov, H. Chao, M. Lamm, H. M. Meyer III, M. Chi, X. Sun, T. Aytug, S. Dai*, S. M. Mahurin*
ACS Appl. Mater. Interfaces 2024, **16**, 2, 2251–2262

- Reduction of CO₂ to porous carbon
- Li₂CO₃–Na₂CO₃–K₂CO₃ eutectic mixture
- Uses molten salts at temperature as low as 450°C
- High coulombic efficiency



Low-Temperature Molten Salt Electrochemical CO₂ Upcycling for Advanced Energy Materials

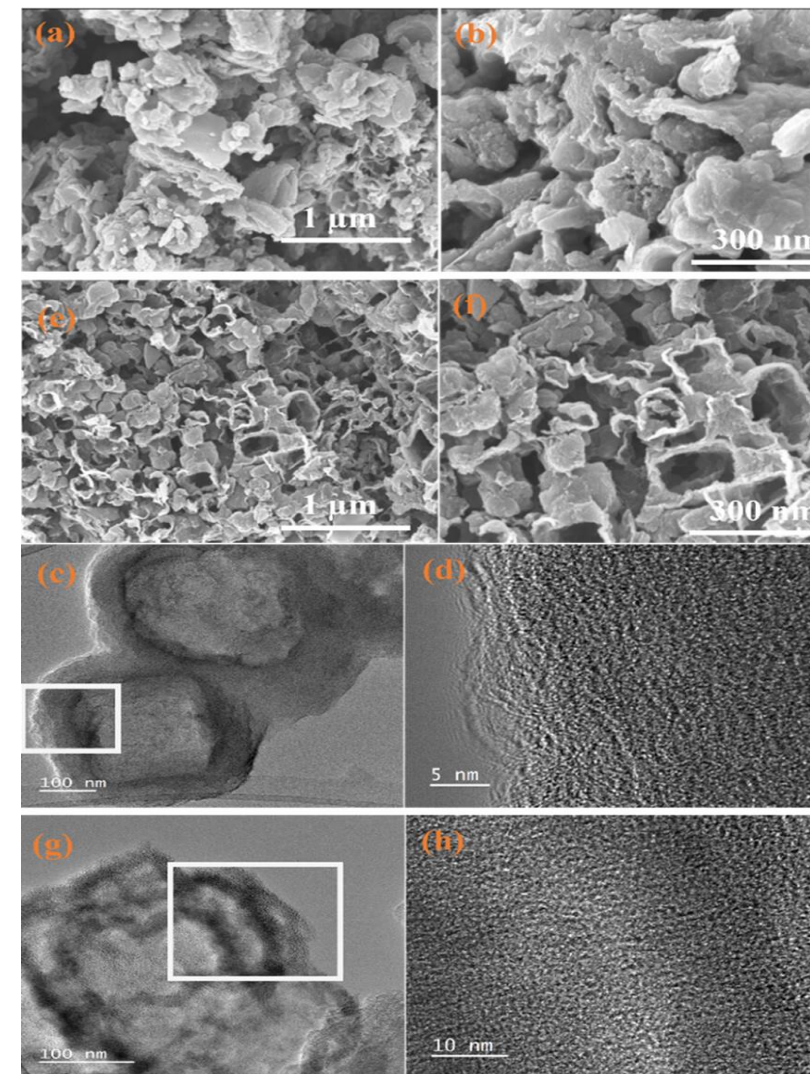


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ACS Appl. Mater. Interfaces 2024, **16**, 2, 2251–2262

- Synthesised carbons have various architectures
- High BET surface areas up to 608 m²/g
- Both amorphous and crystalline regions for Li⁺ intercalation
- Carbons had tuneable electrochemical properties



High-Performance CO₂ Capture from Air by Harnessing the Power of CaO- and Superbase-Ionic-Liquid-Engineered Sorbents

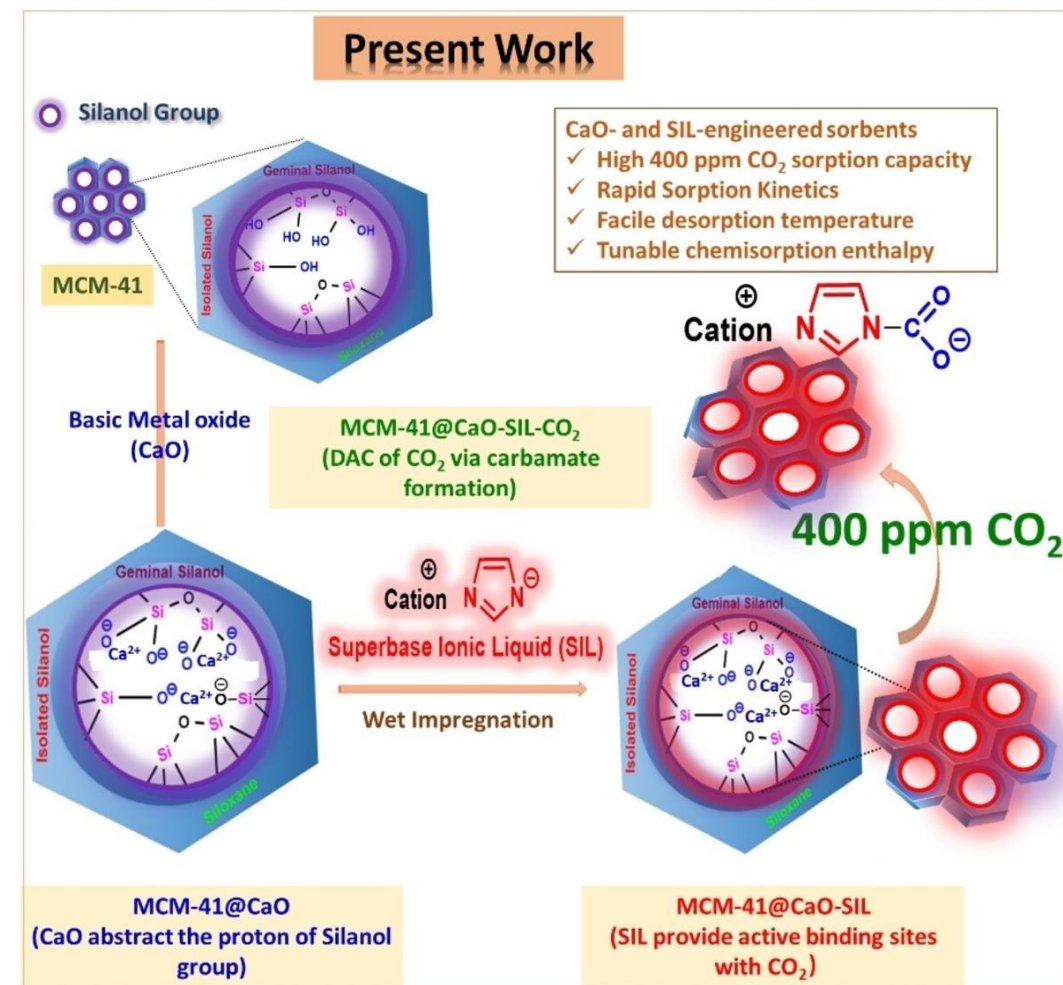


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D. Moitra, N. Mokhtari-Nori, K. M. Siniard, L. Qiu, J. Fan, Z. Dong, W. Hu, H. Liu, De-en Jiang, H. Lin, J. Hu, M. Li, Z. Yang, S. Dai, *ChemSusChem*, 2023, **16**, e2023008

- Hybrid material for direct air capture
- High surface area and fast reaction kinetics
- Can strip CO₂ at low P_{CO₂} (400 ppm)
- Reactive imidazole IL used for chemical sorption



High-Performance CO₂ Capture from Air by Harnessing the Power of CaO- and Superbase-Ionic-Liquid-Engineered Sorbents

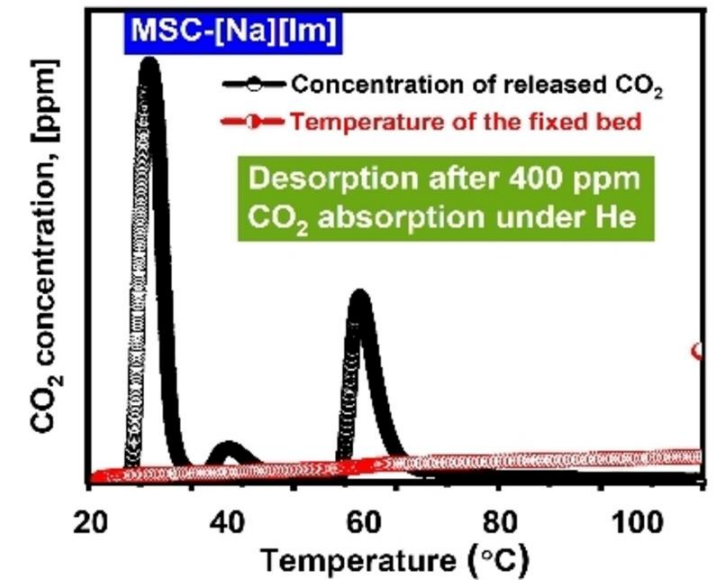
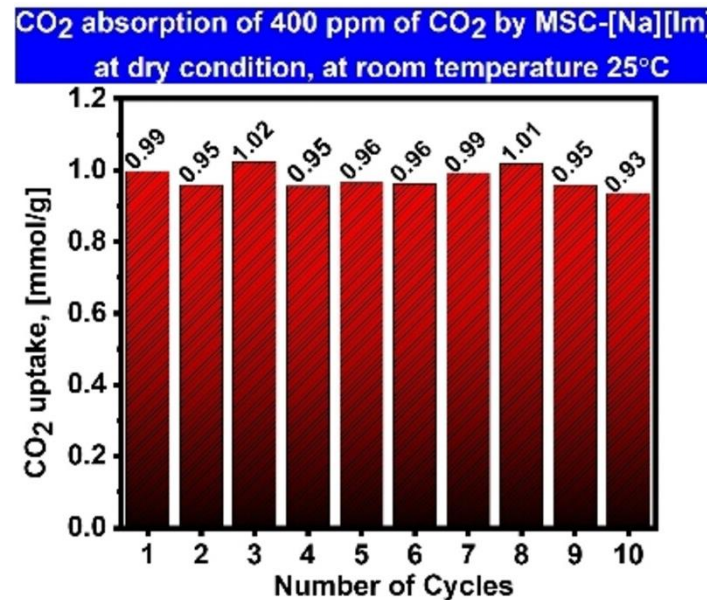
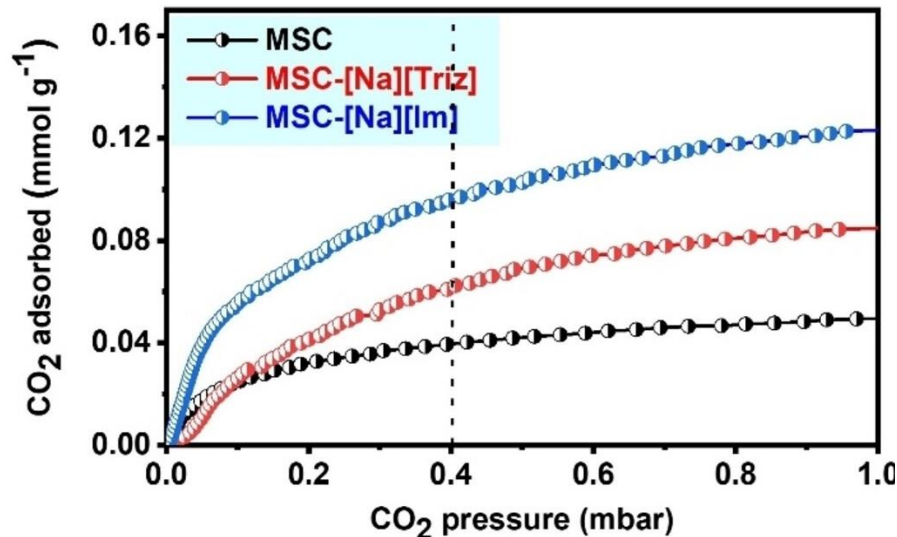


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- Low temperature complete regeneration (70 °C)
- 3 step desorption (Adsorbed, CaO, Imidazolate)
- Gas sorption is more than doubled by addition of IL in MSC



Surpassing the Performance of Phenolate-derived Ionic Liquids in CO₂ Chemisorption by Harnessing the Robust Nature of Pyrazolonates

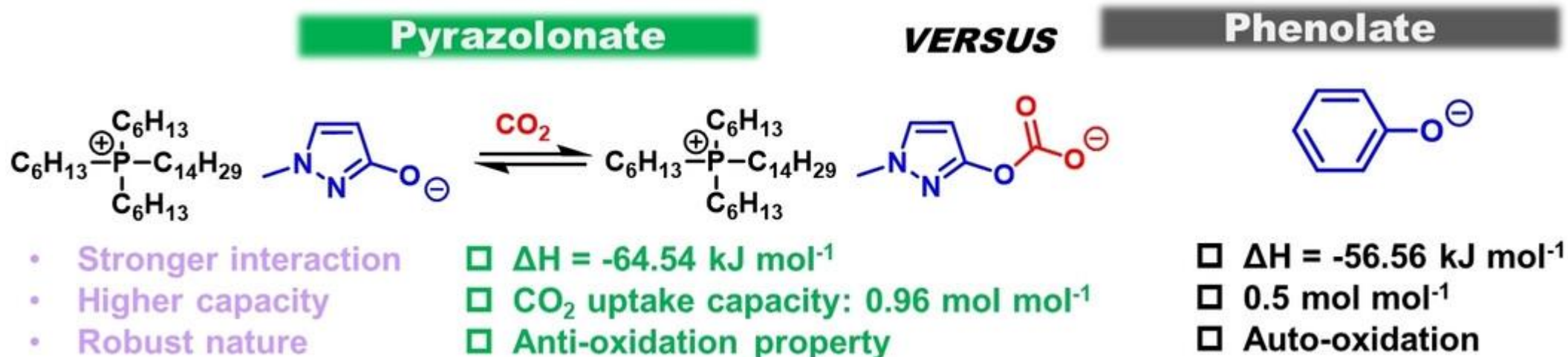


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L. Qiu, Y. Fu, Z. Yang, A. C. Johnson, C. Do-Thanh, B. P. Thapaliya, S. M. Mahurin, L. He, De-en Jiang, S. Dai
ChemSusChem, 2023, e202301329

- New chemical sorption system for CO₂ capture
- Pyrazanolate replaces phenolate as anion
- Higher mole fraction uptake capacity
- No auto oxidation to quinones (problem with phenolate) or Ylide formation



Surpassing the Performance of Phenolate-derived Ionic Liquids in CO₂ Chemisorption by Harnessing the Robust Nature of Pyrazolonates



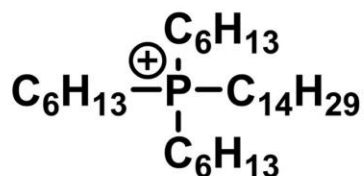
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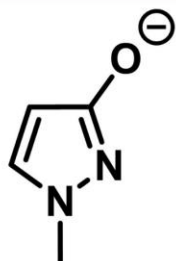
- Capacity greatly influenced by anion structure
- Can be fully regenerated over 10 times (60 °C)
- More negative ΔG for pyrazolate than phenolate

Cation

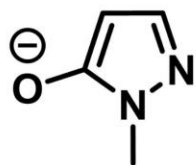


[P₆₆₆₁₄]

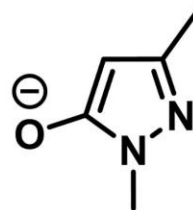
Anion



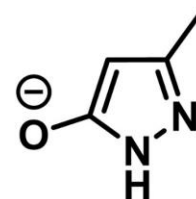
[3-HMPz]



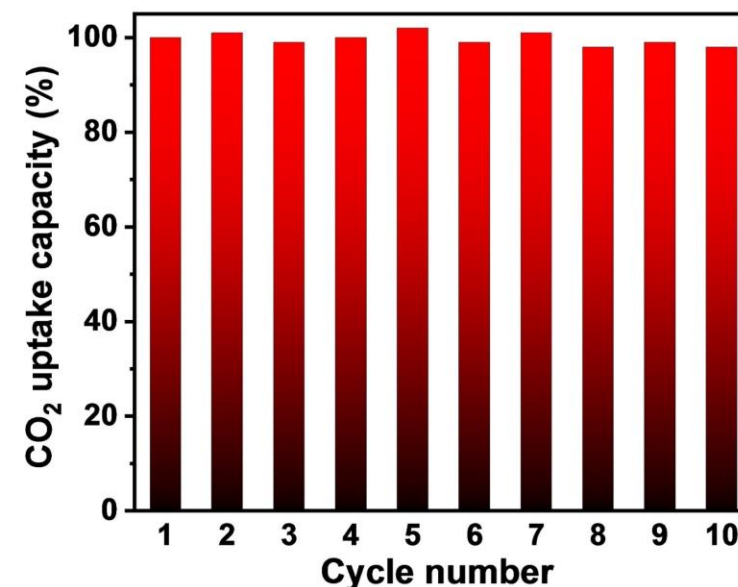
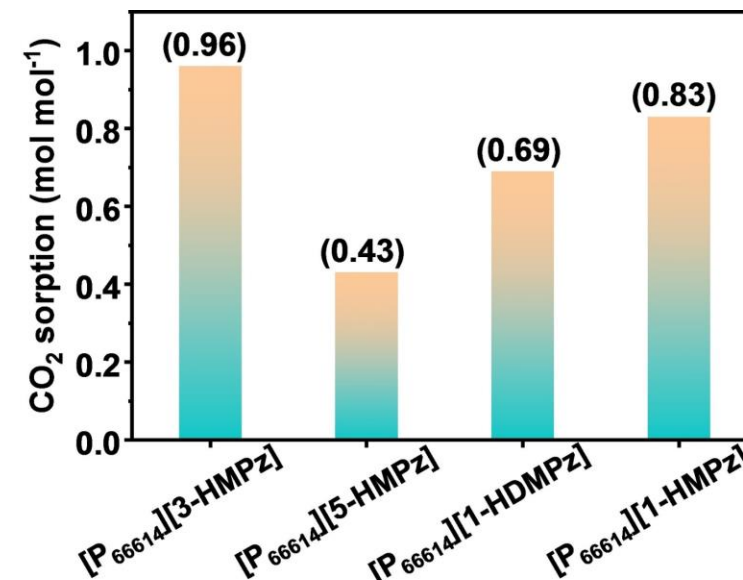
[5-HMPz]



[1-HDMPz]



[1-HMPz]



Exploring the Effect of Different Anions and Cations on the Solubility of CO₂ in Nitrile Imidazolium-Based Ionic Liquids with Sulfonated-Based Anions

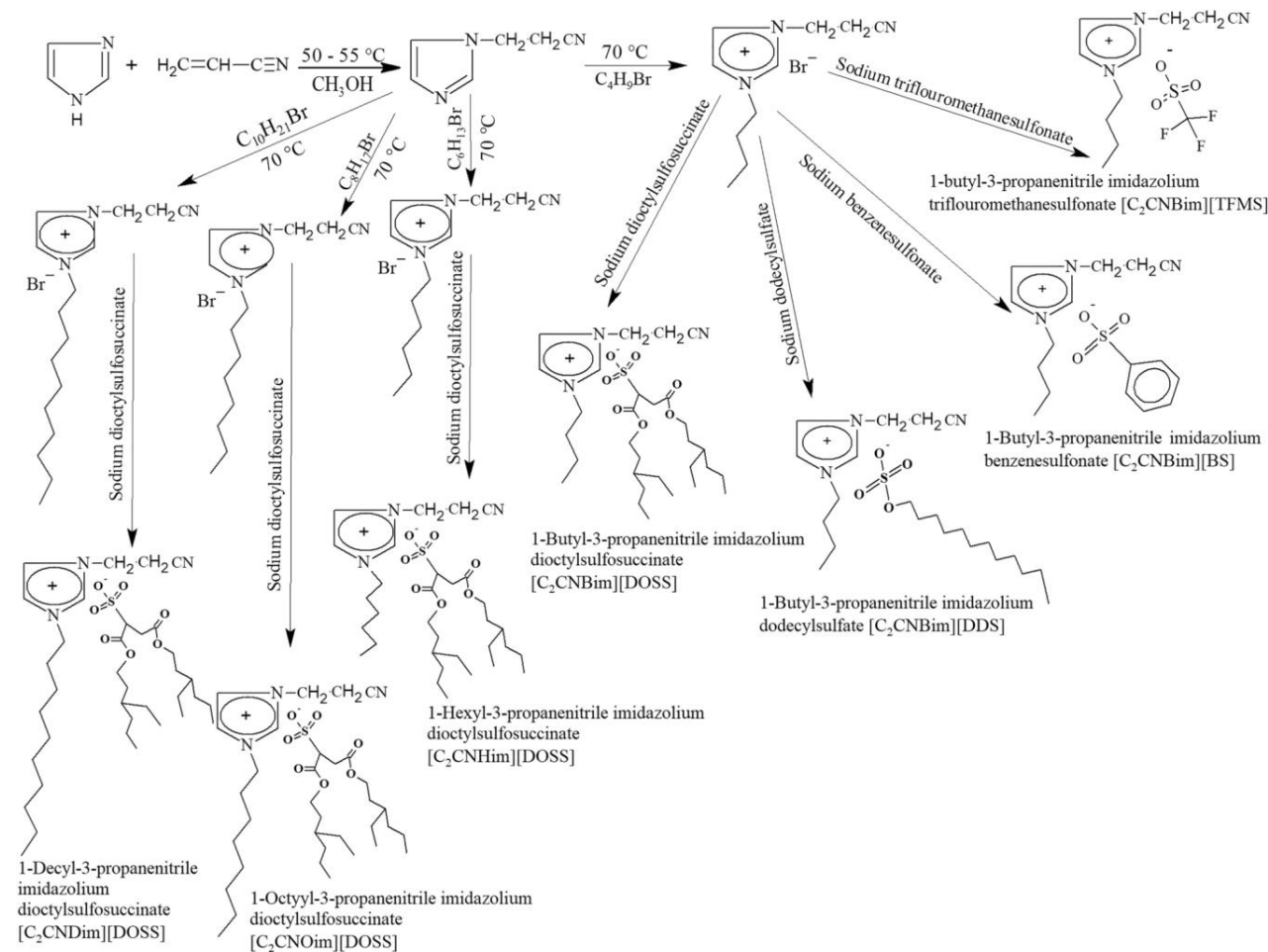


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A. K. Ziyada, A. Osman, A. A. Elbashir, A. M. Khan, C. D. Wilfred, *J. Chem. Eng.* 2024

- Systematically studied structure relation to CO₂ capacity
- Experiments carried out using gravimetric apparatus
- Temperature effects on CO₂ solubility studied between 298-358 K



