Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Does the active hydrogen atom on the hydantoin anion affect the physical properties, CO_2 capture and conversion of ionic liquid?

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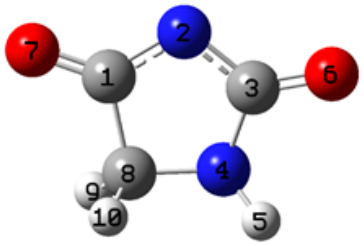
The method for estimating the enthalpy (−Δ*H*) of intermolecular H-bonds.

According to literature[1], the enthalpy (−Δ*H*) of intermolecular H-bonds in 1:1 H-bonded complexes in liquid phases (solutions) could be evaluated as follows:

$$-\Delta H\ [\mathrm{kcal\cdot mol^{-1}}] = 0.33\left(\Delta\nu\ [\mathrm{cm^{-1}}] - 40\right)^{1/2} \quad (1)$$

where $\Delta v = v\mathrm{XH}_{\mathrm{free}} - v\mathrm{XH}_{\mathrm{bonded}}$ represents the red-shift value of the νXH frequency caused by the formation of the H-bond with the XH group being the proton donor. For $[\mathrm{Hy}]^-$ and $[\mathrm{Hy\cdots Hy}]^-$ of the present study, $v\mathrm{NH}_{\mathrm{free}}$ and $v\mathrm{NH}_{\mathrm{bonded}}$ obtained from DFT calculations are 3656.61 and 3080.43 $\mathrm{cm^{-1}}$, respectively, and Δv = 576.18 $\mathrm{cm^{-1}}$, so ΔH = – 31.95 kJ/mol.

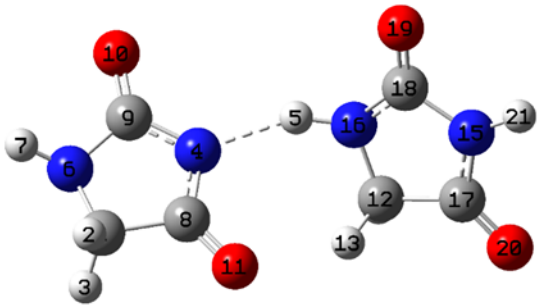
(a) [Hy]⁻



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.109315	-0.277610	0.004160
2	7	0	0.009796	-1.064022	-0.029552
3	6	0	-1.100785	-0.260162	-0.027552
4	7	0	-0.741198	1.118229	-0.163839
5	1	0	-1.374770	1.755364	0.301306
6	8	0	-2.288572	-0.595470	0.060997
7	8	0	2.305631	-0.610886	0.006487
8	6	0	0.689052	1.219155	0.056072
9	1	0	1.212554	1.789462	-0.720933
10	1	0	0.960074	1.638263	1.037421

(b) [Hy···Hy]$^{-}$



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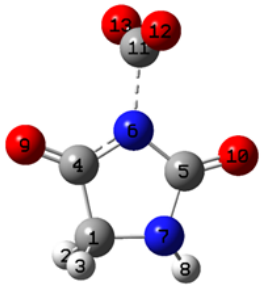
1	6	0	-3.301606	-1.257358	0.572574
2	1	0	-3.522473	-1.278064	1.649886
3	1	0	-3.607743	-2.214820	0.135436
4	7	0	-1.574229	0.184782	-0.183309
5	1	0	0.186950	0.755098	-0.281152
6	7	0	-3.851010	-0.105049	-0.116039
7	1	0	-4.712269	0.326927	0.189165
8	6	0	-1.785313	-1.032005	0.366771
9	6	0	-2.792956	0.796520	-0.399180
10	8	0	-3.000167	1.943526	-0.795538
11	8	0	-0.940153	-1.884755	0.685014
12	6	0	1.676939	-0.713048	-0.774708
13	1	0	1.080952	-1.493581	-0.281549
14	1	0	1.631556	-0.868921	-1.858680
15	7	0	3.307233	0.446559	0.354504
16	7	0	1.214033	0.612654	-0.382147
17	6	0	3.126408	-0.741491	-0.309270
18	6	0	2.134360	1.261389	0.372877
19	8	0	2.070379	2.330152	0.966245
20	8	0	3.965033	-1.615158	-0.486758
21	1	0	4.163111	0.726581	0.809743

(c) $[Hy\text{-}CO_2]^-$



Standard orientation:

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1	6	0	2.137073	0.667382	0.032114
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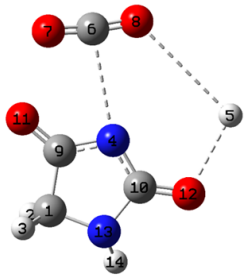
3	1	0	2.705832	1.147970	-0.771193
4	6	0	0.667633	1.135898	-0.009388
5	6	0	0.653208	-1.135954	-0.004564
6	7	0	-0.113525	0.019515	-0.015716
7	7	0	2.005641	-0.768946	-0.139985
8	1	0	2.666473	-1.410426	0.275447
9	8	0	0.325509	2.312891	-0.028001
10	8	0	0.265986	-2.291905	0.094156
11	6	0	-1.825273	0.016748	-0.004413
12	8	0	-2.240702	-0.076299	-1.146213
13	8	0	-2.224297	0.111344	1.143226

(d) $[Hy\text{-}CO_2\cdots H]^-$



Standard orientation:

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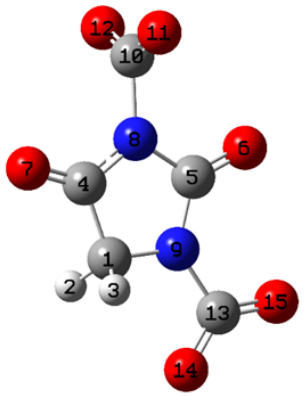
3	1	0	-1.947661	-2.228233	-0.704476
4	7	0	-0.262811	0.371595	-0.042797
5	1	0	-0.188457	3.374007	0.180926
6	6	0	2.610316	0.327487	0.000446
7	8	0	2.700490	0.336444	-1.167067
8	8	0	2.658572	0.361790	1.170014
9	6	0	-0.295715	-0.978670	0.005800
10	6	0	-1.549644	0.838107	-0.041758
11	8	0	0.665109	-1.765126	0.012724
12	8	0	-1.939432	2.012750	0.030957
13	7	0	-2.483083	-0.231042	-0.155852
14	1	0	-3.372527	-0.062055	0.294781

(e) [Hy-2CO_2]$^{2-}$



Standard orientation:

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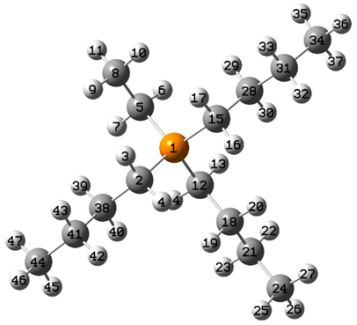
1	6	0	0.803665	1.462836	-0.000004
2	1	0	1.157799	2.009290	0.881831
3	1	0	1.157882	2.009150	-0.881892
4	6	0	-0.716873	1.374323	-0.000046
5	6	0	0.143154	-0.767775	0.000051
6	8	0	0.105529	-1.986514	0.000129
7	8	0	-1.480988	2.346302	-0.000093
8	7	0	-1.027461	0.054686	-0.000020
9	7	0	1.244020	0.080073	0.000118
10	6	0	-2.486360	-0.516664	0.000040
11	8	0	-2.937771	-0.685698	-1.141067
12	8	0	-2.937626	-0.685810	1.141189
13	6	0	2.705096	-0.227875	-0.000042
14	8	0	3.400792	0.823423	-0.000233
15	8	0	3.034603	-1.425555	-0.000003