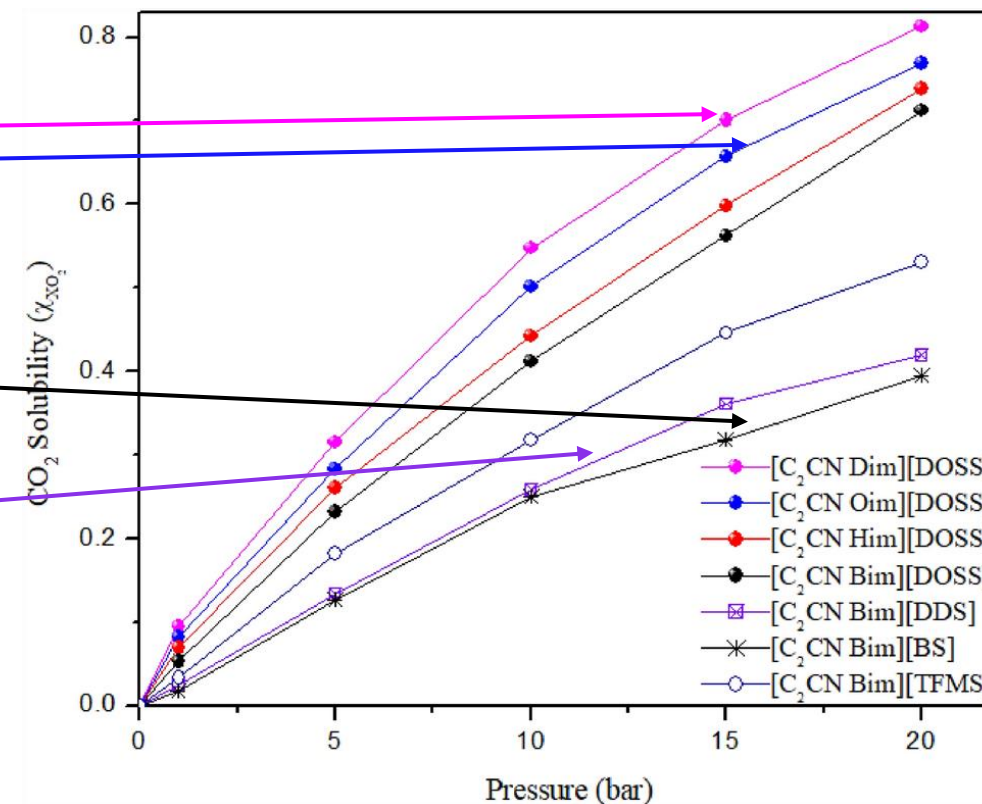
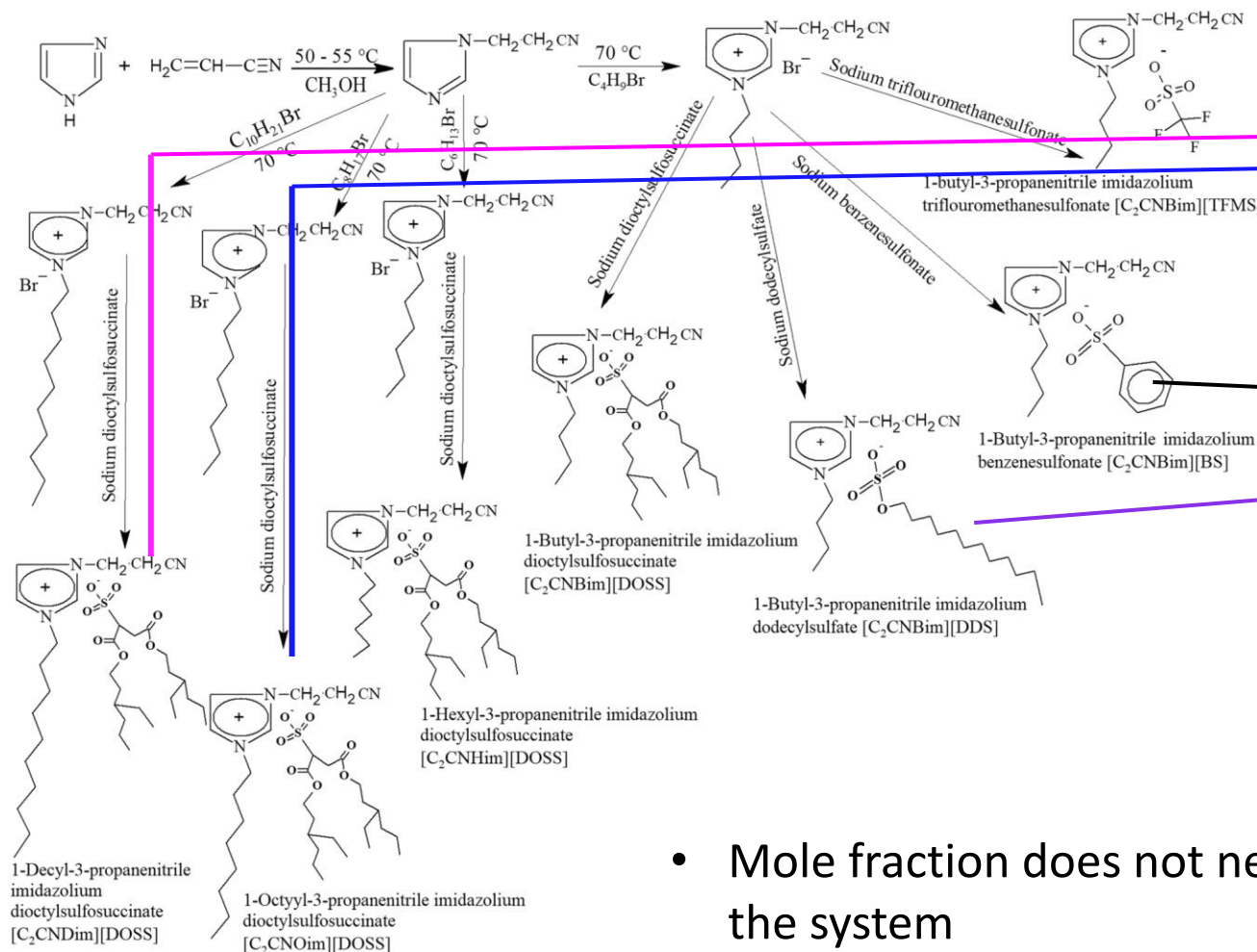
Exploring the Effect of Different Anions and Cations on the Solubility of CO₂ in Nitrile Imidazolium-Based Ionic Liquids with Sulfonated-Based Anions



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A. K. Ziyada, A. Osman, A. A. Elbashir, A. M. Khan, C. D. Wilfred, *J. Chem. Eng.* 2024



- Mole fraction does not necessarily equate to performance of the system



Heterogeneous Catalysis

One-pot synthesis of cyclic carbonates from olefins and CO₂ catalyzed by silica-supported imidazolium hydrogen carbonate ionic liquids

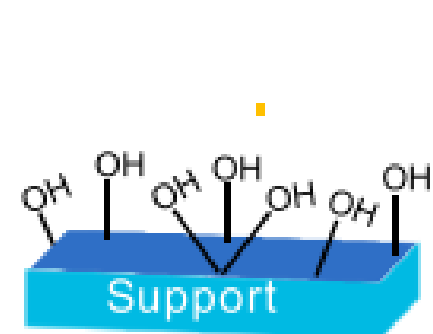


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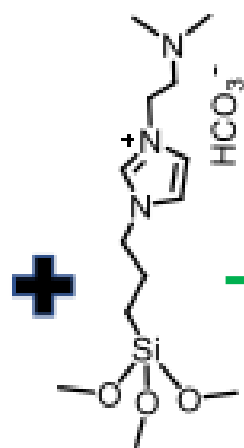
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Zhao, T.; Long, G.; Liang, H.; Xiong, W.; Hu, X. *Microporous and Mesoporous Materials*, 2023, **356**, 112576

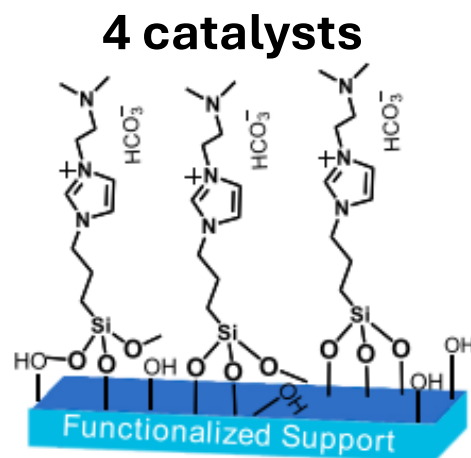
Catalytic results



Silica



Ball Milling



[Im][HCO₃]@SBA-15

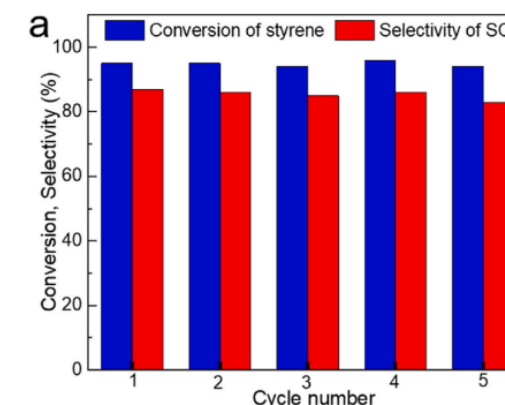
4 catalysts

	Catalyst	Con. (%)	Sel. (%)			Yield of SC (%) ^a
			SC	SO	BA	
1	None	13	0	45	55	0
2	[Im][HCO ₃]@SBA-15	78	72	10	7	56
3	NH ₂ -[Im][HCO ₃]@SBA-15	72	74	12	6	53
4	N(CH ₃) ₂ -[Im][HCO ₃]@SBA-15	80	75	11	10	60
5	N(Et) ₂ -[Im][HCO ₃]@SBA-15	70	76	8	12	53
6 ^b	N(CH ₃) ₂ -[Im][HCO ₃]@SBA-15	50	36	55	9	18
7 ^c	N(CH ₃) ₂ -[Im][HCO ₃]@SBA-15	92	77	6	9	70
8 ^d		9	19	0	0	1.7
9 ^e		99	73	16	11	72
10 ^{c,e}		98	80	6	9	78
11 ^f	N(CH ₃) ₂ -[Im][HCO ₃]@SBA-15	88	78	13	7	69
12 ^g	SBA-15	15	0	3	97	0

100 mg cat.

50 mg cat.
150 mg cat.

H₂O₂
THBP
🏆



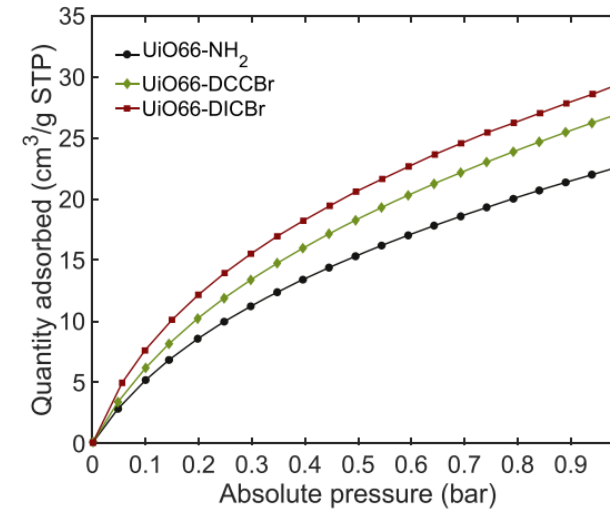
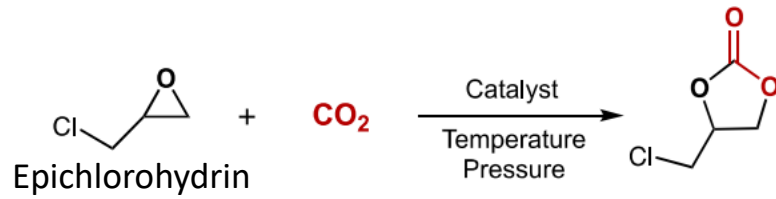
Good recyclability

Post-synthetic modification of Zr-MOFs using guanidine for cyclic carbonate formation catalysis

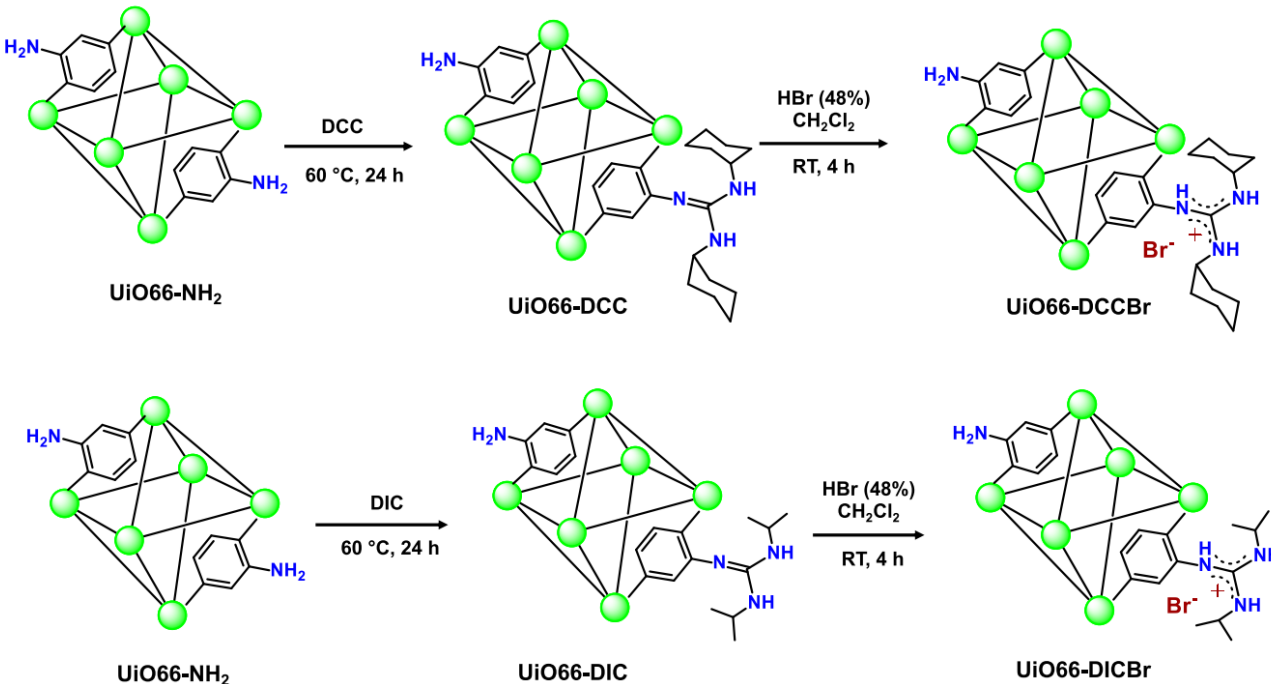


Nataj, S. M. M.; Kaliaguine, S.; Fontaine, F-G. *Catalysis Today*, 2023, **422**, 114216

CO₂ adsorption isotherms 298K



- The grafted materials show better CO₂ adsorption properties



Entry	Catalyst	P (MPa)	T (°C)	time (h)	Yield (%) ^c
1	ZrCl ₄	1.0	100	24	trace
2	UiO66-NH ₂	1.0	100	24	12
3	UiO66-DCC	1.0	100	24	-
4	UiO66-DIC	1.0	100	24	-
5	UiO66-DCCBr	1.0	80	24	76
6	UiO66-DICBr	1.0	80	24	88
7	UiO66-DCCBr	1.0	90	24	96
8	UiO66-DICBr	1.0	90	24	> 99
9	UiO66-DCCBr	0.5	80	24	71
10	UiO66-DICBr	0.5	80	24	75
11	UiO66-DCCBr	0.5	90	16	95
12	UiO66-DICBr	0.5	90	16	> 99

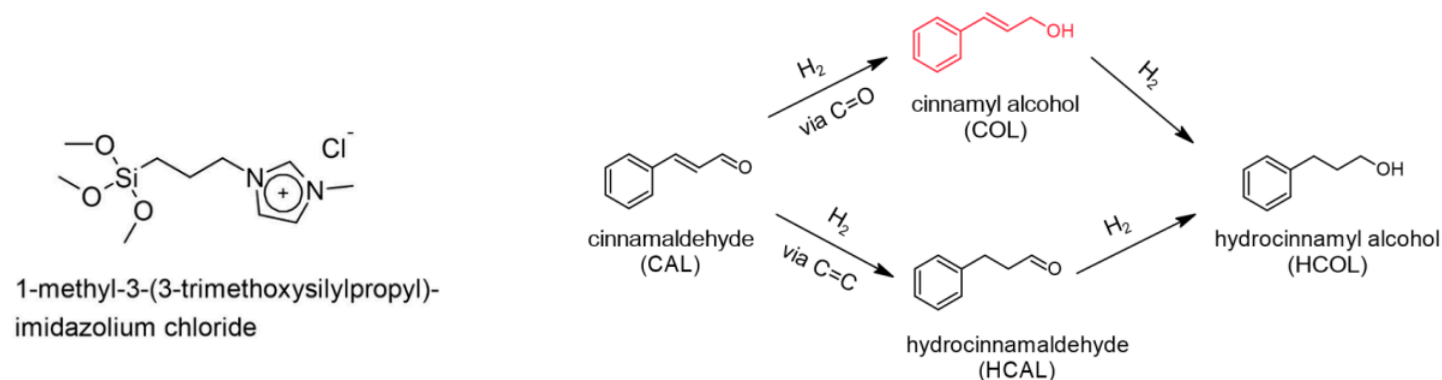
Highly active Pt-Co bimetallic nanoparticles on ionic liquid-modified SBA-15 for solvent-free selective hydrogenation of cinnamaldehyde



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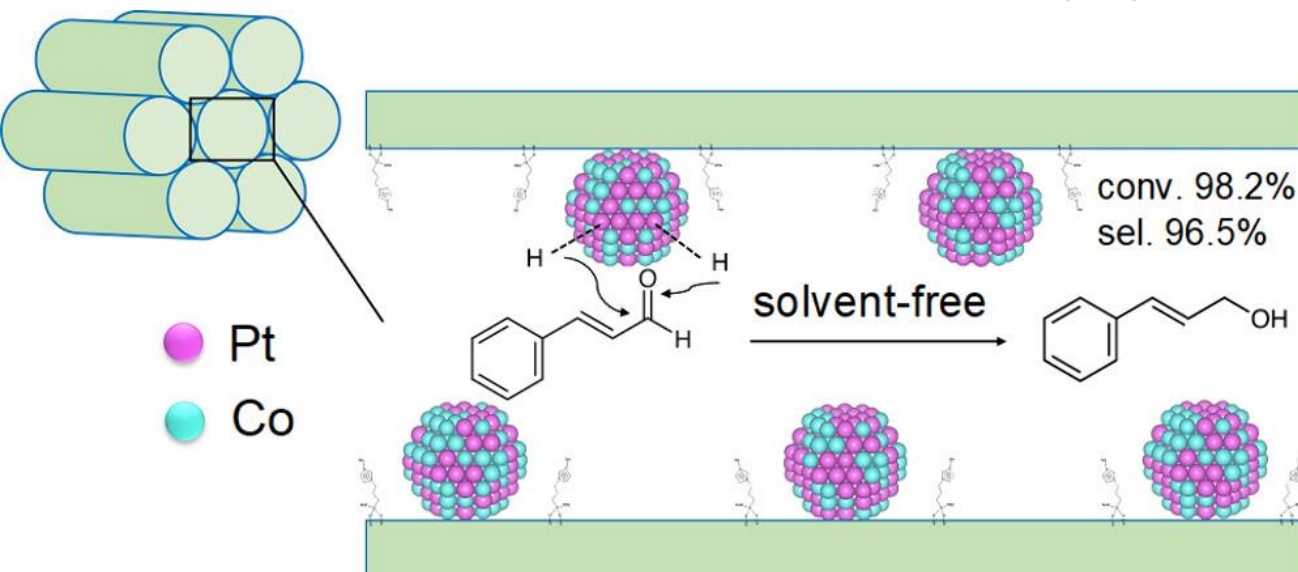
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Kusumawati, E. T.; Sasaki, T.; Shirai, M. *ACS Appl. Nano Mater.* 2023, **6**, 17913-17923



2Pt-2Co/IL@SBA-15
2Pt-2Co/SBA-15

particle size (nm)	
XRD	TEM
1.7	2.4
5.5	6.2



entry	catalyst	CAL conv. (%)	products sel. (%)		
			COL	HCAL	HCOL
1	2Pt-2Co/IL@SBA-15	97.1	96.2	0	3.8
2	2Pt/IL@SBA-15 (A)	3.1	19.9	80.1	0
3	2Co/IL@SBA-15 (B)	trace	—	—	—
4	a mix of A and B	7.9	73.3	19.6	7.2
5	IL@SBA-15	trace	—	—	—
6	2Pt-2Co/SBA-15	20.7	97.9	2.1	0
7	2Pt-2Co/C	73.3	95.2	2.2	2.6

^aReaction condition: CAL 2 mmol, catalyst 20 mg, H₂ 5 MPa, 50 °C, 6 h.