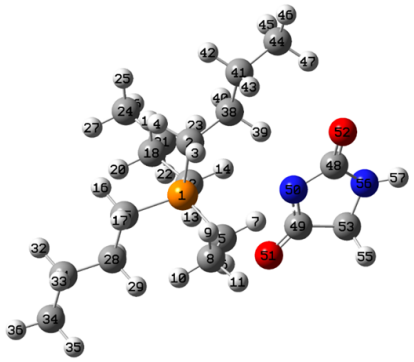
(f) $[P_{4442}]^+$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.000131	-0.582826	0.220716
2	6	0	-1.478183	-0.769711	-0.833755
3	1	0	-1.409181	-1.759799	-1.300334
4	1	0	-1.381049	-0.036271	-1.643208
5	6	0	0.000295	-1.857228	1.532167
6	1	0	0.879226	-1.661279	2.156472
7	1	0	-0.878806	-1.661635	2.156341
8	6	0	0.000631	-3.304928	1.015290
9	1	0	-0.887000	-3.525294	0.415103
10	1	0	0.888498	-3.524954	0.415328
11	1	0	0.000654	-3.992221	1.865115
12	6	0	-0.000106	1.055571	1.024678
13	1	0	0.879153	1.086441	1.679147
14	1	0	-0.879213	1.086065	1.679368
15	6	0	1.478493	-0.769342	-0.833747
16	1	0	1.381218	-0.035876	-1.643161
17	1	0	1.409689	-1.759418	-1.300378
18	6	0	-0.000493	2.250309	0.053577
19	1	0	-0.881758	2.203825	-0.599136
20	1	0	0.880598	2.204205	-0.599395
21	6	0	-0.000670	3.590426	0.805317
22	1	0	0.878788	3.634277	1.461109
23	1	0	-0.879970	3.633911	1.461346
24	6	0	-0.001047	4.791956	-0.144977
25	1	0	-0.886995	4.787429	-0.789849
26	1	0	-0.001159	5.732022	0.413856
27	1	0	0.884725	4.787785	-0.790093
28	6	0	2.823852	-0.600686	-0.104418
29	1	0	2.909667	-1.337121	0.704927
30	1	0	2.875462	0.391174	0.362387
31	6	0	4.012339	-0.766537	-1.064451
32	1	0	3.922310	-0.033014	-1.876388
33	1	0	3.959924	-1.757785	-1.533525
34	6	0	5.360685	-0.596525	-0.357402
35	1	0	5.486386	-1.336906	0.440585
36	1	0	6.188926	-0.721368	-1.060566
37	1	0	5.450934	0.399541	0.090376
38	6	0	-2.823576	-0.601289	-0.104436
39	1	0	-2.909233	-1.337682	0.704966
40	1	0	-2.875397	0.390595	0.362294
41	6	0	-4.012034	-0.767473	-1.064446
42	1	0	-3.922176	-0.033986	-1.876435
43	1	0	-3.959401	-1.758742	-1.533450
44	6	0	-5.360410	-0.597715	-0.357393
45	1	0	-5.450869	0.398355	0.090336
46	1	0	-6.188632	-0.722774	-1.060540
47	1	0	-5.485942	-1.338082	0.440634

(g) $[P_{4442}][Hy]$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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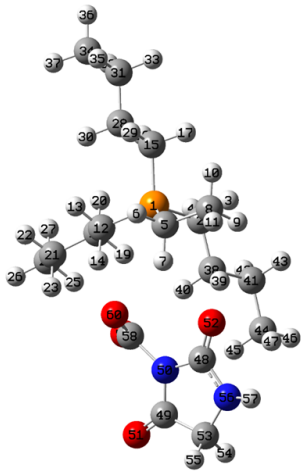
3	1	0	0.047658	1.557263	-2.592417
4	1	0	0.654531	2.616928	-1.324657
5	6	0	0.433907	-1.239486	-1.625336
6	1	0	0.708940	-2.067256	-0.962821
7	1	0	-0.661313	-1.231789	-1.609154
8	6	0	1.014924	-1.381133	-3.038181
9	1	0	0.745155	-0.540612	-3.687346
10	1	0	2.106034	-1.473889	-3.036609
11	1	0	0.610183	-2.287107	-3.498523
12	6	0	0.566875	0.208262	1.019258
13	1	0	0.927851	-0.764942	1.368490
14	1	0	-0.524717	0.139633	1.082210
15	6	0	2.706090	0.565915	-1.003735
16	1	0	2.951536	1.535026	-0.553751
17	1	0	2.882345	0.664774	-2.081419
18	6	0	1.132800	1.380070	1.833529
19	1	0	0.787885	2.337645	1.418910
20	1	0	2.230337	1.394095	1.783147
21	6	0	0.701341	1.291922	3.304628
22	1	0	1.033411	0.330327	3.716911
23	1	0	-0.394790	1.284232	3.353767
24	6	0	1.253834	2.442645	4.151689
25	1	0	0.908892	3.412488	3.773689
26	1	0	0.930946	2.357893	5.194332
27	1	0	2.350469	2.451771	4.141659
28	6	0	3.585350	-0.545802	-0.407143
29	1	0	3.309232	-1.515323	-0.840515
30	1	0	3.397601	-0.627896	0.670765
31	6	0	5.080236	-0.290958	-0.643054
32	1	0	5.352564	0.681274	-0.210151
33	1	0	5.266424	-0.211208	-1.722756
34	6	0	5.965364	-1.389559	-0.044841
35	1	0	5.730873	-2.366772	-0.482277
36	1	0	7.025869	-1.187223	-0.225732
37	1	0	5.818874	-1.467384	1.038605
38	6	0	-1.399007	1.928545	-0.998428
39	1	0	-1.956967	0.988168	-1.018284
40	1	0	-1.367439	2.233992	0.055307
41	6	0	-2.155875	2.985314	-1.811540
42	1	0	-1.592039	3.930277	-1.823922
43	1	0	-2.221756	2.648870	-2.855919
44	6	0	-3.567391	3.214602	-1.257018
45	1	0	-3.523151	3.630808	-0.243163
46	1	0	-4.129524	3.916614	-1.882561
47	1	0	-4.114464	2.268203	-1.200550
48	6	0	-3.464834	-1.062070	0.121558
49	6	0	-1.747555	-2.315032	0.773224
50	7	0	-2.085692	-1.176141	0.130493
51	8	0	-0.595880	-2.744621	0.974621
52	8	0	-4.119047	-0.192235	-0.461348
53	6	0	-3.020785	-3.049470	1.246511
54	1	0	-2.968576	-3.256868	2.321209
55	1	0	-3.119584	-4.004319	0.712038
56	7	0	-4.040692	-2.077922	0.896331
57	1	0	-4.997224	-2.334179	0.698891

(h) $[P_{4442}][Hy\text{-}CO_2]$



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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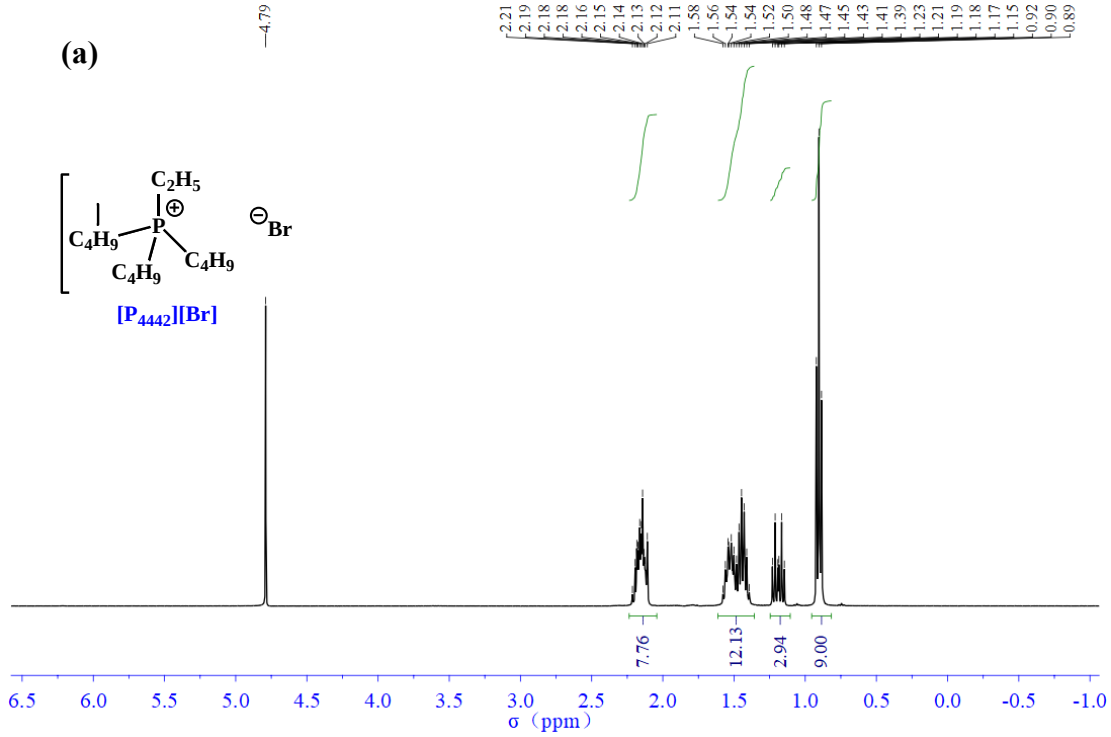
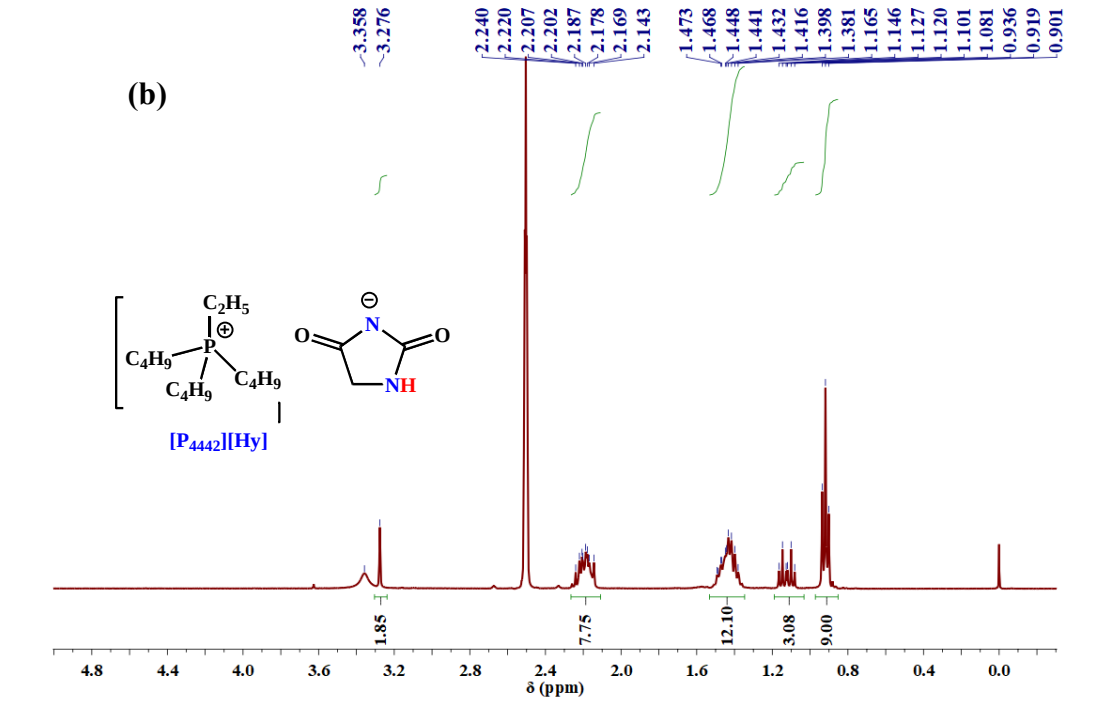
4	1	0	-1.324042	0.467701	2.505036
5	6	0	-1.201983	-1.673407	-0.767186
6	1	0	-1.774746	-1.599796	-1.698802
7	1	0	-0.161952	-1.440499	-1.025566
8	6	0	-1.319107	-3.064980	-0.133023
9	1	0	-0.694408	-3.145084	0.761120
10	1	0	-2.350388	-3.327335	0.130713
11	1	0	-0.951850	-3.810071	-0.843472
12	6	0	-1.537373	1.277149	-0.547912
13	1	0	-2.388709	1.400989	-1.229452
14	1	0	-0.639403	1.147189	-1.167533
15	6	0	-3.567399	-0.542565	0.673437
16	1	0	-3.879369	0.343117	1.241508
17	1	0	-3.648386	-1.398319	1.354328
18	6	0	-1.383056	2.495304	0.376073
19	1	0	-0.536683	2.330390	1.050490
20	1	0	-2.282027	2.641889	0.993737
21	6	0	-1.095396	3.762377	-0.439863
22	1	0	-1.913877	3.934295	-1.153322
23	1	0	-0.184340	3.583395	-1.021495
24	6	0	-0.910827	4.996182	0.448853
25	1	0	-0.068083	4.856262	1.135336
26	1	0	-0.703954	5.887890	-0.151924
27	1	0	-1.807019	5.197412	1.049651
28	6	0	-4.473973	-0.748488	-0.550375