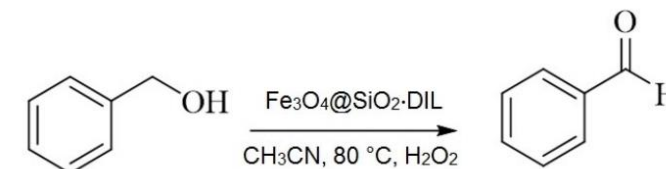
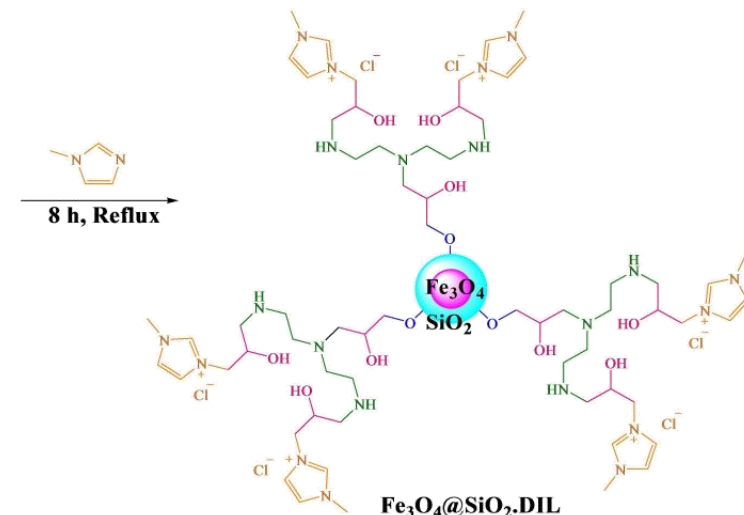
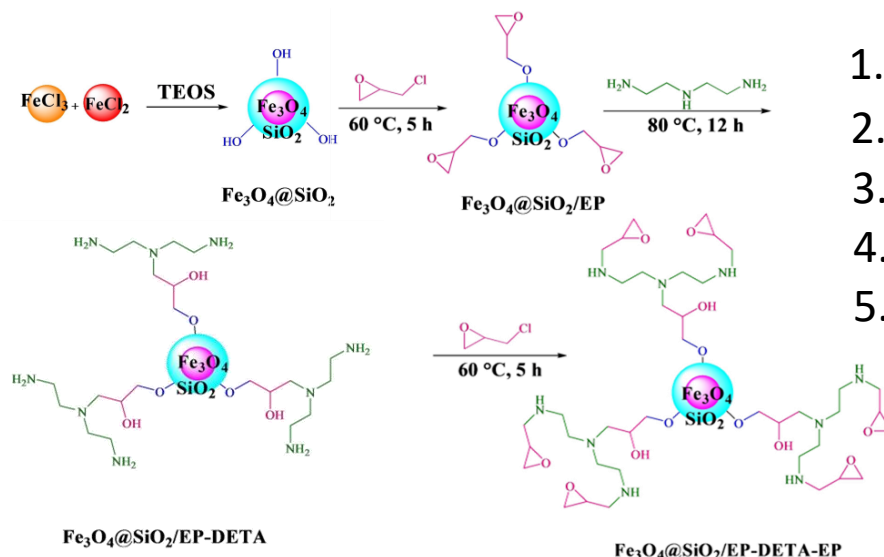
Preparation of dicationic ionic liquid immobilized on $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and evaluation of its catalytic efficiency in the oxidation of alcohols



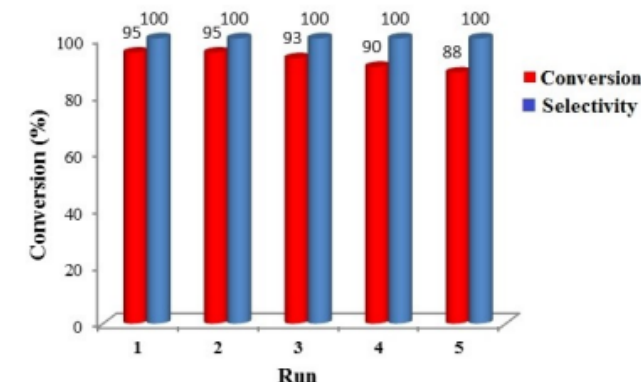
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Ebadi, A.; Vadie, S.; Shojaei, S. *Chemistry Select*, 2023, **8**, 1-8



Reaction Condition	Time (h)	Conversion (%)	Selectivity of benzaldehyde (%)	Ref
Triple-shell hollow $\text{CuNiFe}_2\text{O}_4$ spheres, H_2O , 80 °C, H_2O_2	4	98	100	36
$\text{MnO}_2/\text{HAP-10}$, toluene, 80 °C, O_2	2	48	97	40
2% $\text{V}_2\text{O}_5/\text{STO}$, acetonitrile, 80 °C, TBHP	3	70	88	41
5% $\text{Co}_3\text{O}_4/\text{HCS}$, DMF, 110 °C, O_2	8	50	63	42
$\text{Pd}(\text{Co})\text{OH}_2$, Solvent-free, 160 °C, O_2	4	33	80	43
Au/TiO_2 , Solvent-free, 80 °C, TBHP, MW irradiation	1	69.3	99.1	44
$\text{La}_{0.3}\text{Ce}_{0.7}\text{CoO}_3$, toluene, 88 °C, O_2	1	95	95	45
$\text{Fe}_3\text{O}_4@\text{SiO}_2\cdot\text{DIL}$, CH_3CN , 80 °C, H_2O_2	5	95	100	This work



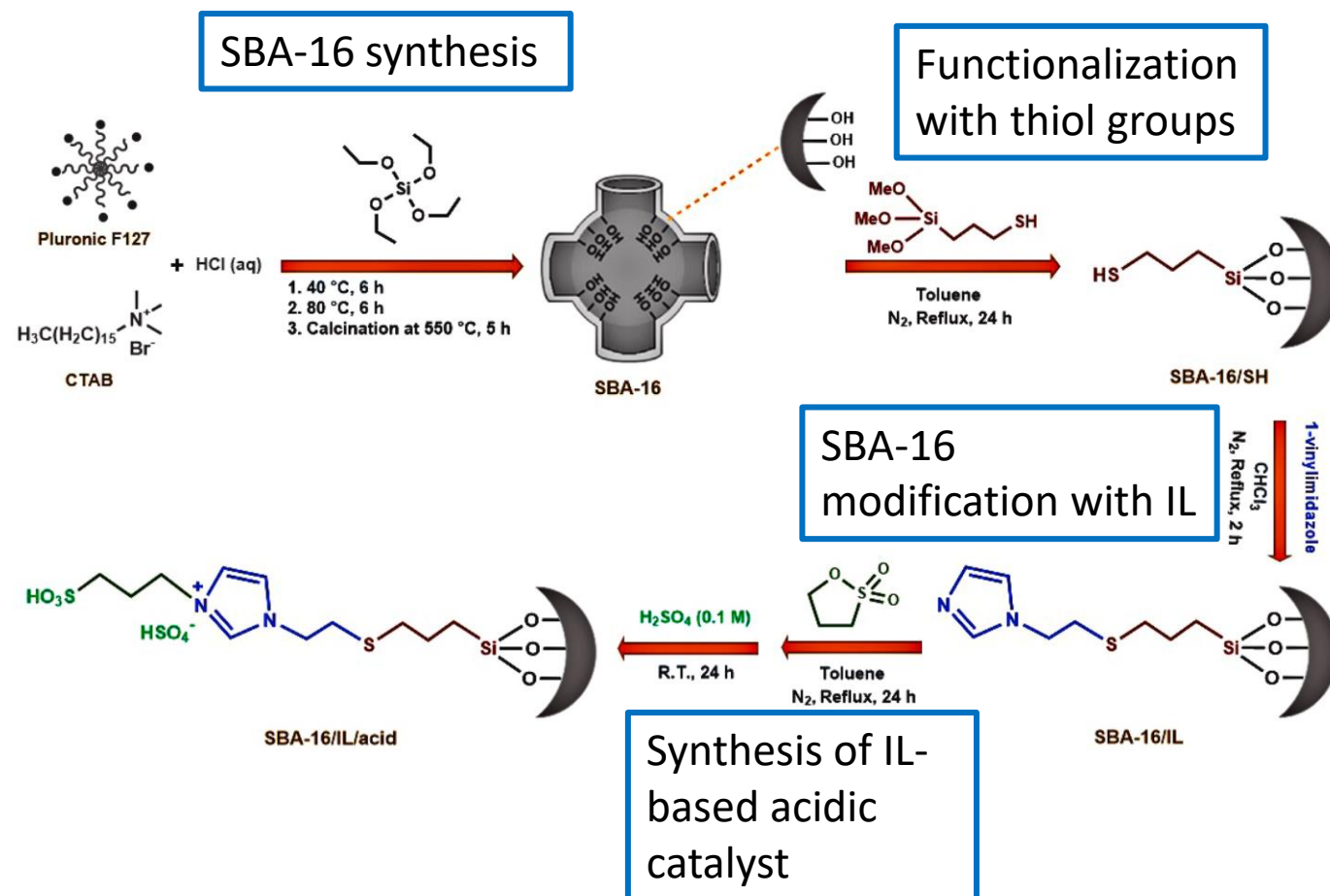
Sulfonated ionic liquid immobilized SBA-16 as an active solid acid catalyst for the synthesis of biofuel precursor 5-hydroxymethylfurfural from fructose

Niakan, M.; Masteri-Farahani, M.; Seidi, F. *Renewable Energy*, 2023, **212**, 50-56

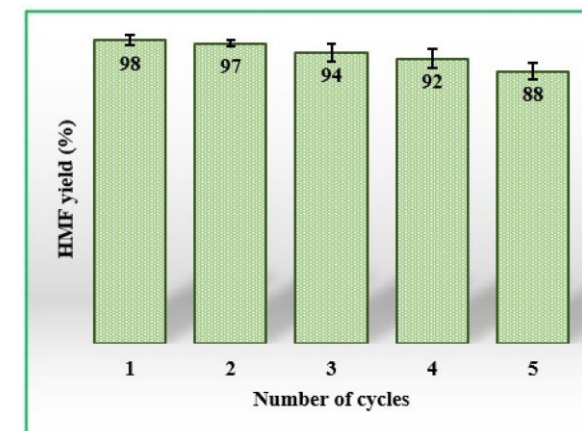


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Fructose amount (mg)	Catalyst (mg)	Solvent	T (°C)	Time (min)	HMF yield (%)	Ref
50	Si-1-IL-HSO ₄ (40)	DMSO	130	30	63	[24]
100	Cr(Salen)-IM-HSO ₄ -MCM-41 (50)	DMSO	120	180	83.5	[25]
90	PW12-ILs-C4-HNS (60)	DMSO	100	120	93.7	[26]
50	PS-Tet-SO ₃ H (30)	DMSO	150	120	86	[27]
36	b-MPOS (25)	DMSO	135	20	86	[39]
100	PrSO ₃ H/GF (30)	DMSO	120	60	87	[10]
300	Aquivion@silica (163)	DMSO	90	120	85	[40]
100	SO ₄ ²⁻ /TiO ₂ (50)	DMSO	150	360	74.7	[41]
100	COP-SO ₃ H/SB (55)	DMSO	120	60	78	[42]
150	SBA-16/IL/acid (15)	DMSO	120	30	98	[This work]





Electrocatalysis

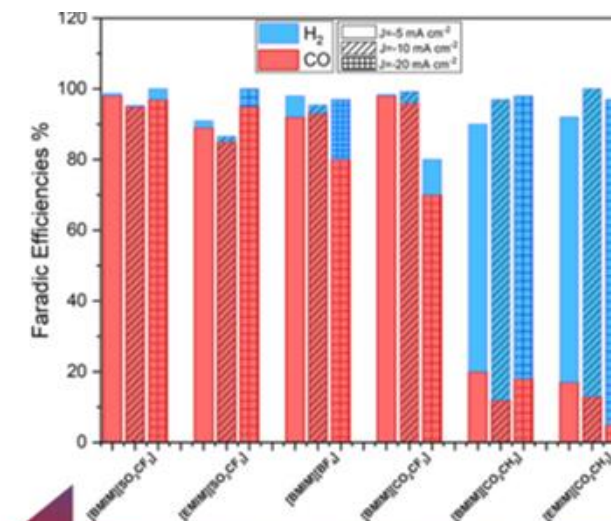
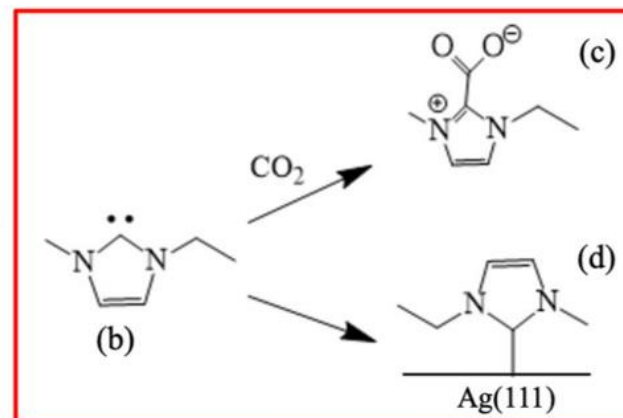
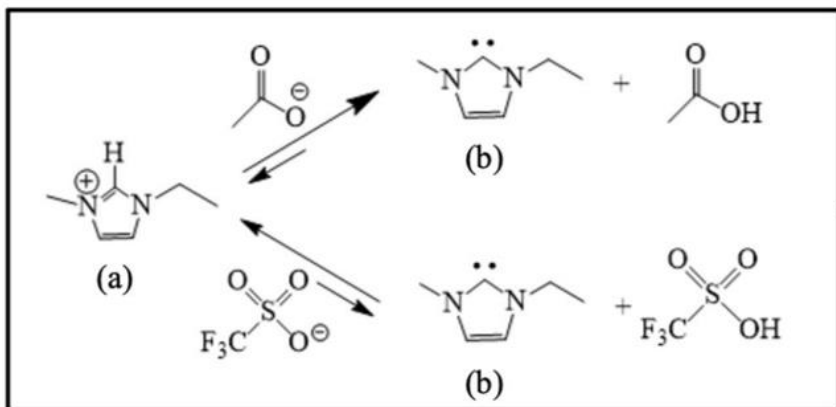
Understanding the role of imidazolium-based ionic liquids in the electrochemical CO₂ reduction reaction



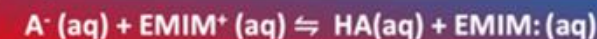
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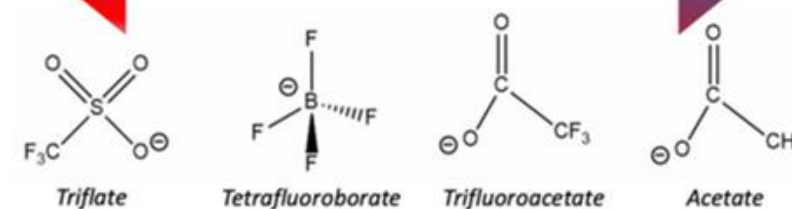
A. Fortunati, F. Risplendi, M. Re Fiorentin, G. Cicero, E. Parisi, M. Castellino, E. Simone, B. Iliev, T. J. S. Schubert, N. Russo, S. Hernández, *Communications Chemistry*, 2023, **6**, 84



CO₂RR



HER



The role of the anion:

- ILs with fluorinated anions favour the reduction reaction of CO₂ to CO

Understanding the role of imidazolium-based ionic liquids in the electrochemical CO₂ reduction reaction

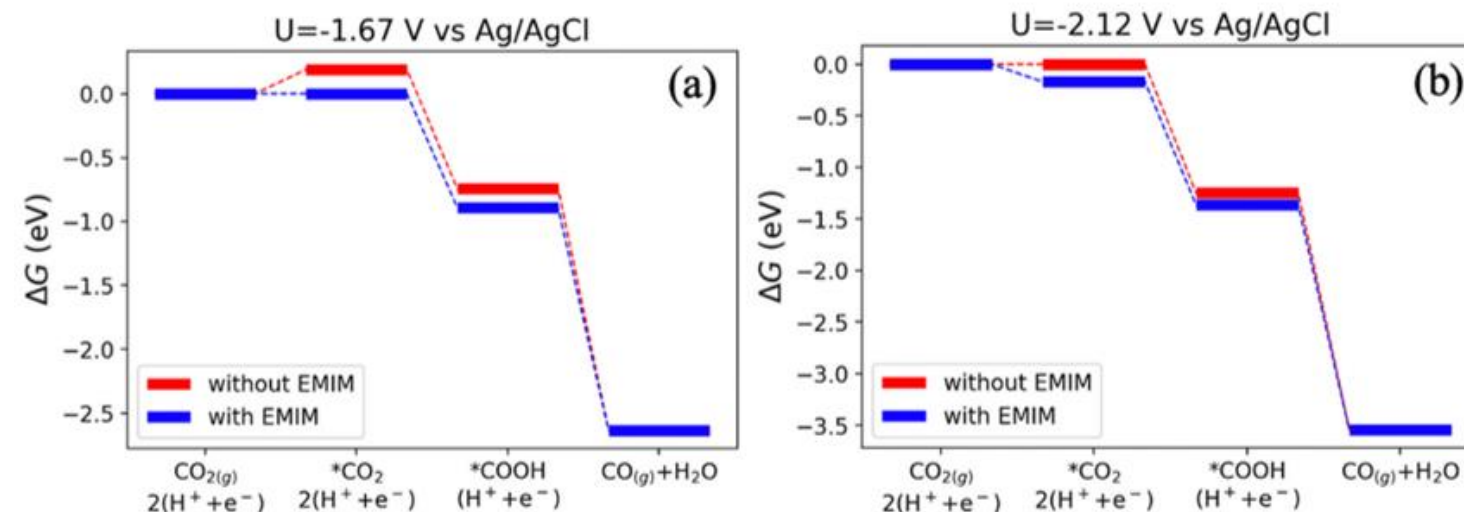
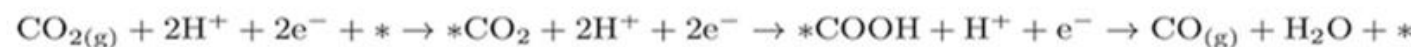


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A. Fortunati, F. Risplendi, M. Re Fiorentin, G. Cicero, E. Parisi, M. Castellino, E. Simone, B. Iliev, T. J. S. Schubert, N. Russo, S. Hernández, *Communications Chemistry*, 2023, **6**, 84

The role of the cation:



- The presence of the IL cation in the form ([EMIM]⁺ or [BMIM]⁺) helps to stabilize the activation of the CO₂ at the interface of the Ag electrode
- Helps to decrease the overpotential of the first-rate determining step and of all the reaction intermediates involved in the electrochemical reduction of CO₂ to CO

A Bifunctional Ionic Liquid for Capture and Electrochemical Conversion of CO₂ to CO over Silver

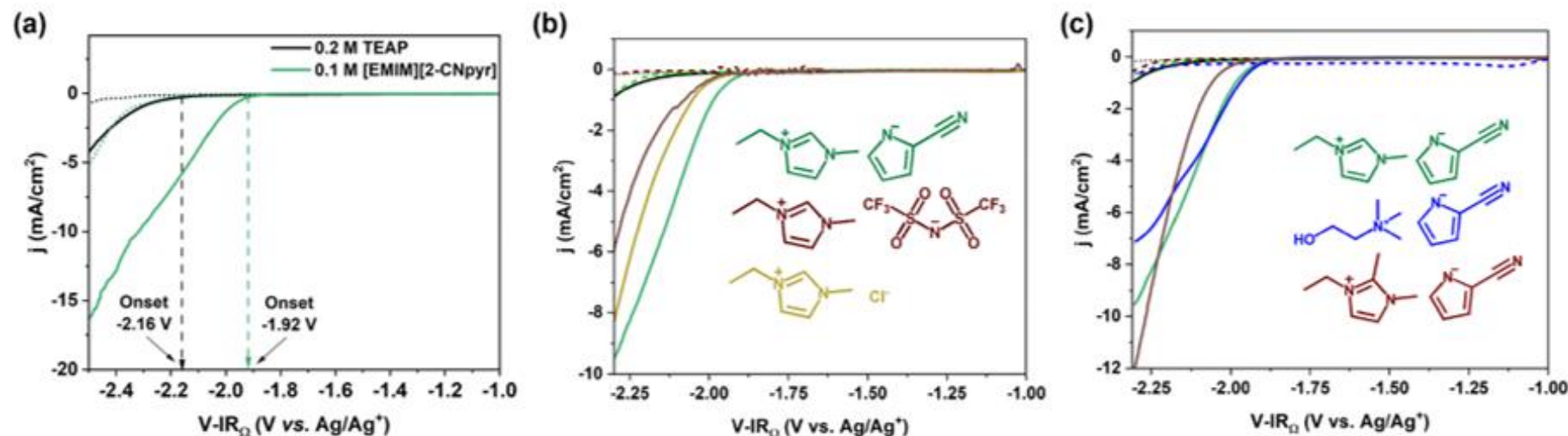


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S. Dongare, O. K. Coskun, E. Cagli, K. Y. C. Lee, G. Rao, R. D. Britt, L. A. Berben, B. Gurkan*, *ACS Catal.* 2023, **13**, 12

- The exact mechanism by which ILs with imidazolium cations lower the activation energy was unclear



- The co-catalytic activity of the reactive IL [EMIM][2-CNpyr] was studied
- Investigated the roles of the carboxylate and carbamate species
- Identified reaction products – agreed with previous paper

A Bifunctional Ionic Liquid for Capture and Electrochemical Conversion of CO₂ to CO over Silver



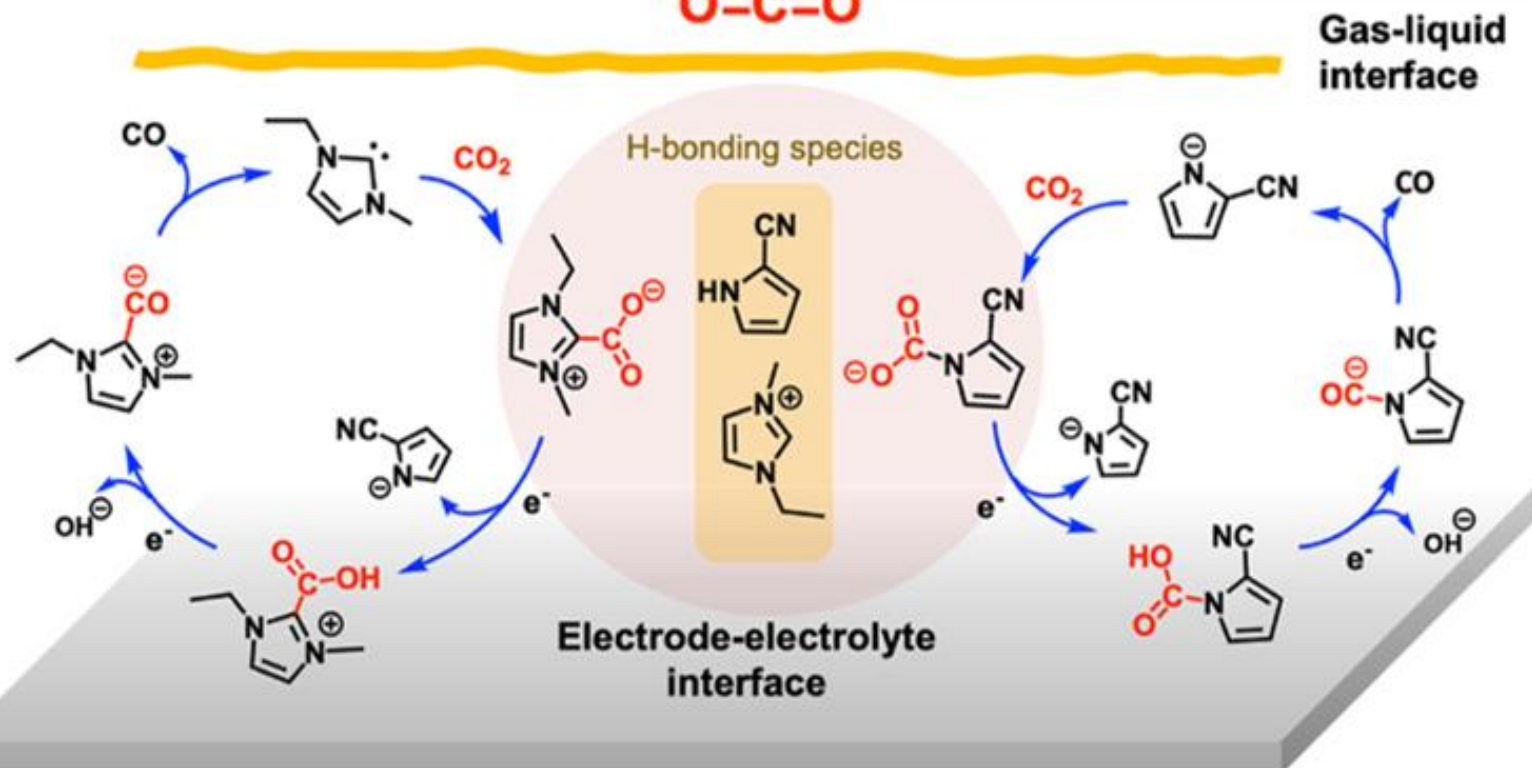
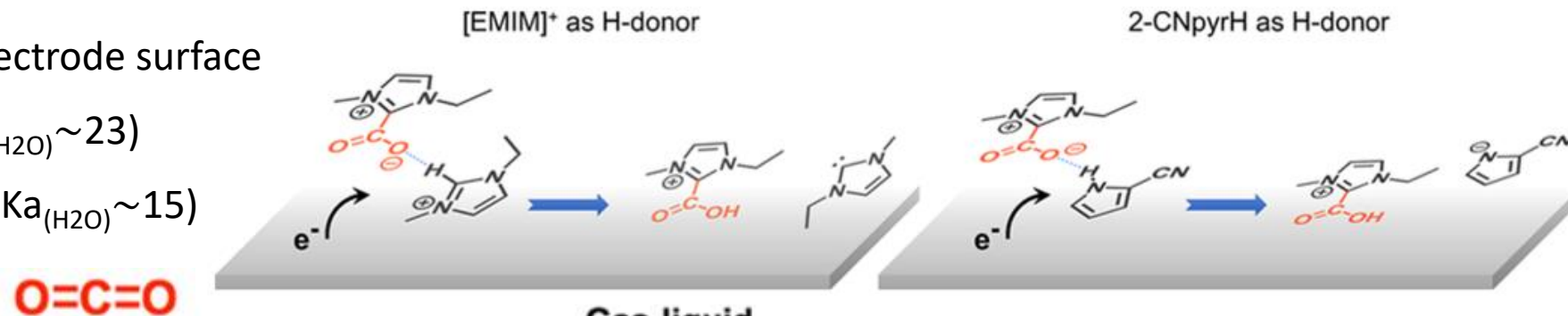
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S. Dongare, O. K. Coskun, E. Cagli, K. Y. C. Lee, G. Rao, R. D. Britt, L. A. Berben, B. Gurkan*, *ACS Catal.* 2023, **13**, 12