29	1	0	-4.166103	-1.652617	-1.090725
30	1	0	-4.360229	0.087854	-1.251785
31	6	0	-5.952734	-0.874832	-0.157305
32	1	0	-6.260249	0.030317	0.383562
33	1	0	-6.067980	-1.709778	0.547149
34	6	0	-6.867557	-1.089434	-1.367535
35	1	0	-6.599165	-2.004143	-1.908729
36	1	0	-7.914942	-1.177255	-1.061833
37	1	0	-6.793825	-0.252602	-2.071679
38	6	0	0.590129	-0.366166	1.847647
39	1	0	0.932912	-1.205051	1.234170
40	1	0	0.932555	0.541126	1.341777
41	6	0	1.245928	-0.449534	3.230518
42	1	0	0.915422	0.398010	3.847404
43	1	0	0.913005	-1.361013	3.747699
44	6	0	2.776132	-0.442706	3.119017
45	1	0	3.122237	0.464437	2.611459
46	1	0	3.249412	-0.485235	4.105695
47	1	0	3.127977	-1.301687	2.535975
48	6	0	3.010408	-1.520721	-0.647456
49	6	0	4.349353	0.314991	-1.038676
50	7	0	3.048428	-0.151567	-0.942572
51	8	0	4.726120	1.437369	-1.304777
52	8	0	2.014447	-2.223933	-0.520539
53	6	0	5.263367	-0.892648	-0.782262
54	1	0	5.953005	-0.670197	0.038370
55	1	0	5.843770	-1.102998	-1.688473
56	7	0	4.310243	-1.935176	-0.454156
57	1	0	4.513185	-2.922759	-0.468824
58	6	0	1.794431	0.693681	-1.158242
59	8	0	1.726288	1.694092	-0.434120
60	8	0	1.015975	0.209520	-1.998218