Two possible interactions on the electrode surface

- C2 proton of [EMIM]⁺ ($pK_{a(H_2O)} \sim 23$)
- -NH proton of 2-CNpyrH ($pK_{a(H_2O)} \sim 15$)



Efficient electrocatalytic reduction of CO₂ to CO on highly dispersed Ag nanoparticles confined by Poly(ionic liquid)

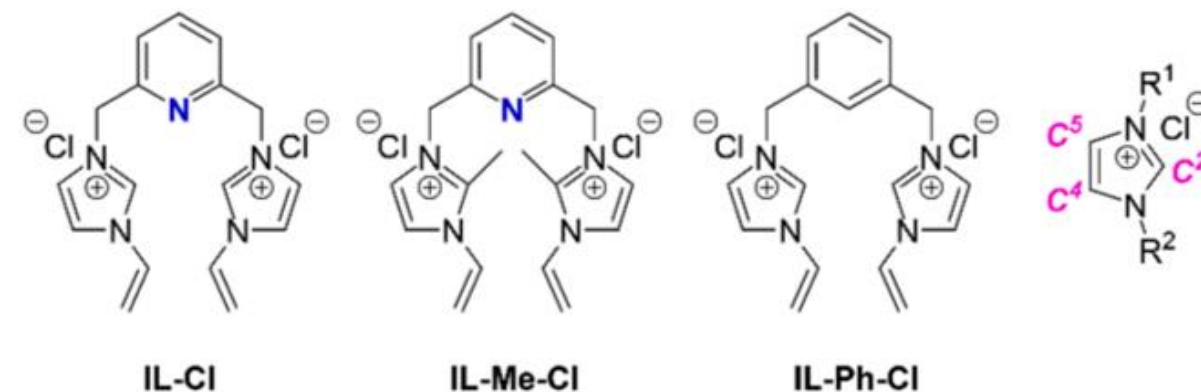
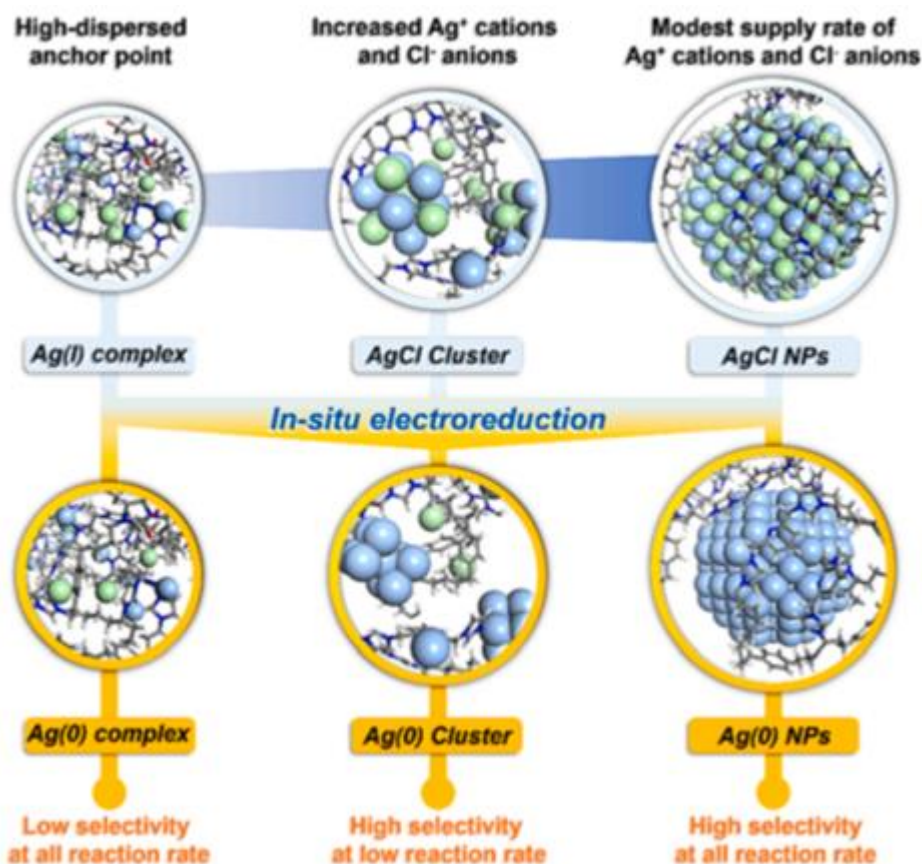


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G. Duan, X. Li, Y. Du, B. Xu*, *ACS Catal.* 2023, **10**, 2

- Polyionic liquids (PILs) impregnated with silver salts
 - dosage and type of silver salt
 - structure of PIL



- Corresponding complexes, clusters, and nanoparticles were obtained in the inner domain.
- The distribution of Ag–Cl species in the PIL is highly correlated to both the microstructure of PIL and silver salts used.

Efficient electrocatalytic reduction of CO₂ to CO on highly dispersed Ag nanoparticles confined by Poly(ionic liquid)

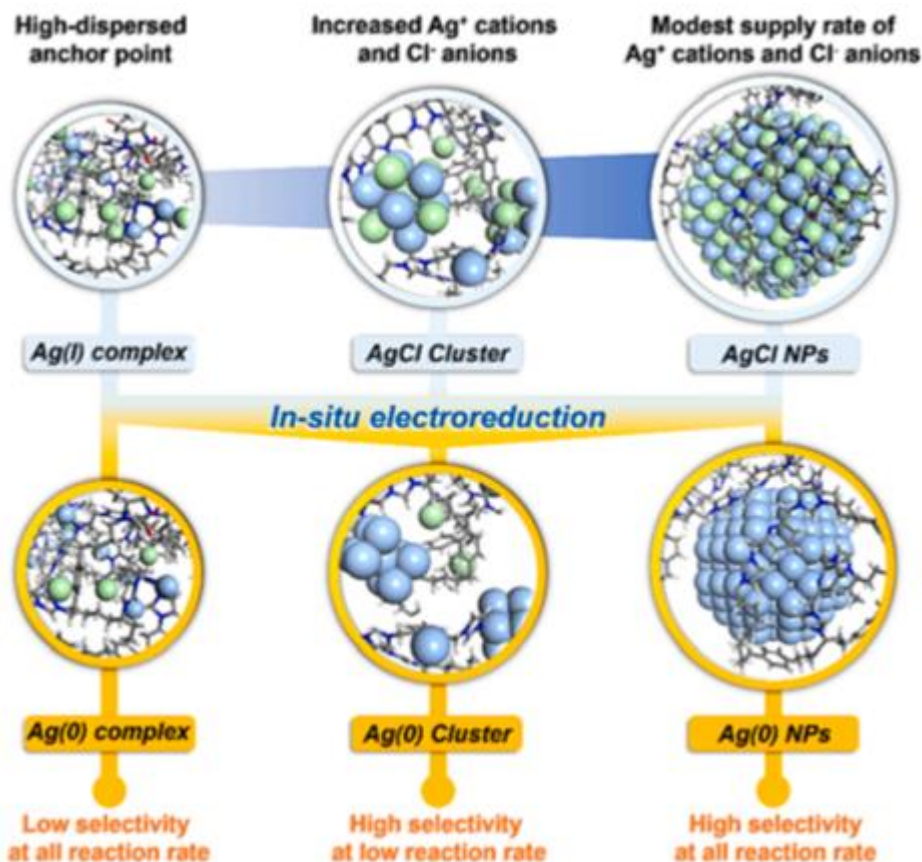
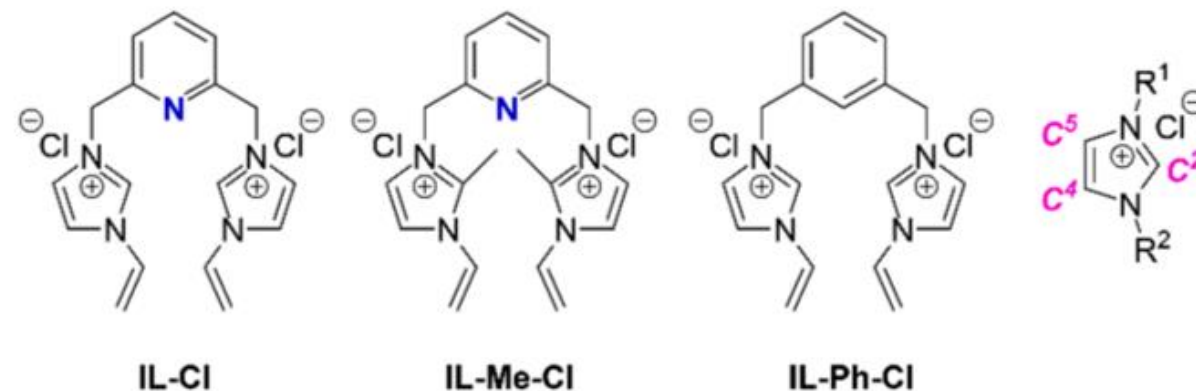


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G. Duan, X. Li, Y. Du, B. Xu*, *ACS Catal.* 2023, **10**, 2

- Polyionic liquids (PILs) impregnated with silver salts
 - dosage and type of silver salt
 - structure of PIL



- Initial reduction of Ag–Cl species to Ag(0) mainly accounts for the CO₂ reduction activity
- The CO₂ reduction performance of PIL-Ag hybrids varies greatly
- PIL-Cl@AgOAc-1.0 mainly consisting of AgCl NPs was selected as the optimized electrocatalyst taking both reactivity and stability into account

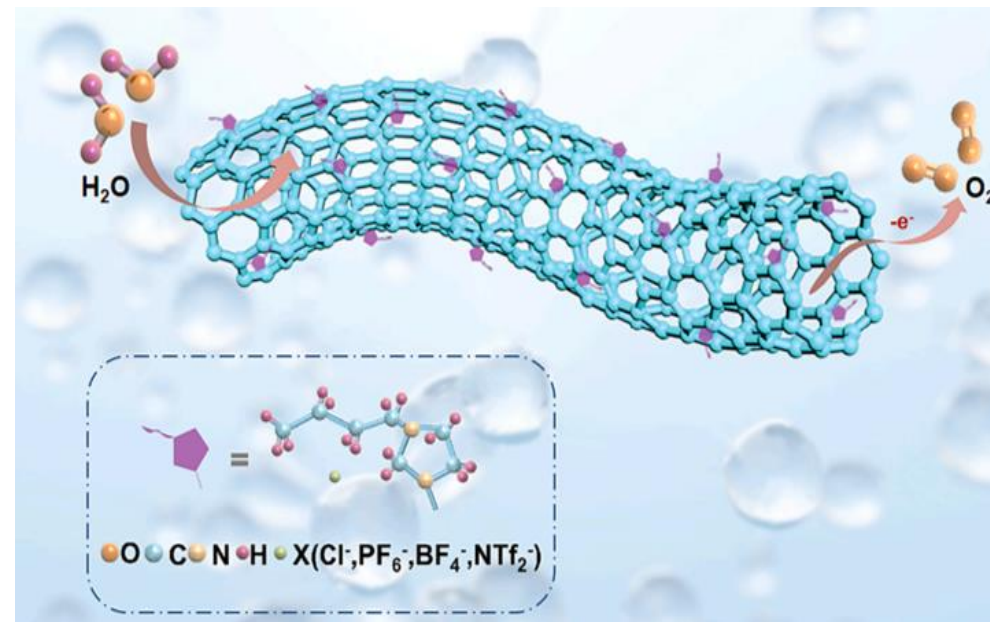
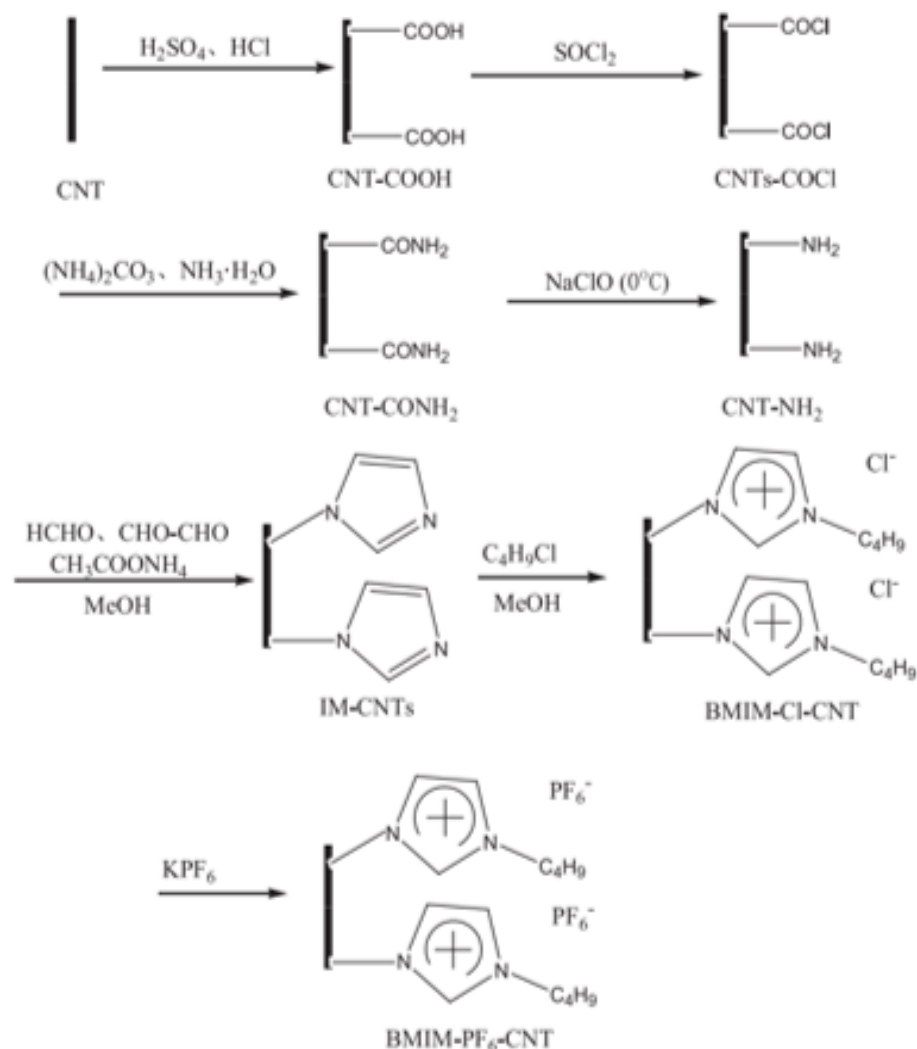
Ionic liquid in-situ functionalized carbon nanotube film as self-supported metal-free electrocatalysts for oxygen evolution



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T. Li*, Y. Wang, T. Chen, G. Wang*, C. Qiu*, W. Hu*, *Chemical Engineering Journal*, 2024, **484**, 149767



- An innovative organic functionalization strategy, where the imidazolium-based IL was in-situ synthesized and directly immobilized on the surface of CNT simultaneously
- Effective way to tune the structure of CNT and improve catalytic activity

Ionic liquid in-situ functionalized carbon nanotube film as self-supported metal-free electrocatalysts for oxygen evolution

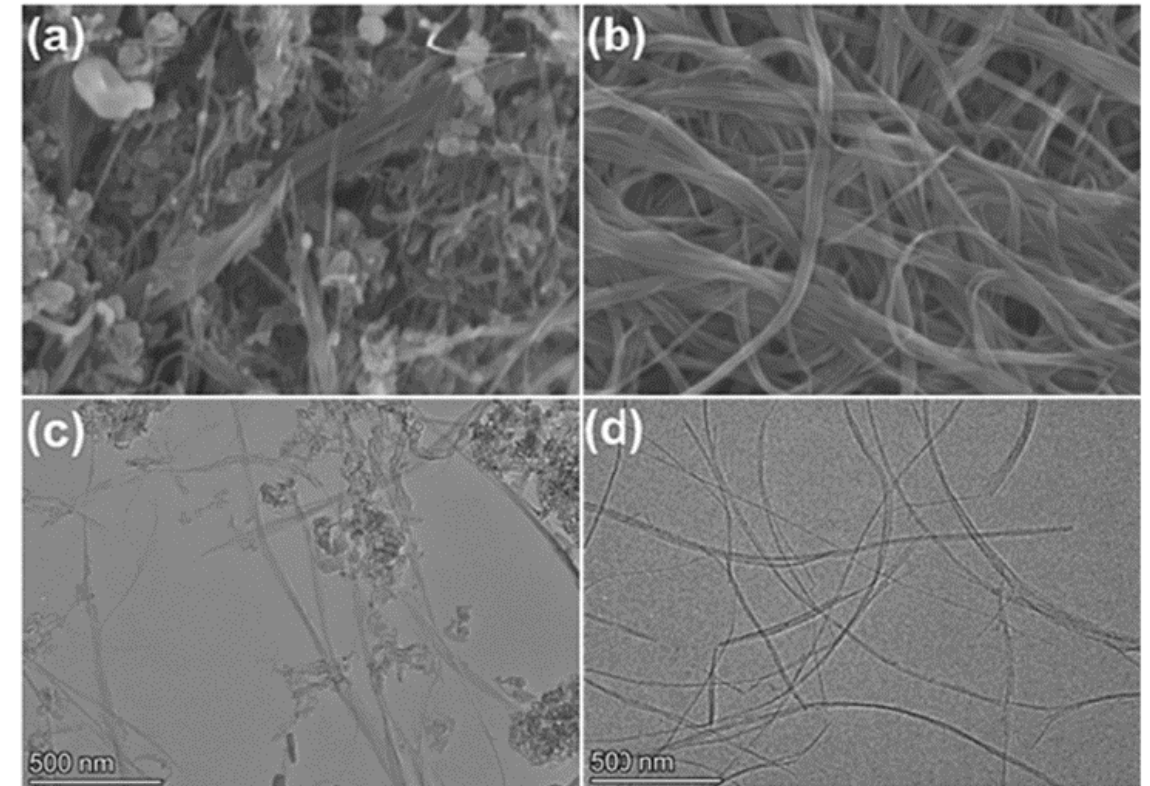


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T. Li*, Y. Wang, T. Chen, G. Wang*, C. Qiu*, W. Hu*, *Chemical Engineering Journal*, 2024, **484**, 149767

- IL-CNT exhibited excellent electrocatalytic performance for the oxygen evolution reaction
- IL-CNT powder material can also self-assemble to form a carbon film
- This IL cation direct bonding remarkably improved the oxygen evolution catalytic activity – great potential for practical applications



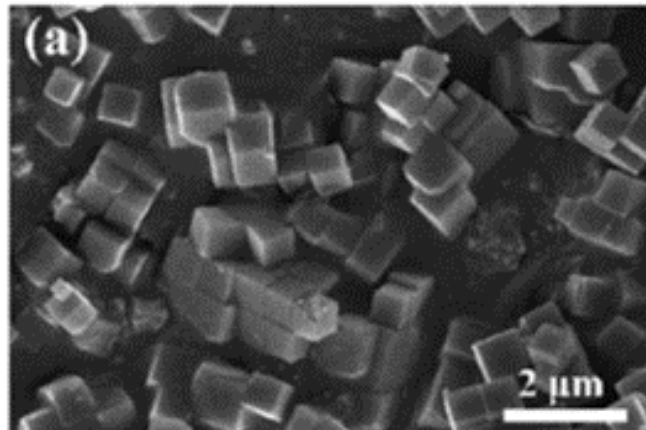
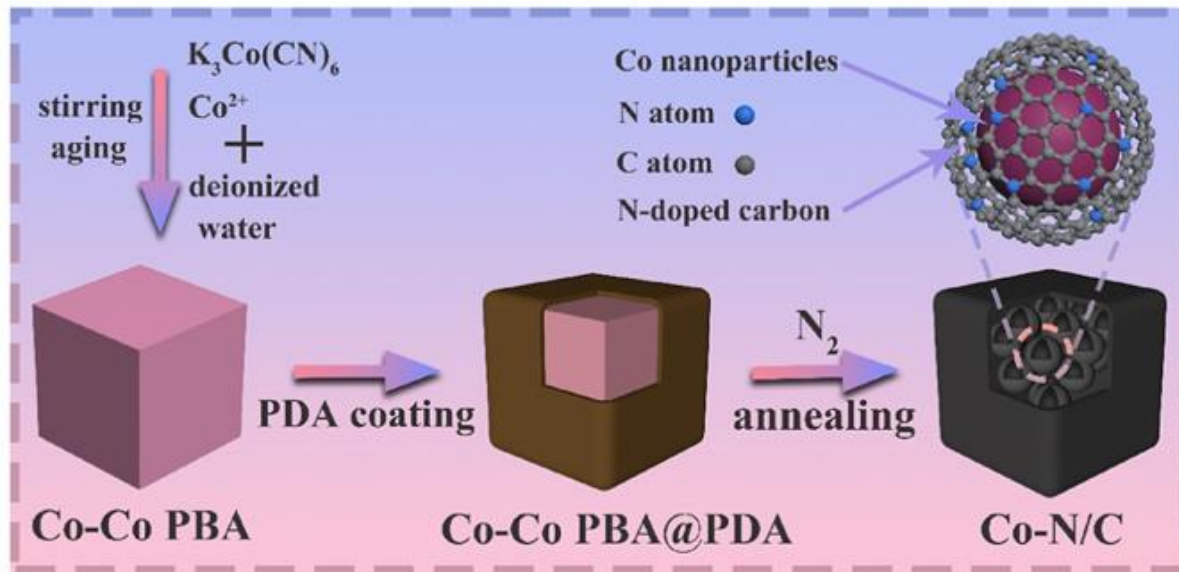
Double-Layer Carbon Encapsulated Co Particles Combined with Ionic Liquid for Enhancing Electrochemical Detection of Oxygen



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W. Yin, J. Liu*, Q. Liu, J. Zhu, M. Zhang*, P. Liu, R. Li, J. Wang, *ACS Sustainable Chem. Eng.*, 2023, **11**, 7



- Synthesized the nitrogen-doped carbon encapsulated Co particles embedded in hollow square box microcubes derived from Prussian blue analogue precursors
- Explored the effects of carbon materials encapsulated with the metallic particle catalyst
- Ionic liquid [C4mpyrr][TFSI] and Co-N/C microcubes synthesized
- Co-N/C was introduced into [C4mpyrr][TFSI] – enhanced the sensor's electrochemical sensing performance.

Double-Layer Carbon Encapsulated Co Particles Combined with Ionic Liquid for Enhancing Electrochemical Detection of Oxygen

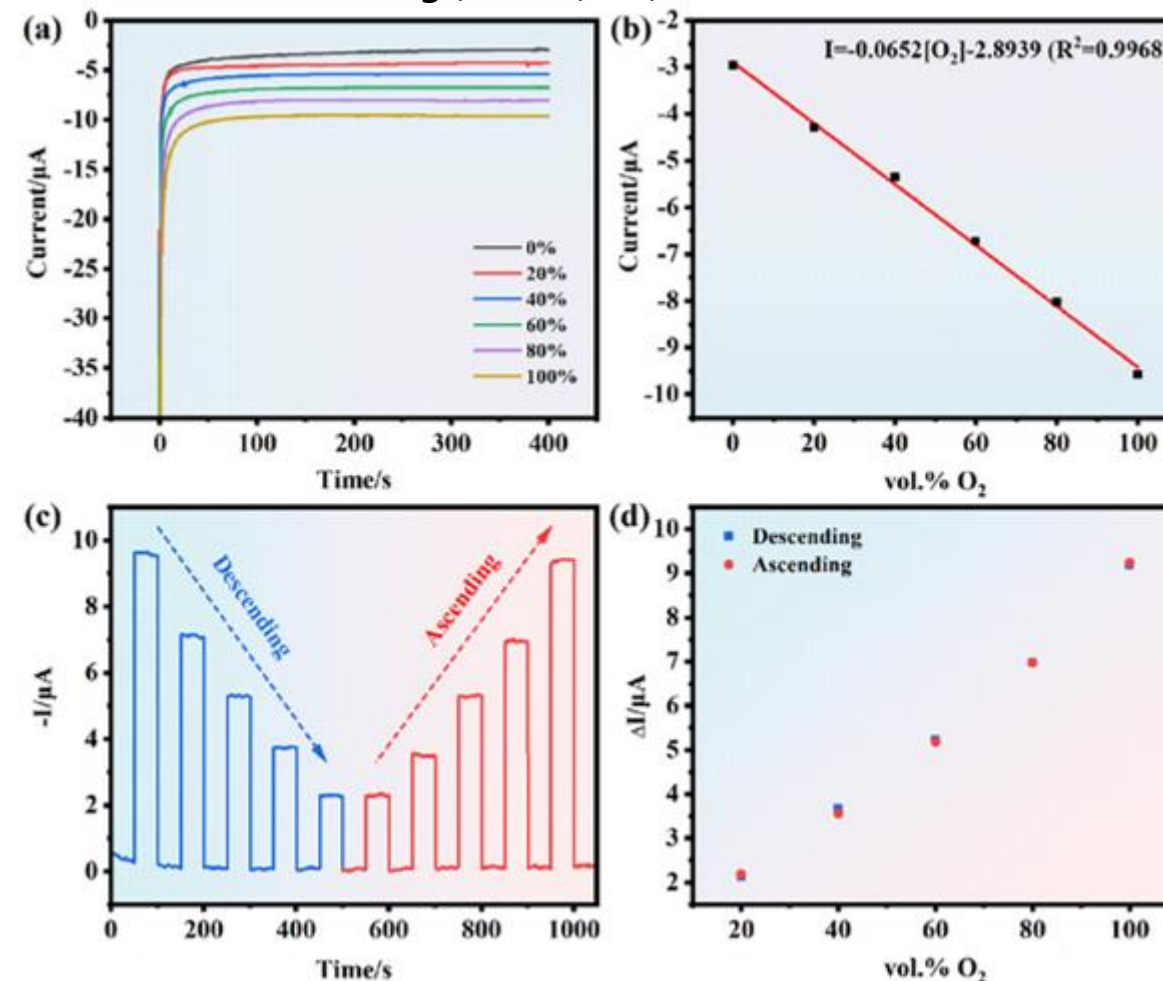


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W. Yin, J. Liu*, Q. Liu, J. Zhu, M. Zhang*, P. Liu, R. Li, J. Wang, *ACS Sustainable Chem. Eng.*, 2023, **11**, 7

- Significant improvement in O₂ sensing when Co-N/C/[C4mpyrr][TFSI] used compared to [C4mpyrr][TFSI]
- The addition of Co-N/C improves oxygen reduction, enhancing the electrochemical O₂ sensor performance





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Polymers

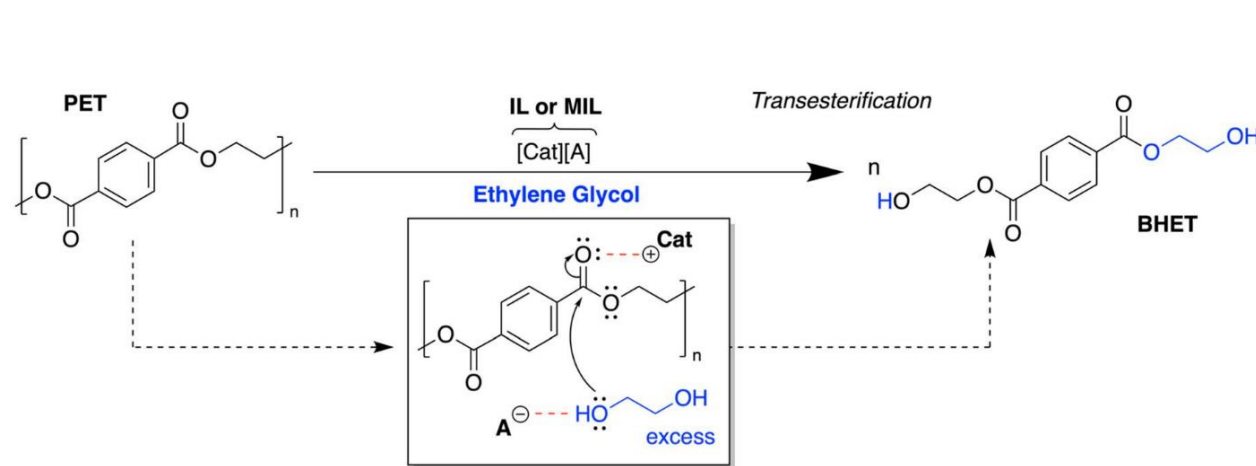
Understanding the important variables to optimize glycolysis of polyethylene terephthalate with lanthanide-containing ionic liquids



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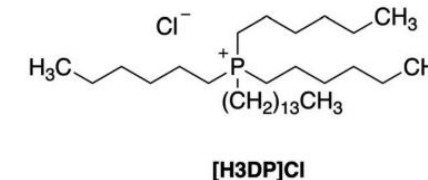
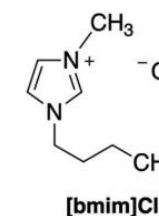
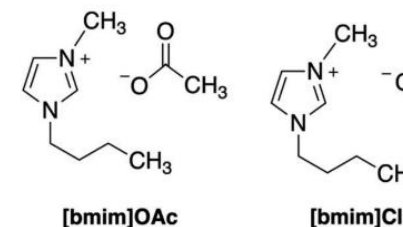
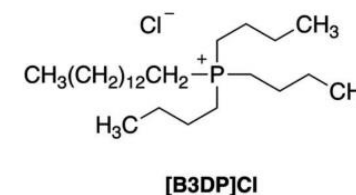
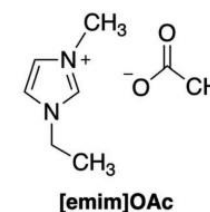
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N.G. Bush, C. H. Dinh, C. L. Cattertona and M. E. Fieser, *RSC Sustainability*, 2023, **1**, 938

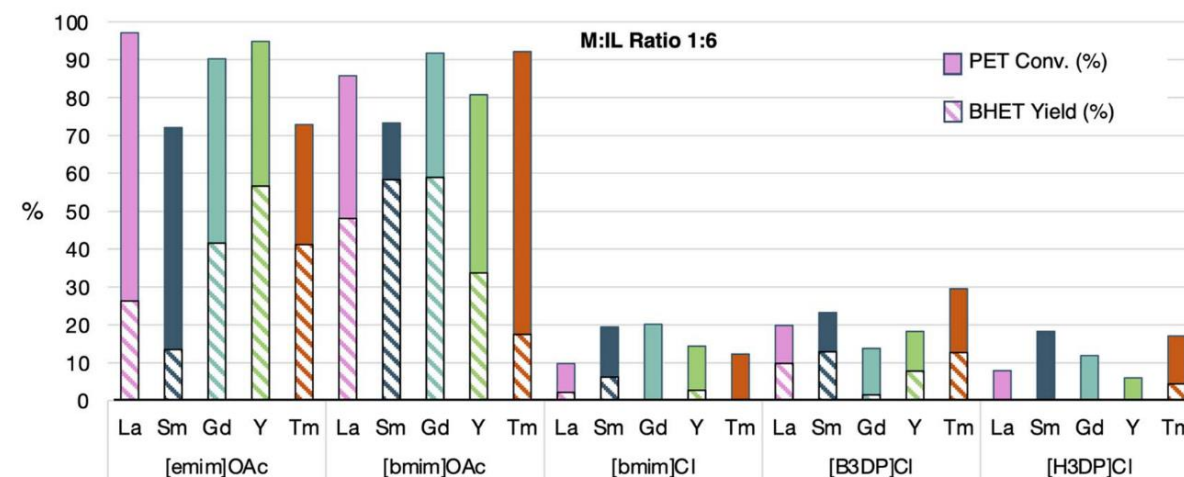


Metal Salts:

LaCl₃ · 7H₂O
SmCl₃ · 6H₂O
GdCl₃ · 6H₂O
YCl₃ · 6H₂O
TmCl₃ · 6H₂O



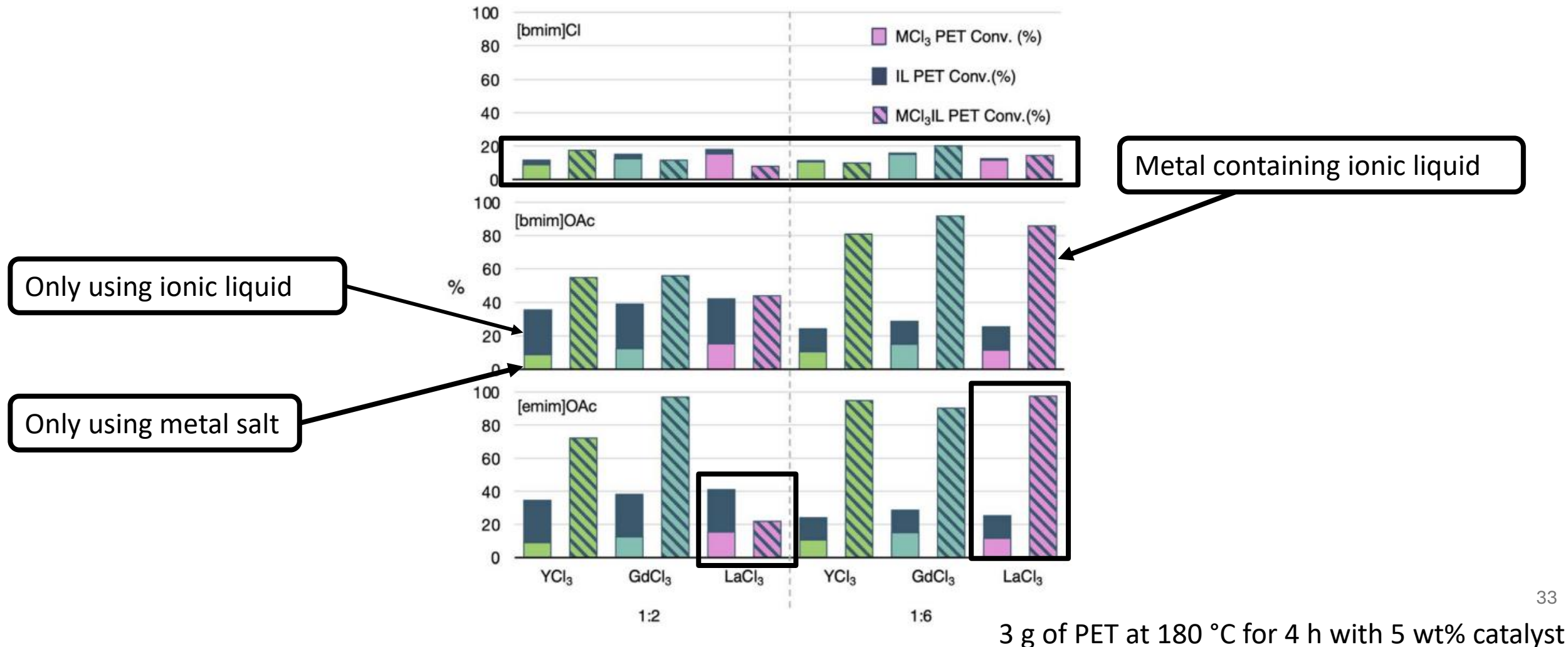
- Yttrium and gadolinium were identified to be the most promising metals to pursue further, as both showed high PET conversions with both ratios of metal salt to IL



Understanding the important variables to optimize glycolysis of polyethylene terephthalate with lanthanide-containing ionic liquids



N.G. Bush, C. H. Dinh, C. L. Cattertona and M. E. Fieser, *RSC Sustainability*, 2023, **1**, 938



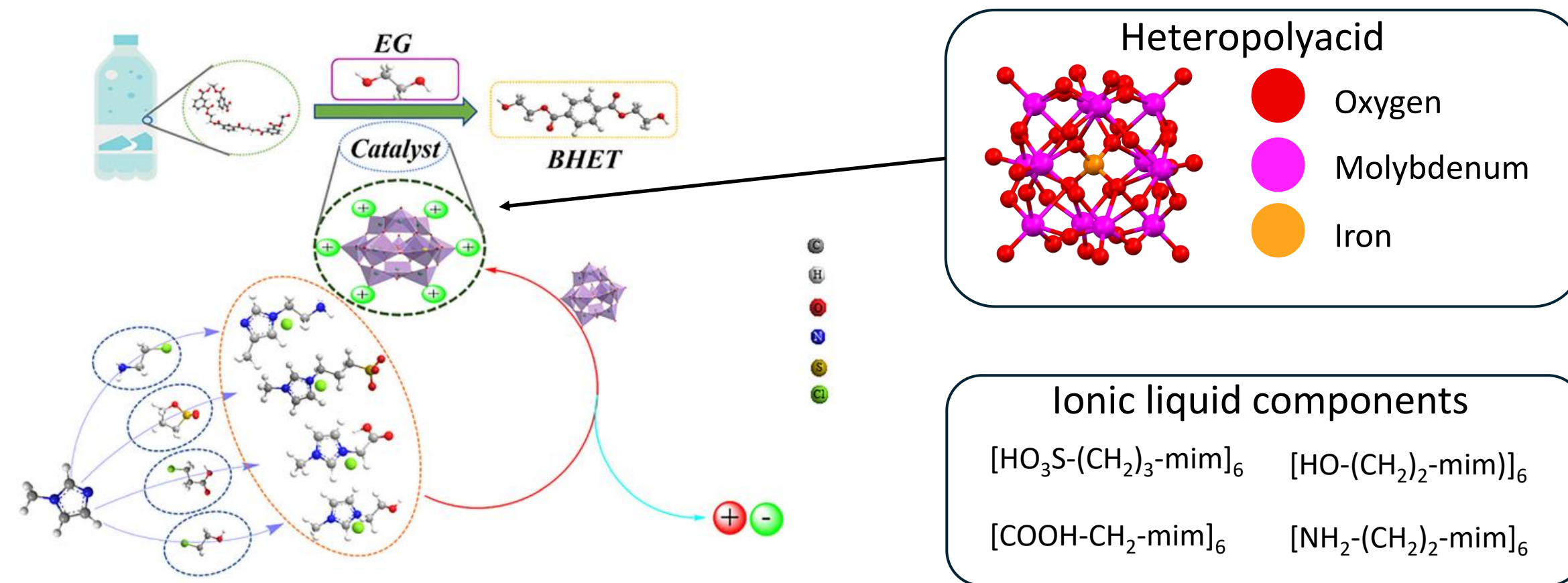
Preparation of functionalised heteropolyacid ionic liquids and their application in catalytic degradation of bottle-grade polyester



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B. Liu, B. Liu, Z. Liao, J. Zhang and L. Guo. *New J. Chem.*, 2023, **47**, 19943



Preparation of functionalised heteropolyacid ionic liquids and their application in catalytic degradation of bottle-grade polyester



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B. Liu, B. Liu, Z. Liao, J. Zhang and L. Guo. *New J. Chem.*, 2023, **47**, 19943

No	Catalyst	D/%	Y _B /%	Further reaction optimisation
1	[HSO ₃ -(CH ₂) ₃ -mim] ₆ [Fe(H ₂ O)FeMo ₁₁ O ₃₉]	100	85.26	100 % conversion of PET 91.92 % yield of BHET 0.2 % catalyst loading at 196 °C for 3 h
2	(COOH-CH ₂ -mim) ₆ [Fe(H ₂ O)FeMo ₁₁ O ₃₉]	100	82.88	
3	[HO-(CH ₂) ₂ -mim] ₆ [Fe(H ₂ O)FeMo ₁₁ O ₃₉]	100	77.34	
4	[NH ₂ -(CH ₂) ₂ -mim] ₆ [Fe(H ₂ O)FeMo ₁₁ O ₃₉]	100	73.38	
5	Bmim ₆ [Cu(H ₂ O)TiMo ₁₁ O ₃₉]	100	72.3	Literature comparison
6	Bmim ₆ [Pb(H ₂ O)TiMo ₁₁ O ₃₉]	100	67.68	
7	Bmim ₆ [Fe(H ₂ O)FeMo ₁₁ O ₃₉]	100	65.38	
8	Bmim ₇ [Pb(H ₂ O)FeMo ₁₁ O ₃₉]	99.6	62.46	
9	Zn(OAc) ₂	94.17	60.35	

Note: D—alcoholysis rate, Y_B—the yield of BHET

0.5% catalyst loading at 190 °C for 5 h

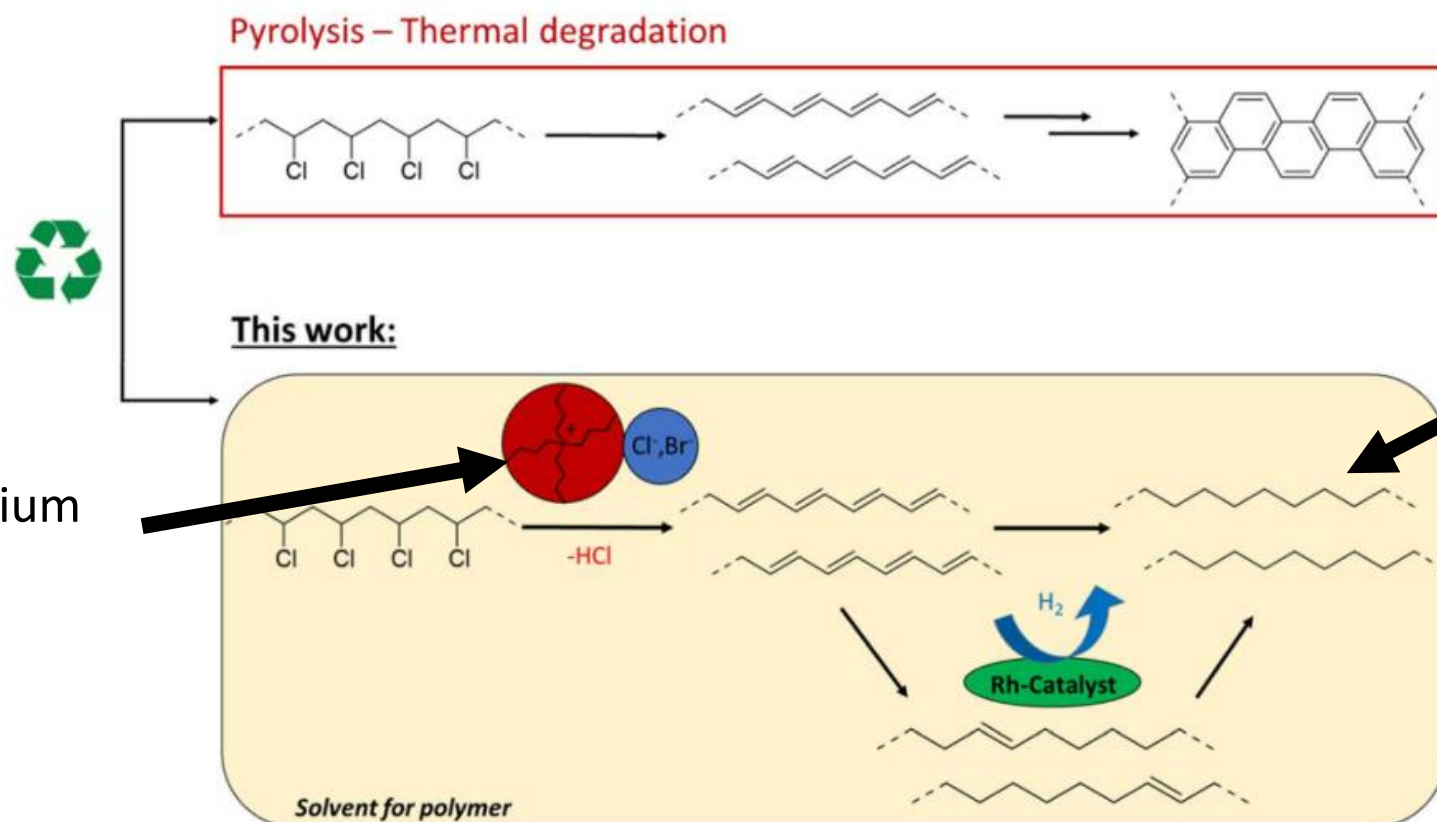
Catalytic tandem dehydrochlorination–hydrogenation of PVC towards valorisation of chlorinated plastic waste



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G. O'Rourke, T. Hennebel, M. Stalpaert, A. Skorynina, A. Bugaev, K. Janssens, L. Van Emelen, V. Lemmens, R. D. O. Silva, C. Colemonts, P. Gabriels, D. Sakellariou a and D. De Vos. *Chem. Sci.*, 2023, **14**, 4401



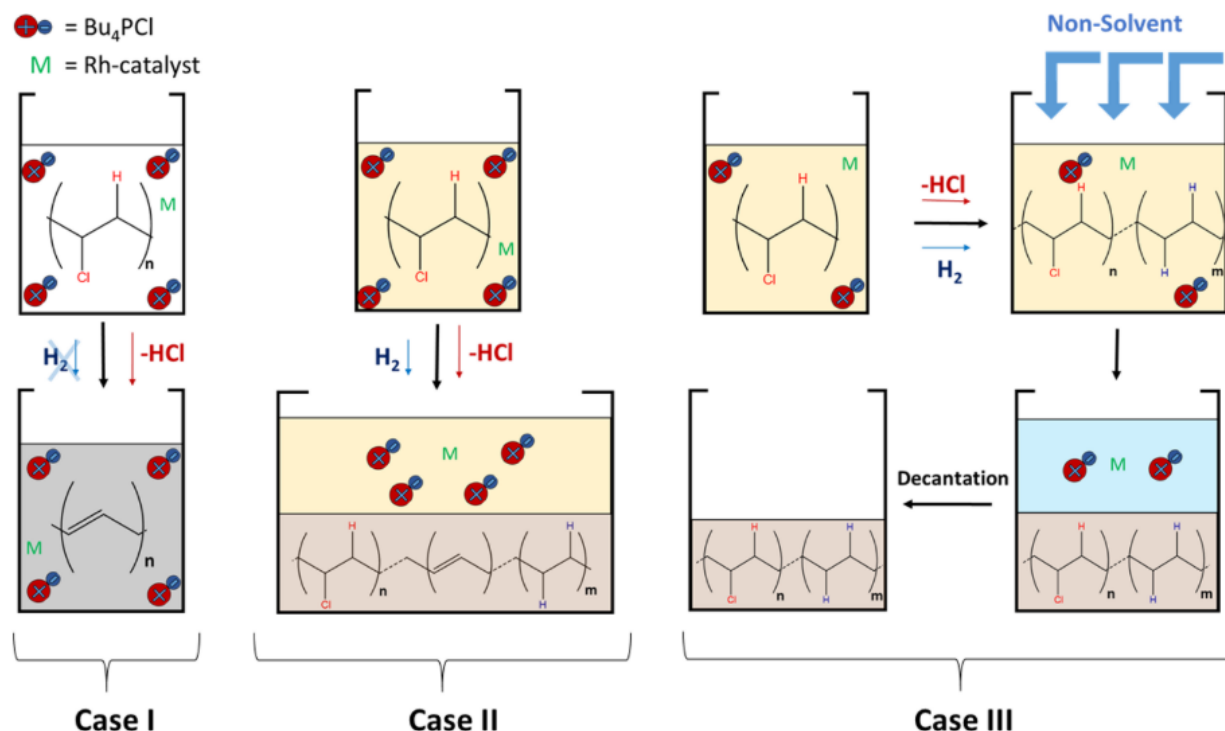
Catalytic tandem dehydrochlorination–hydrogenation of PVC towards valorisation of chlorinated plastic waste



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81% dehydrochlorination is reached in 2 h, with the hydrogenation proceeding smoothly with minimal catalyst use of 0.5–2.0 mol% Rh.