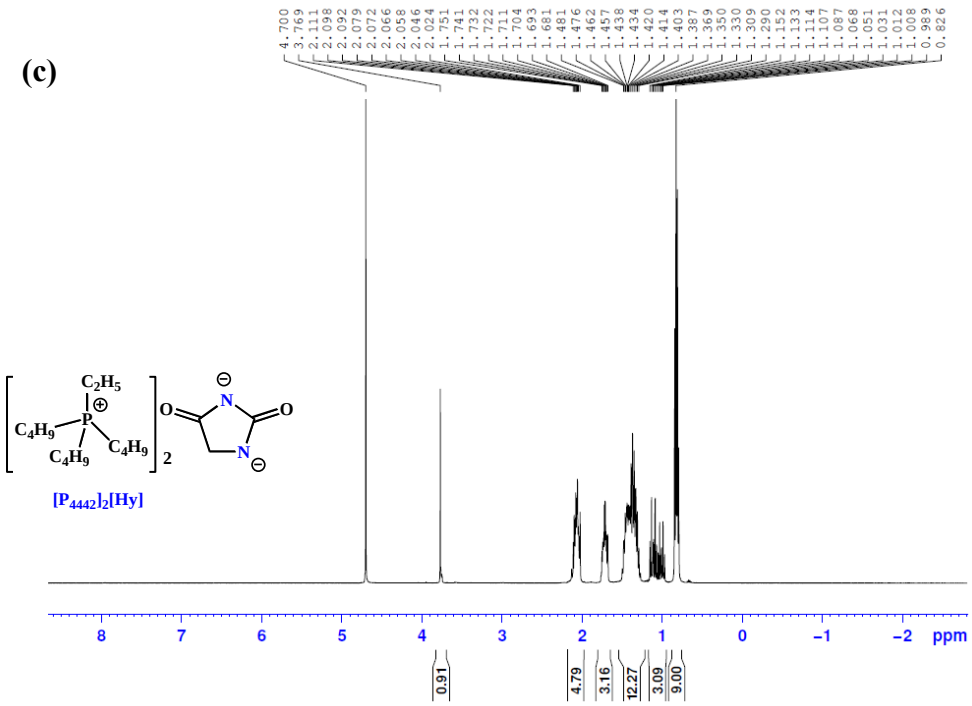
Fig. S1 The Cartesian coordinates of the optimized structures at the B3LYP-D3/6-311++G (d, p) level.