Case I : Reaction in pure ionic liquid only leads to dehydrochlorination

Case II: an excess of ionic liquid in a solvent, the polymer precipitates spontaneously during reaction

Case III : a limited amount of ionic liquid in a solvent, spontaneous precipitation is avoided, and largely saturated products are obtained

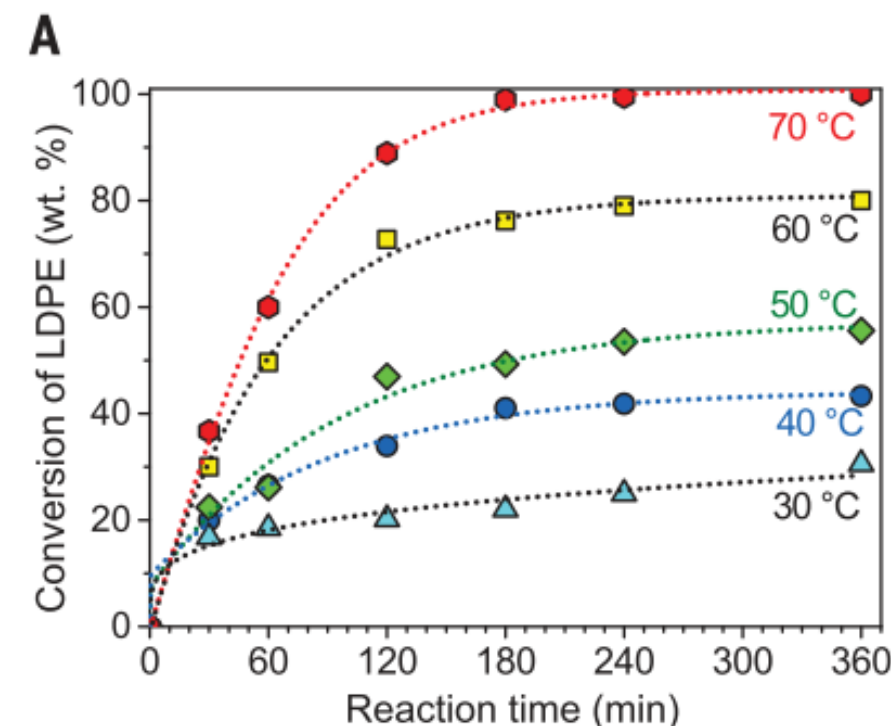
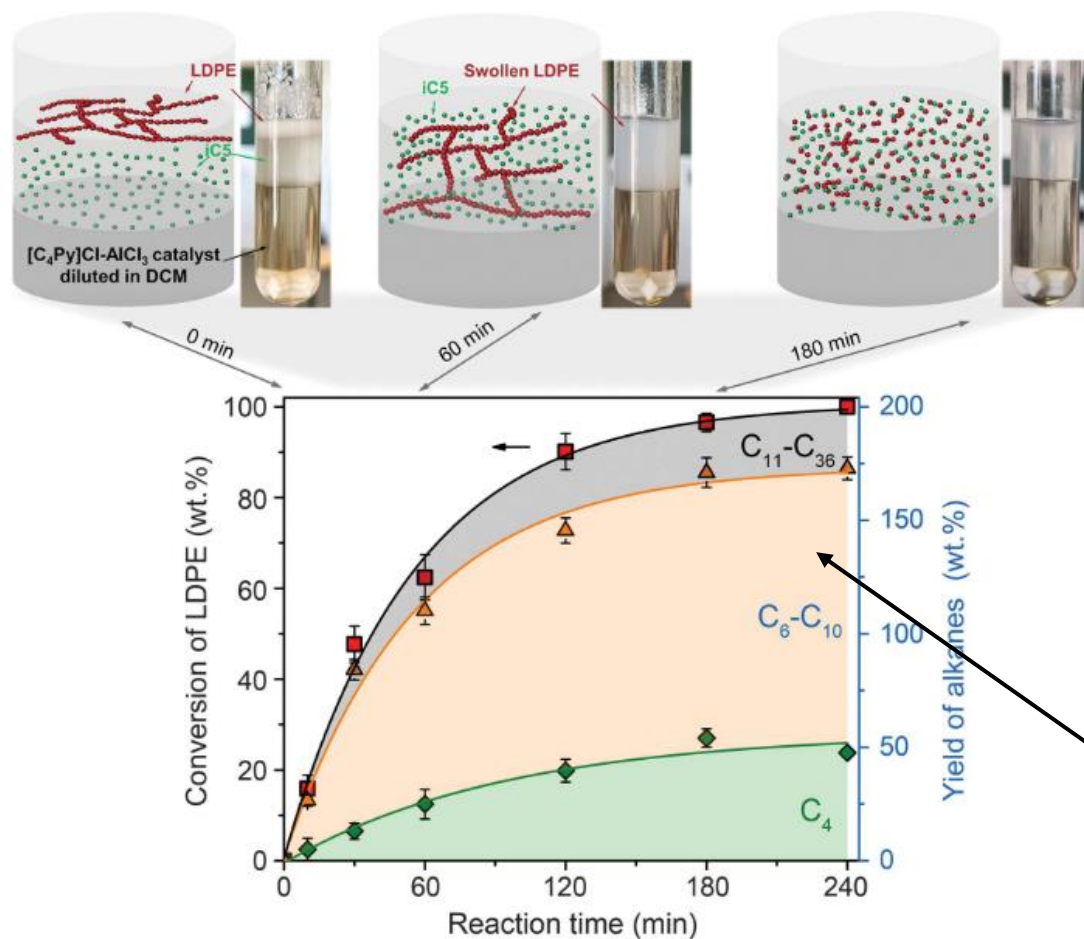
Low-temperature upcycling of polyolefins into liquid alkanes via tandem cracking-alkylation



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W. Zhang, S. Kim, L. Wahl, R. Khare, L. Hale, J. Hu, D. M. Camaioni, O. Y. Gutiérrez, Y. Liu, J. A. Lercher, *Science*, 2023, **379**, 807-811



Full conversion of polyolefin to produce a distribution of products

LDPE, 200 mg; iC_5 , 800 mg; $[C_4Py]Cl-AlCl_3$, 3 mmol; TBC as an additive, 5 mg; DCM, 3 ml; and temperature, 70°C.

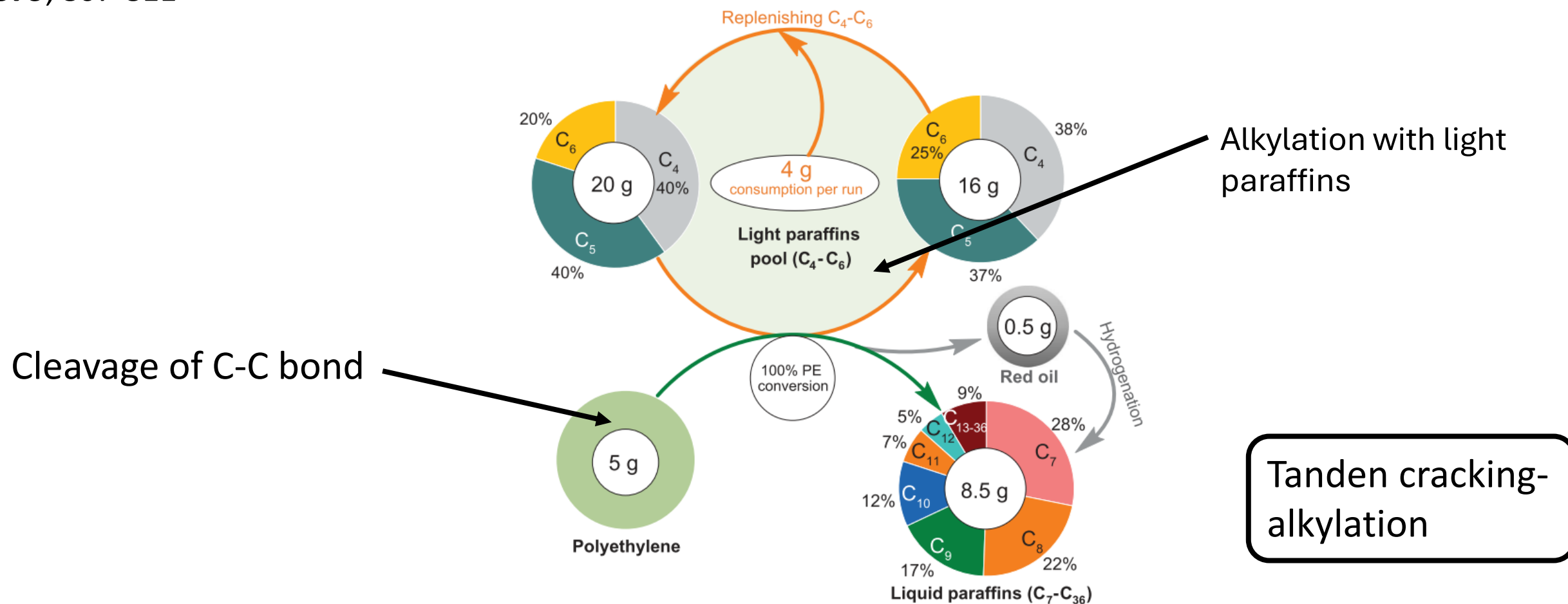
Low-temperature upcycling of polyolefins into liquid alkanes via tandem cracking-alkylation



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Polyethylene reaction with light paraffin mixture – 70° C for 2 h



Liquid-liquid separation

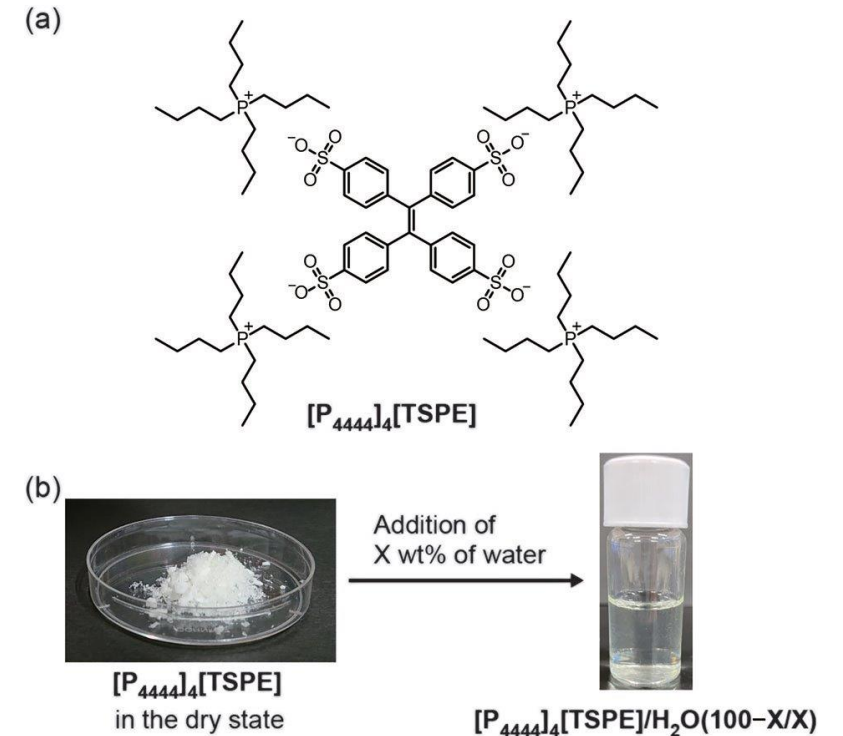
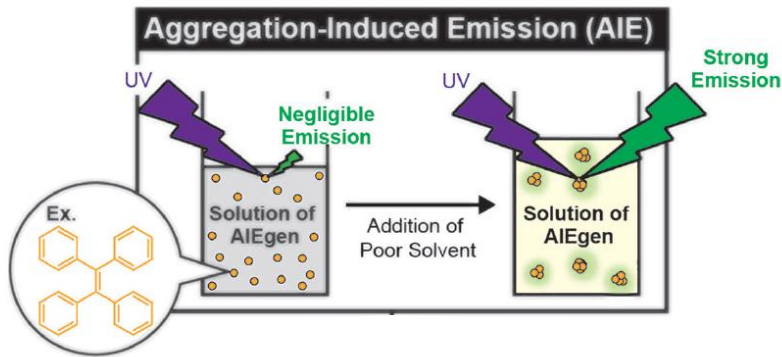
Thermally Reversible On-Off Switching of Aggregation-induced Emission via LCST Phase Transition of Ionic Liquids in Water



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H. Iwasawa, D. Uchida, Y. Hara, M. Tanaka, N. Nakamura, H. Ohno, and T. Ichikawa*, *Adv. Optical Mater.* 2023, **11**, 2301197



AIE : a phenomenon in which a class of π -conjugated molecules show strong photoluminescence in aggregated states and negligible emission in the solution states.

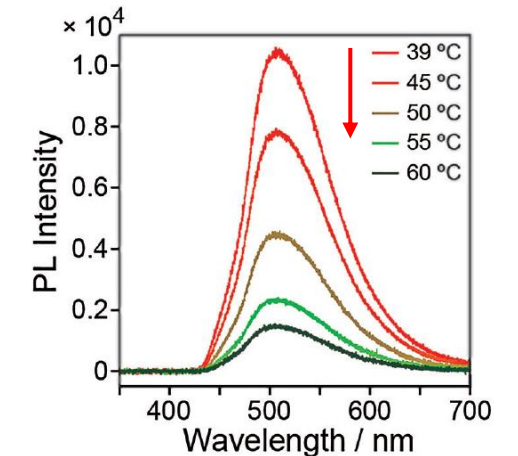
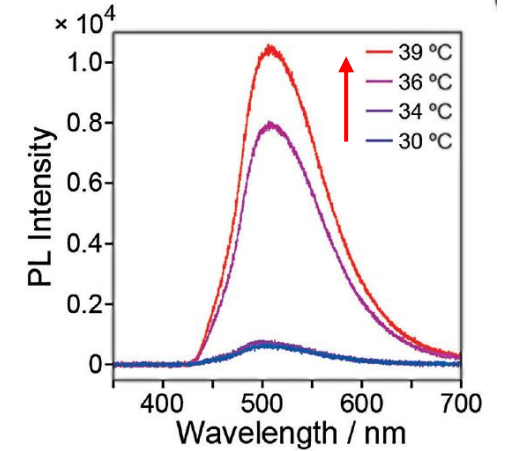
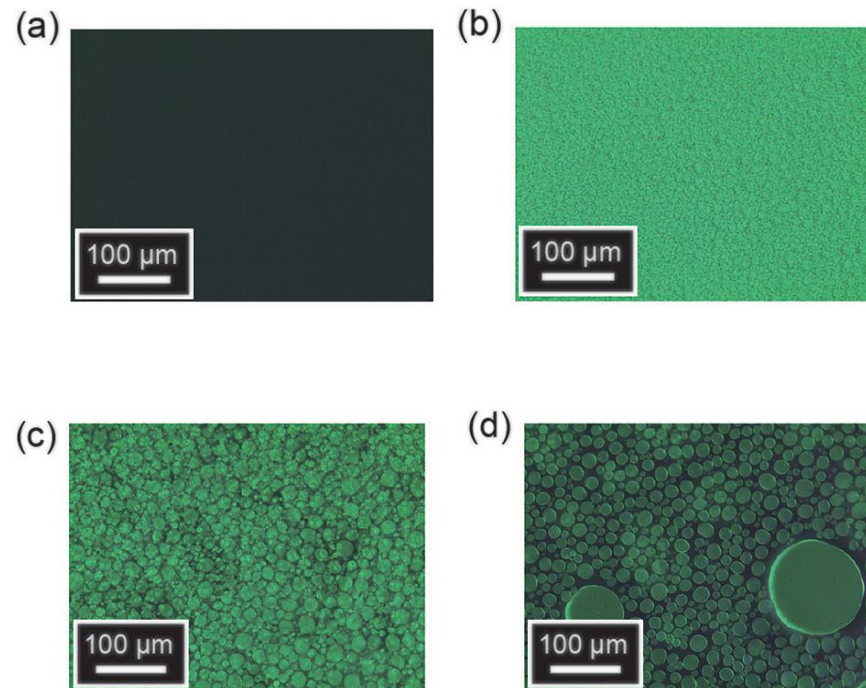
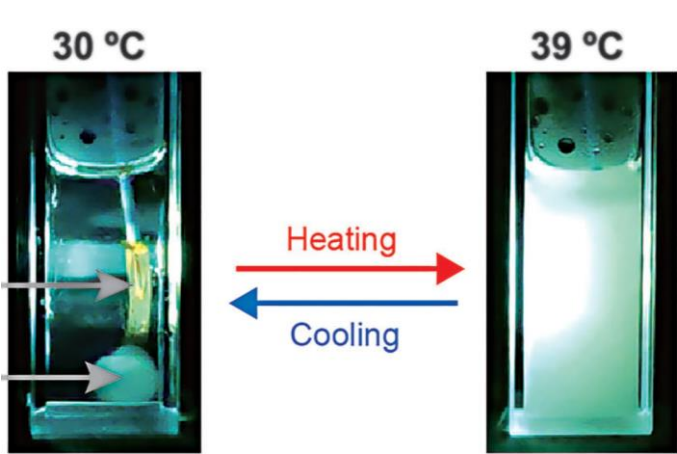
Thermally Reversible On-Off Switching of Aggregation-induced Emission via LCST Phase Transition of Ionic Liquids in Water



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H. Iwasawa, D. Uchida, Y. Hara, M. Tanaka, N. Nakamura, H. Ohno, and T. Ichikawa*, *Adv. Optical Mater.* 2023, 11, 2301197



1. The strongest photoluminescence around the LCST phase transition temperature
2. Application: Photoluminescent materials with high sensitivity to temperature

Thermo-switchable hydrophobic solvents formulated with weak acid and base for greener separation processes

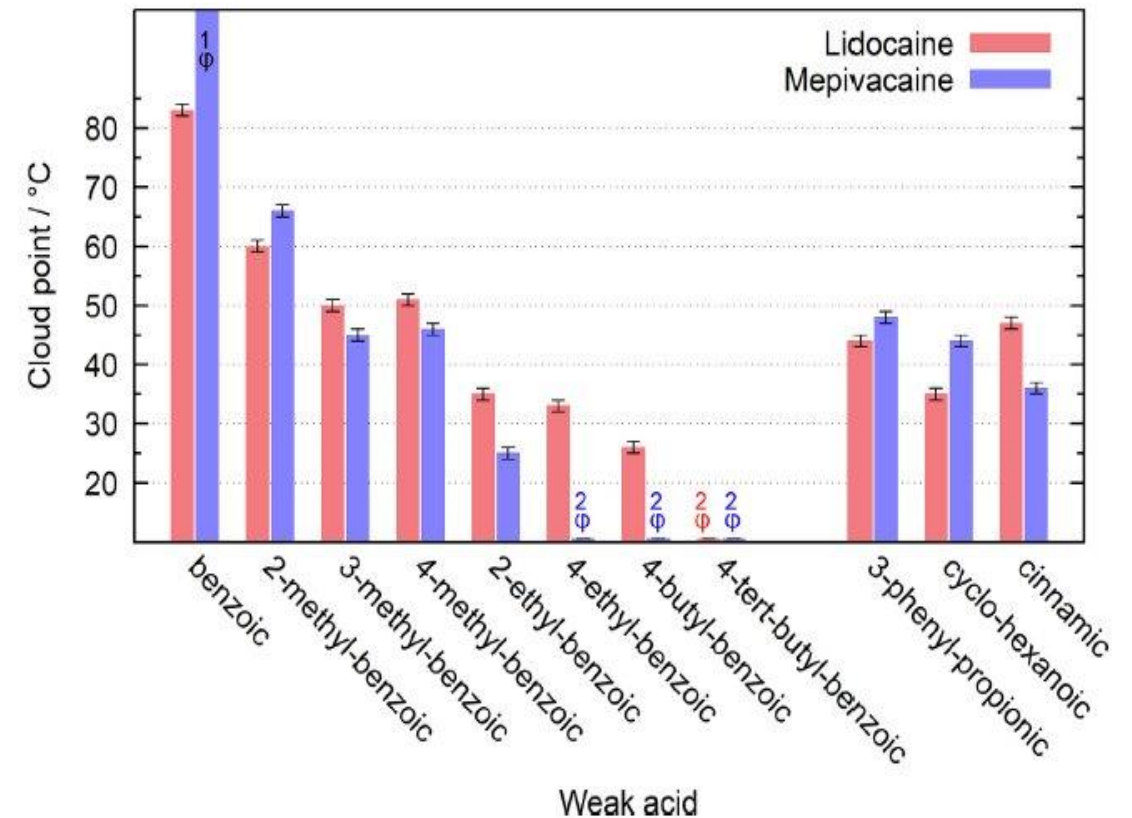
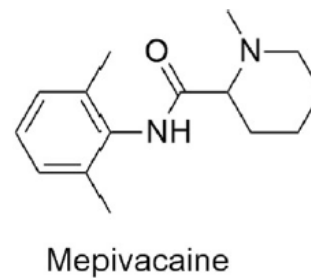
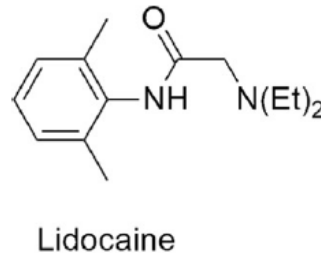
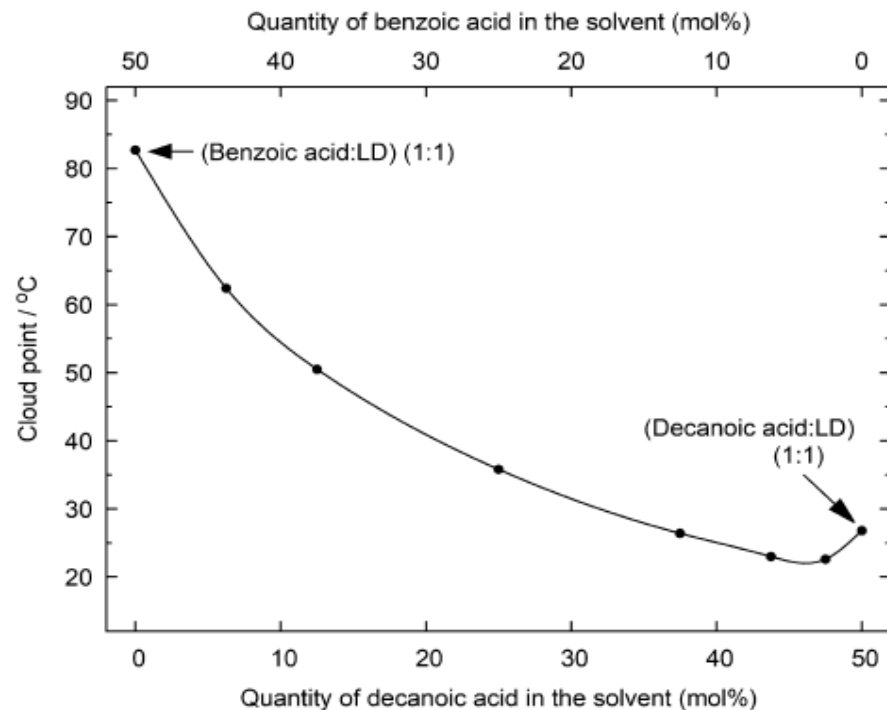


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J. C. Corzo, K. B. Busserolles, J. Coxam, A. Gautier, J. M. Andanson*, *J. Mol. Liq.* 2023, **377**, 121468

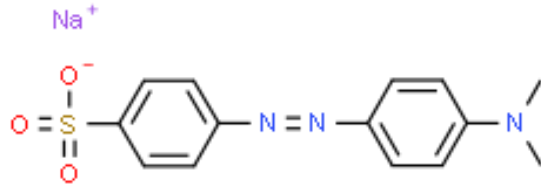
1. Deep Eutectic solvents show LCST phenomena,
2. Cloud point temperature can be adjusted based on acid: base ratio



Thermo-switchable hydrophobic solvents formulated with weak acid and base for greener separation processes



J. C. Corzo, K. B. Busserolles, J. Coxam, A. Gautier, J. M. Andanson*, *J. Mol. Liq.*, 2023, **377**, 121468



Achieved 99% extraction of anionic dye, methyl orange, with tested solvents.

	Solvent	(Acid:base) (mol%)	Cloud point	EE ⁵
1	Decanoic acid:LD	(50:50)	27 °C	99 %
2	Decanoic acid:LD	(50:50)	27 °C	99 %
3	Pentanoic acid:LD	(50:50)	57 °C	89 %
4	Pentanoic acid:LD	(68:32)	33 °C	89 %
5	Pentanoic acid:LD	(68:32)	33 °C	90 %
6	2EB ¹ acid:LD	(50:50)	35 °C	96 %
7	2EB ¹ acid:LD	(50:50)	35 °C	99 %
8	3PP ² acid:LD	(50:50)	44 °C	99 %
9	3PP ² acid:LD	(35:65)	31 °C	97 %
10	3PP ² acid:LD	(35:65)	31 °C	99 %
11	Decanoic acid ³	100 % ³	–	2 %
12	LD in octanol ⁴	10 wt% ⁴	–	50 %

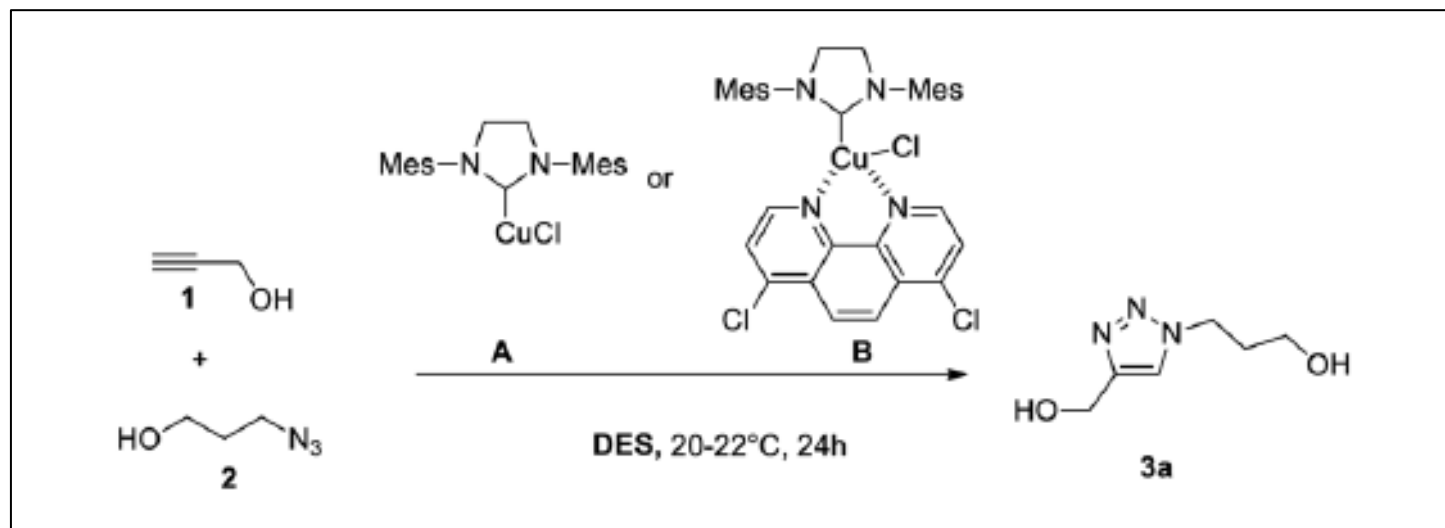
Thermo-switchable hydrophobic deep eutectic solvent for CuAAC



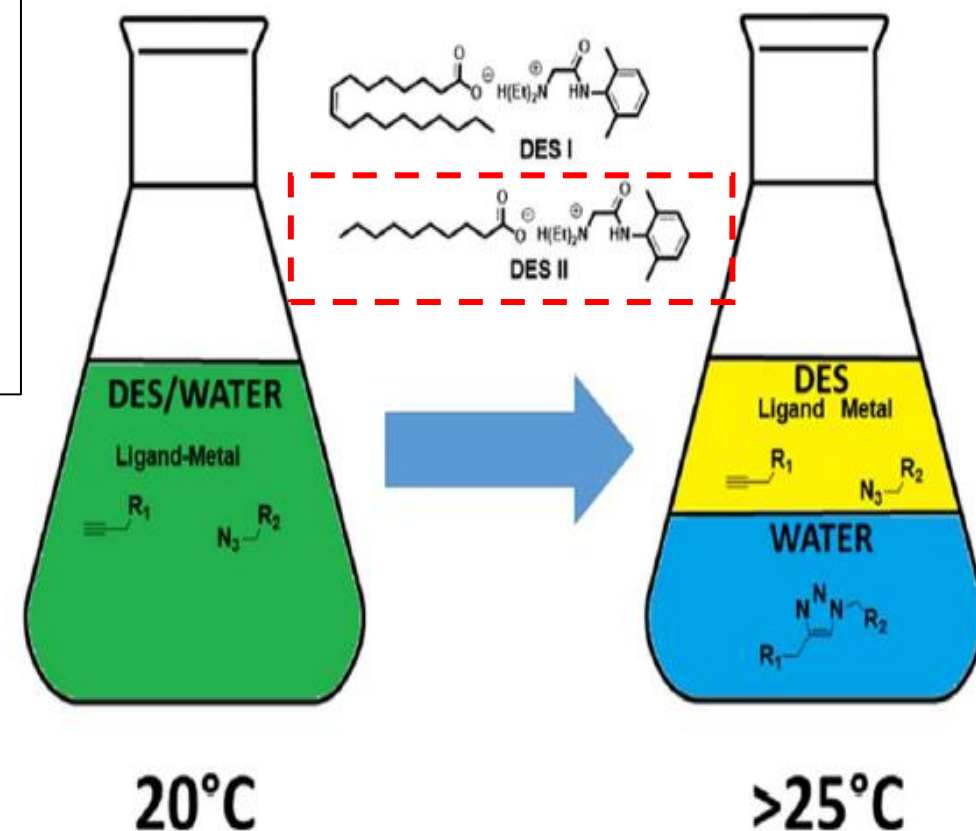
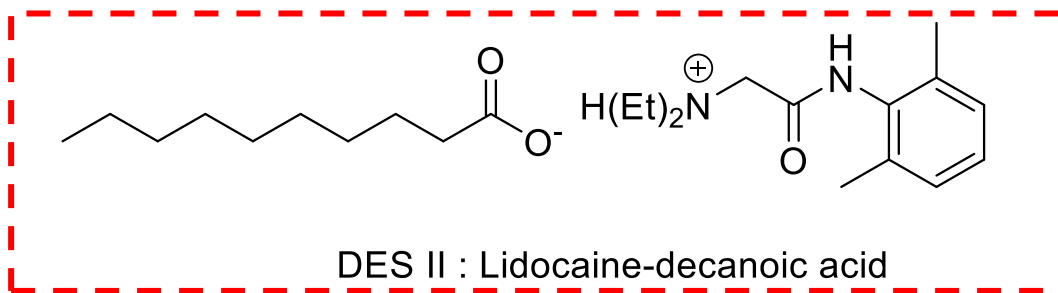
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F. C. Pouget, J. M. Andanson* and A. Gautier *, *RSC Sustainability*, **2023**, 1, 1826–1832



1. Solvent separates into aqueous and organic layers upon thermal trigger,
2. DES acts as a metal trap, providing products with low copper contamination



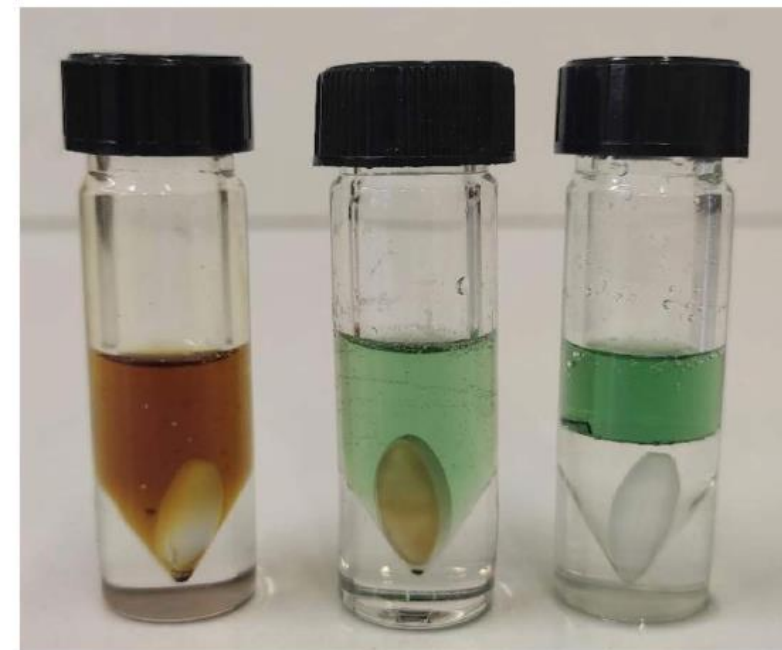
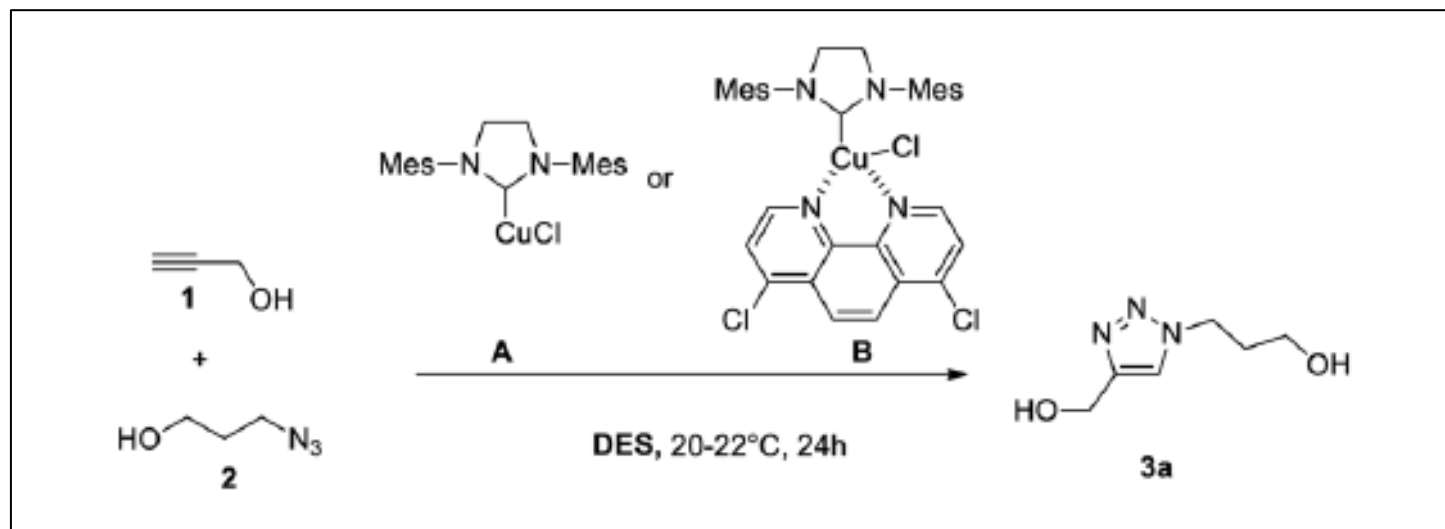
Thermo-switchable hydrophobic deep eutectic solvent for CuAAC



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F. C. Pouget, J. M. Andanson* and A. Gautier *, *RSC Sustainability*, **2023**, 1, 1826–1832



Experiment	1	2	3	4	5
Yield (catalyst) ^a	95% (B)	99% (B)	95% (B)	95% (B)	95% (B)
Copper ^b	0.03%	0.04%	0.02%	0.05%	0.02%
Yield (catalyst) ^a	97% (B)	95% (A)	97% (A)	80% (A)	59% (A)
Copper ^b	0.03%	0.2%	0.07%	0.18%	0.37%

^a Measured by ¹H NMR with 3-trimethylsilyl-1-propanesulfonic acid sodium salt as internal standard. ^b Contamination: mass Cu/total mass.

1. Good yields of alkyne-azide cycloaddition achieved in aqueous layer,
2. Low contamination of products by metals; good reusability of solvents.

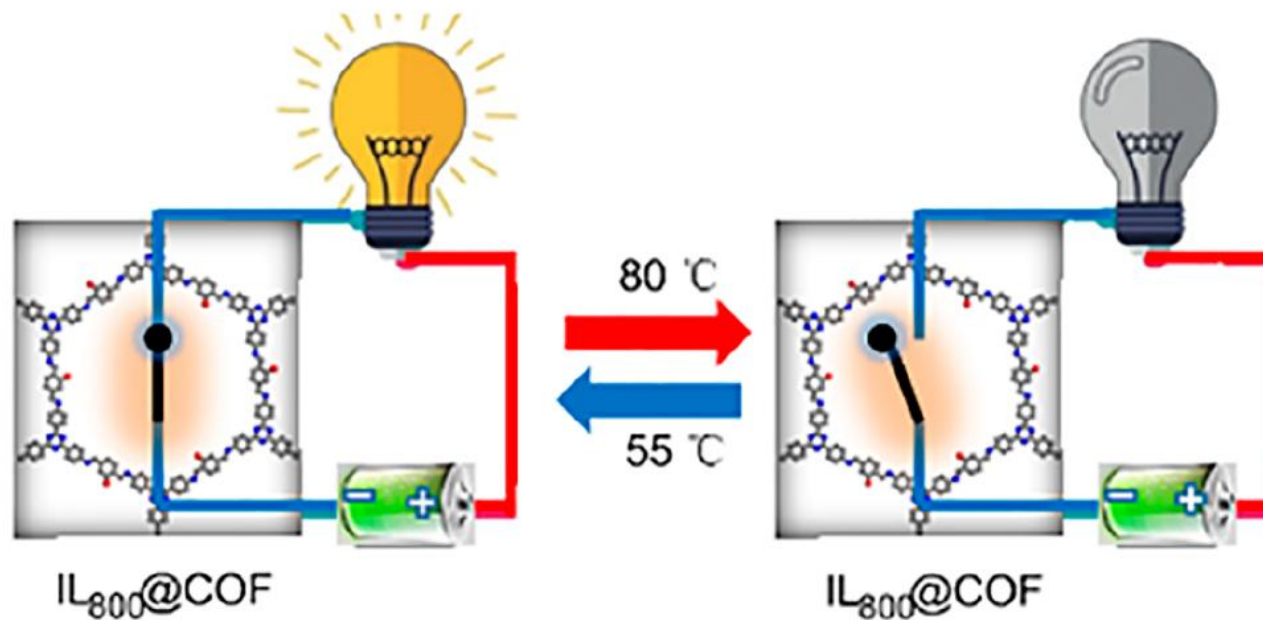
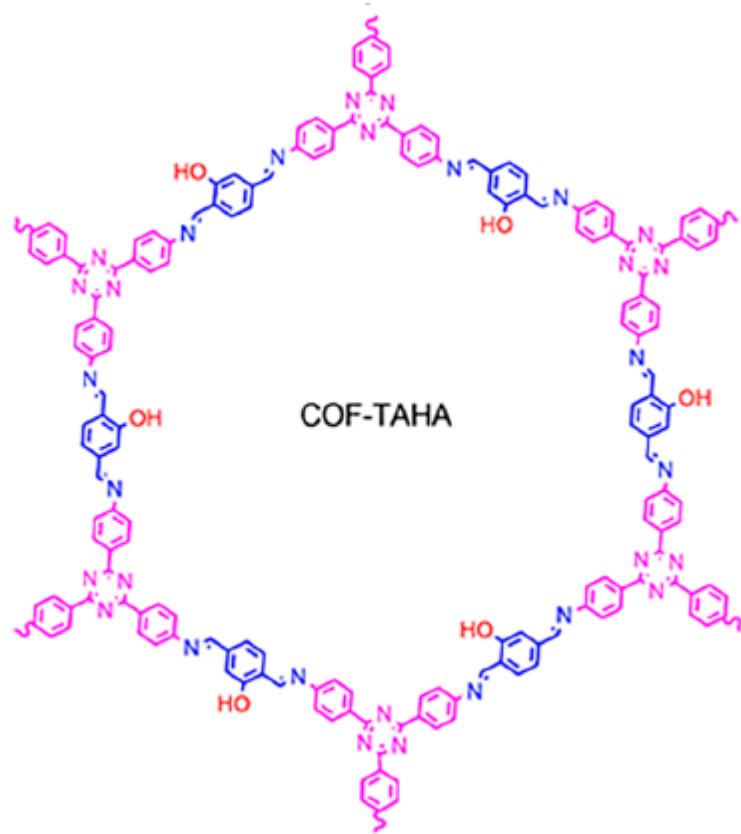
Liquid-liquid Phase separation of Aqueous Ionic Liquids in Covalent Organic Frameworks for Thermal Switchable Proton Conductivity



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Concept

TA: 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline
HA: 2-hydroxyterephthalaldehyde

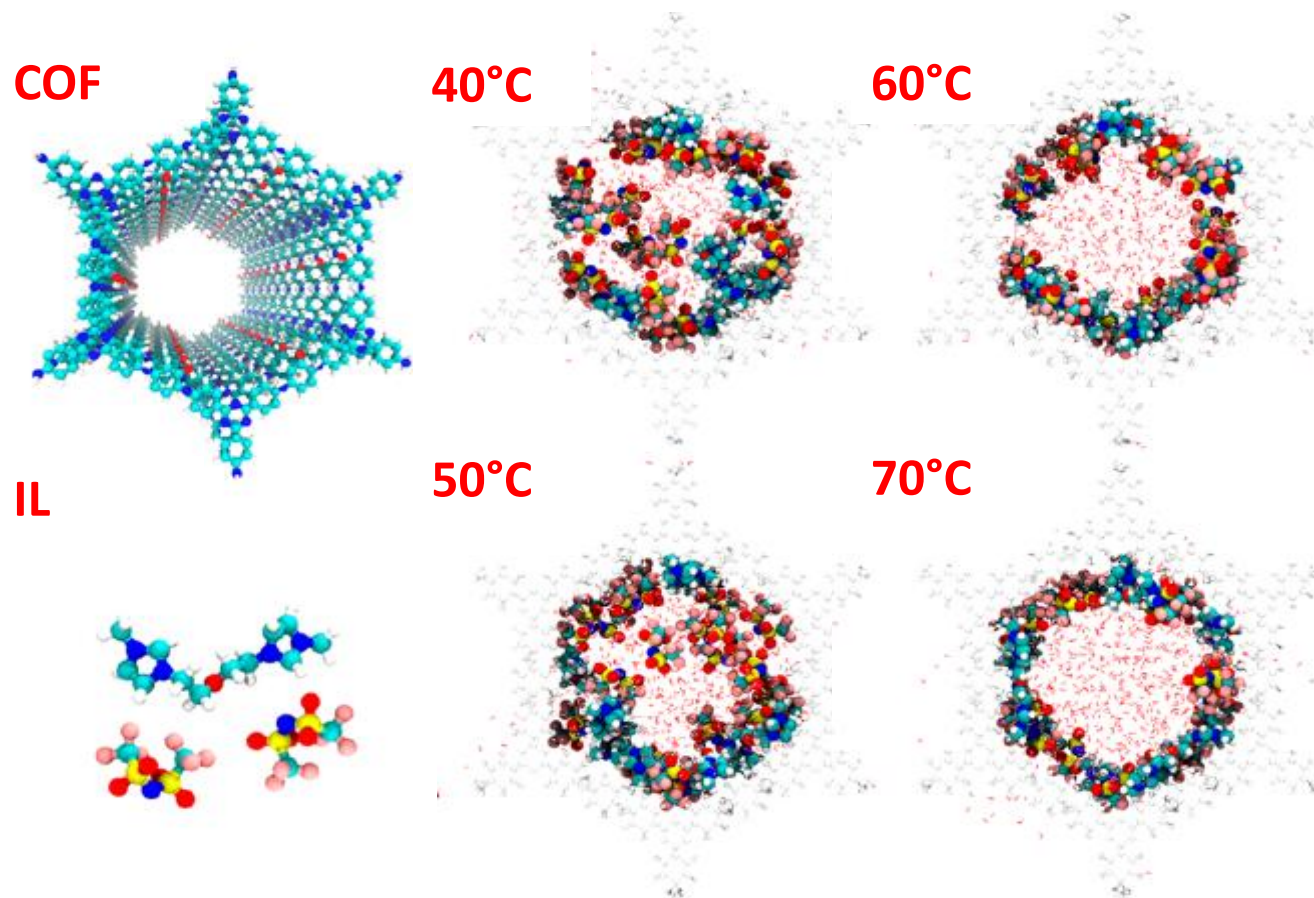
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Molecular Dynamics simulations used to study phase separation in IL@COF hybrids

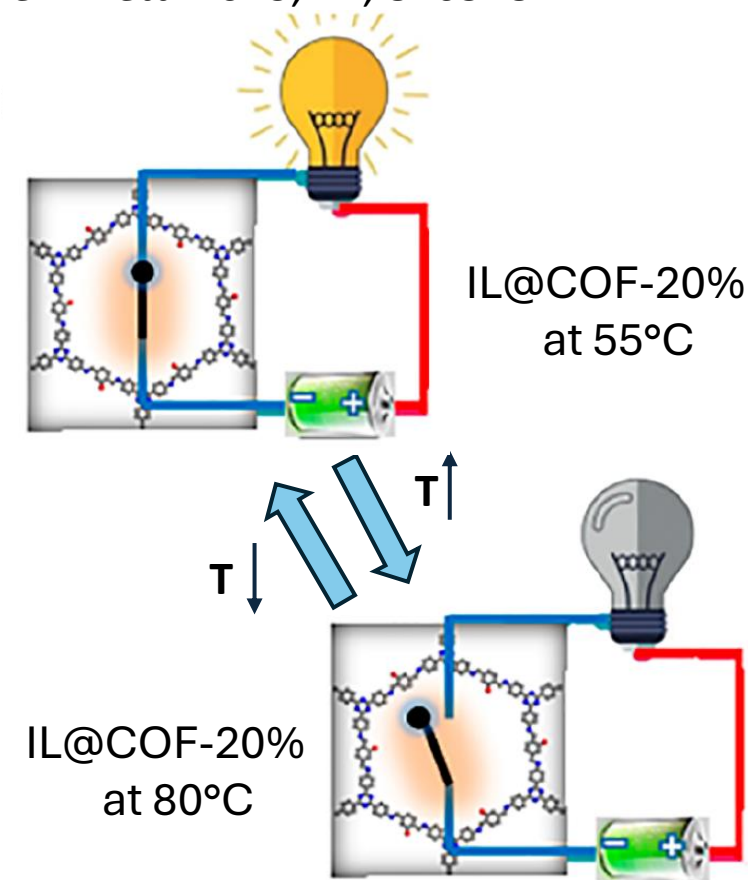
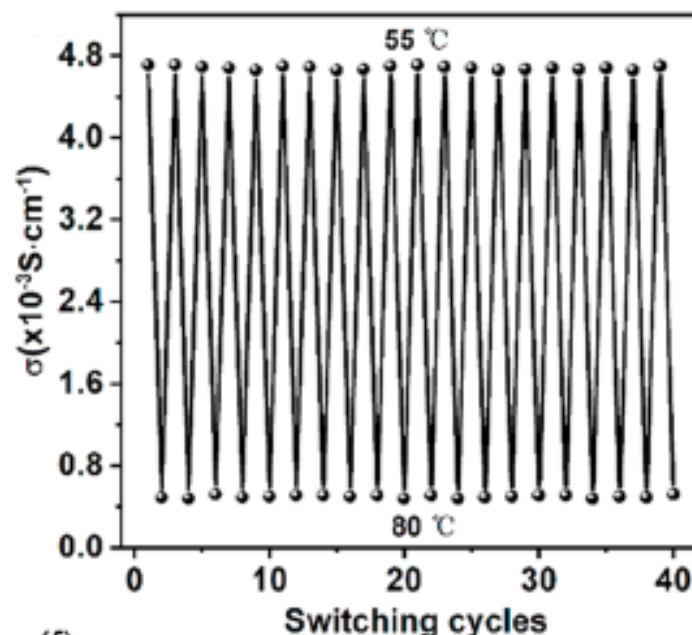
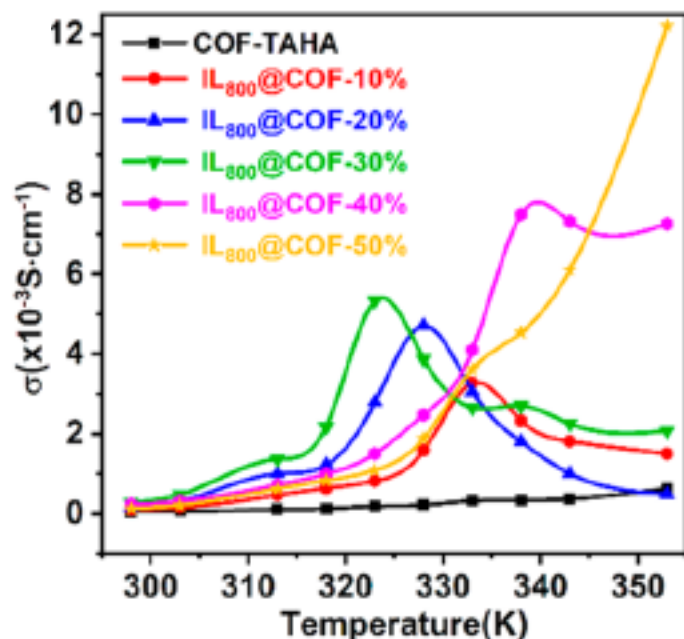
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Conductivity performance of the IL@COF hybrids

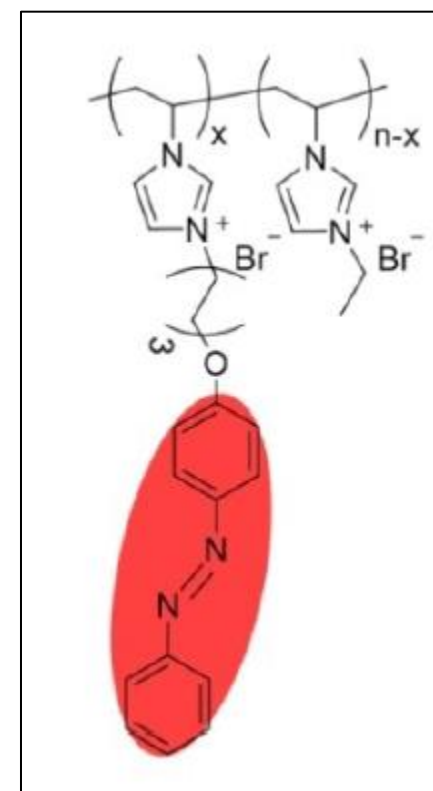
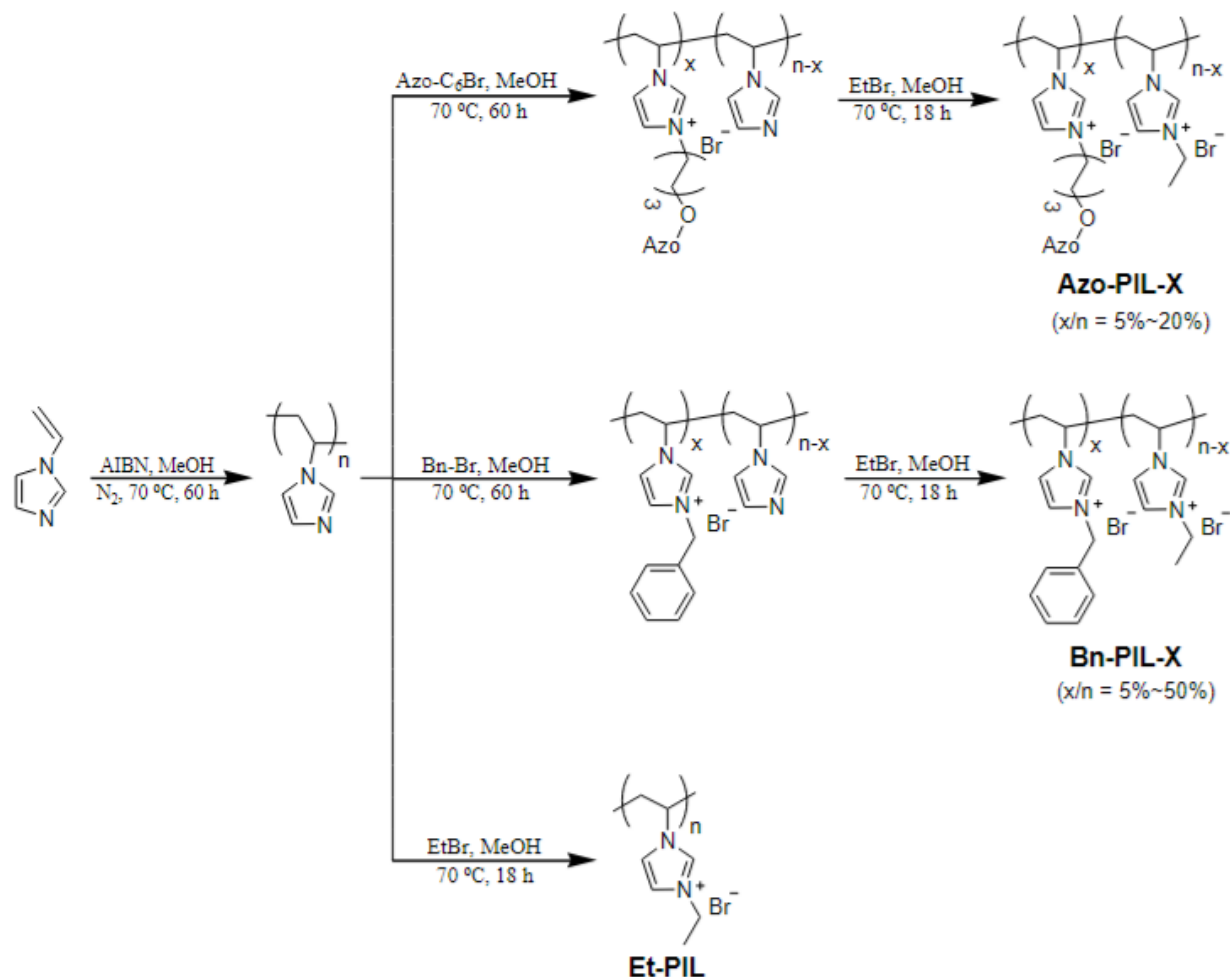
Up/Down Tuning of Poly(Ionic Liquids) in Aqueous Two-phase System



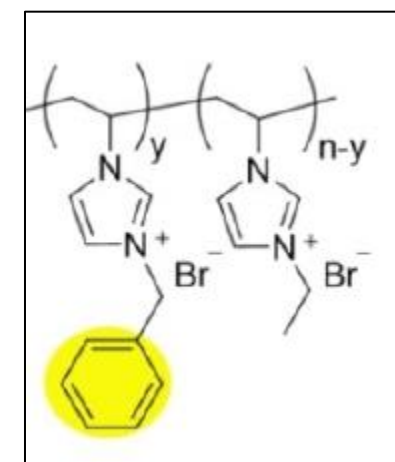
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Azobenzene modified-Poly(Ionic liquid)-X



Benzyl modified-Poly(Ionic liquid)-X

X: molar percentage of corresponding alkyl bromide w.r.t imidazole repeat units

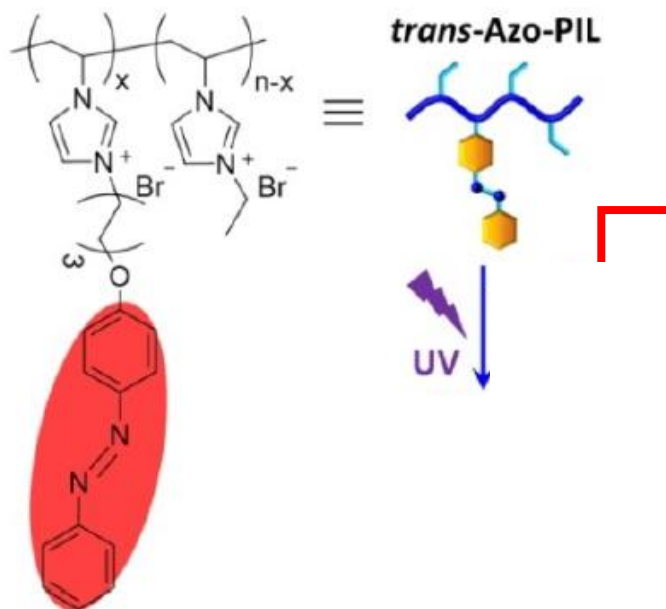
Up/Down Tuning of Poly(Ionic Liquids) in Aqueous Two-phase System



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Aqueous Two-phase System:

1. Grafting degree (GD) tuned-
2. Thermo-tuned migration
3. Light irradiation tuned-

Up/Down Tuning of Poly(Ionic Liquids) in Aqueous Two-phase System

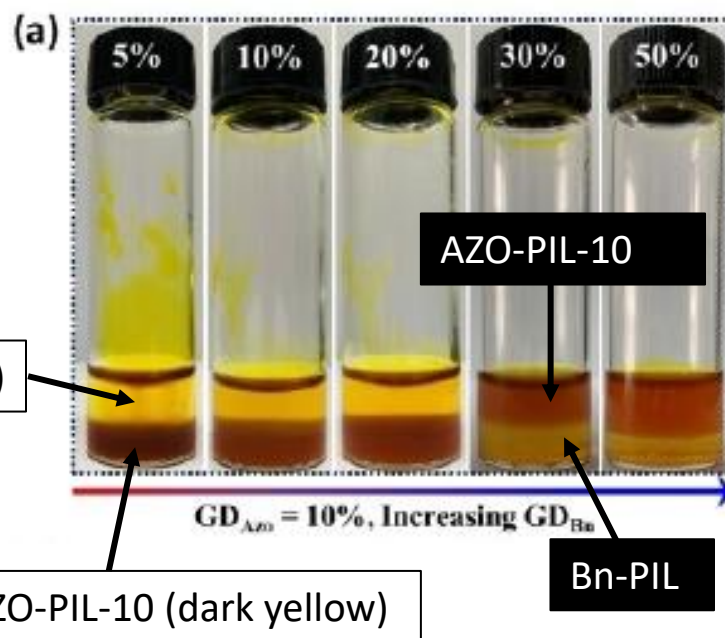


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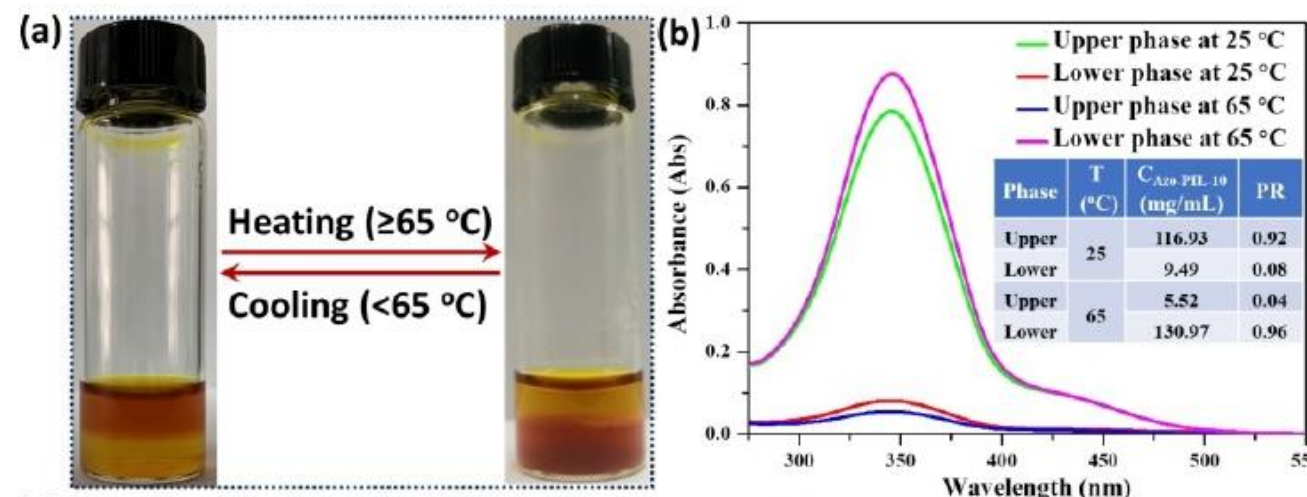
Y. Tang, Y. Zhang, X. Chen, X. Xie, N. Zhou, Z. Dai,* and Y. Xiong*, *Angew. Chem. Int. Ed.* **2023**, 62, e202215722

1. Grafting degree (GD) tuned-



Hydrodynamic Diameter (D_h) of AZO-PIL & Bn-PIL decreased with increasing GD_{azo} & GD_{Bn}

2. Thermo-tuned migration



Hydrodynamic Diameter (D_h) of AZO-PIL-10 & Bn-PIL-30 decreased with increasing temperatures,

Decrease is more for AZO-PIL-10 than for Bn-PIL-30

Up/Down Tuning of Poly(Ionic Liquids) in Aqueous Two-phase System

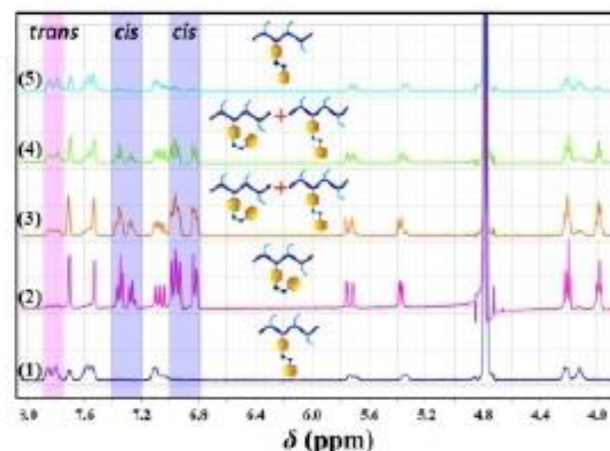


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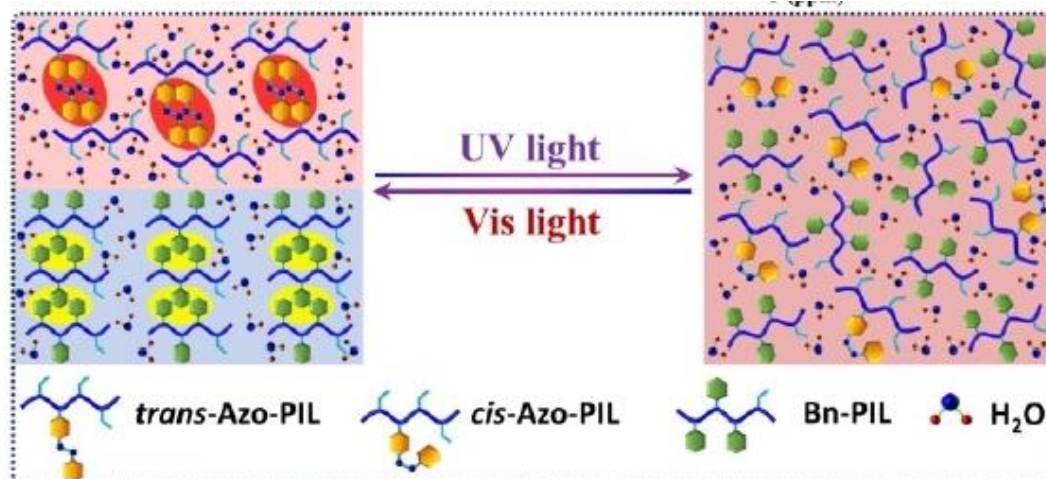
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3. Light irradiation tuned-



Cis-Azo-PIL becomes more compatible with Bn-PIL, leading to formation of homogeneous single-phase solution, that can be reversed





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Published as part of Chemical Reviews *virtual special issue* "Ionic Liquids for Diverse Applications".

Pankaj Bharmoria,* Alesia A. Tietze, Dibyendu Mondal, Tejwant Singh Kang, Arvind Kumar,* and Mara G Freire*

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David Mecerreyes,* Nerea Casado, Irune Villaluenga, and Maria Forsyth



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Catalytic depolymerization of polyester plastics toward closed-loop recycling and upcycling

Yujing Weng, ^{†a,b} Cheng-Bin Hong, ^{†a} Yulong Zhang*^b and Haichao Liu ^a

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Viewpoint

Ionic-Liquid-Mediated Deconstruction of Polymers for Advanced Recycling and Upcycling

Ty Christoff-Tempesta and Thomas H. Epps, III*



Cite This: *ACS Macro Lett.* 2023, **12**, 1058–1070



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Ionic liquids and electrocatalysis



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Role of Ionic Solvents in the Electrocatalytic CO₂ Conversion and H₂ Evolution Suppression: from Ionic Liquids to Deep Eutectic Solvents

Alejandro Leal-Duaso,^[a, b] Yanis Adjaz,^[a] and Carlos M. Sánchez-Sánchez^{*,[a]}

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Short Review

Ionic liquid derived electrocatalysts for electrochemical water splitting

Tianhao Li ^{a,b,*}, Weihua Hu ^{a,*}

 *molecules*



Review

Ionic Liquids as Promisingly Multi-Functional Participants for Electrocatalyst of Water Splitting: A Review

Chenyun Zhang ¹, Puyu Qu ¹, Mei Zhou ¹, Lidong Qian ¹, Te Bai ¹, Jianjiao Jin ¹ and Bingwei Xin ^{2,*}

Ionic liquids – general knowledge



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Microwave Encounters Ionic Liquid: Synergistic Mechanism, Synthesis and Emerging Applications

Zhenyu Zhao, Hong Li,* and Xin Gao*



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- **Everyone who contributed to this presentation**