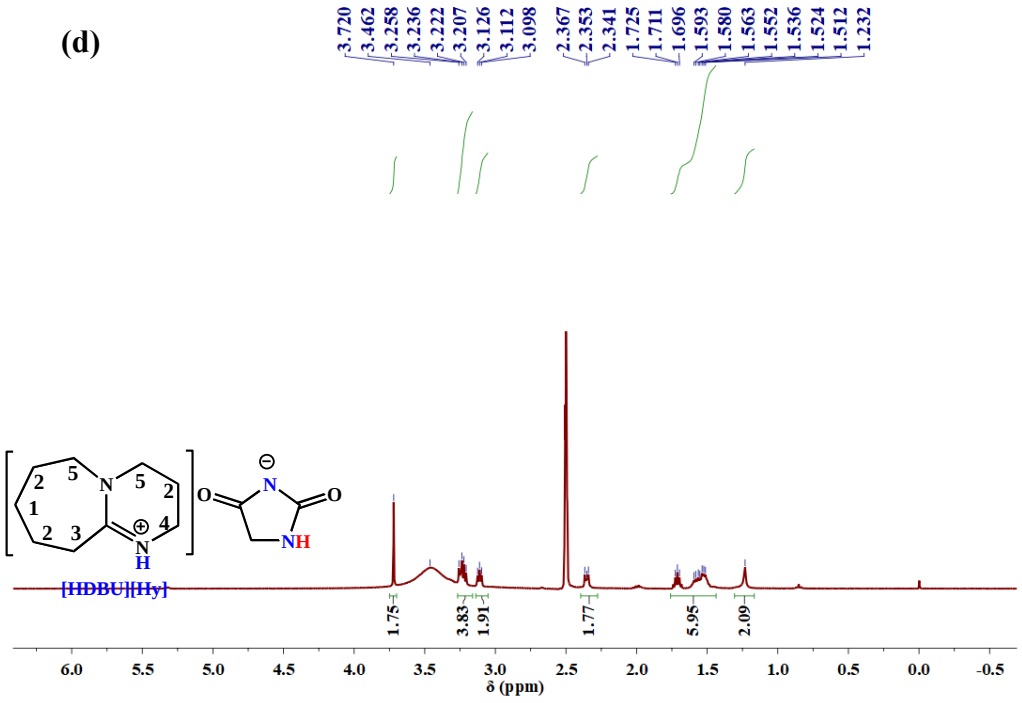
(a). $[P_{4442}][Br]$ (D_2O): cation, 0.89-0.92 (t, 9H, CH_3), 1.15-1.23 (m, 3H, CH_3), 1.39-1.56 (m, 12H, CH_2), 2.11-2.21 (m, 8H, PCH_2) ppm.



(b). $[P_{4442}][Hy]$ (DMSO-d_6): cation, 0.90-0.94 (m, 9H, CH_3), 1.08-1.17 (m, 3H, CH_3), 1.38-1.47 (m, 12H, CH_2), 2.14-2.24 (m, 8H, PCH_2) ppm; anion, 3.28 (s, 2H, CH_2), 3.36 (s, N−H) ppm.



(c). $[P_{4442}]_2[Hy]$ (D_2O): cation, 0.83-0.99 (m, 9H, CH_3), 1.01-1.15 (m, 3H, CH_3), 1.29-1.48 (m, 12H, CH_2), 1.68-2.11 (m, 8H, PCH_2) ppm; anion, 3.77 (s, 2H, CH_2) ppm. σδ



(d). [HDBU][Hy] (DMSO-d_6): cation, 1.23(m, 2H, CH_2, 1), 1.52-1.73 (m, 6H, CH_2, 2), 2.34-2.37 (t, 2H, CH_2, 3), 3.10-3.13 (t, 2H, CH_2, 4), 3.21-3.26 (t, 4H, CH_2, 5); anion, 3.72 (s, 2H, CH_2); 3.46 (s, N−H) ppm.

Fig. S2 ^{1}H NMR spectra of ILs. (a), $[P_{4442}][Br]$ (D_2O); (b), $[P_{4442}][Hy]$ (DMSO-d_6); (c), $[P_{4442}]_2[Hy]$ (D_2O); (d), [HDBU][Hy] (DMSO-d_6).

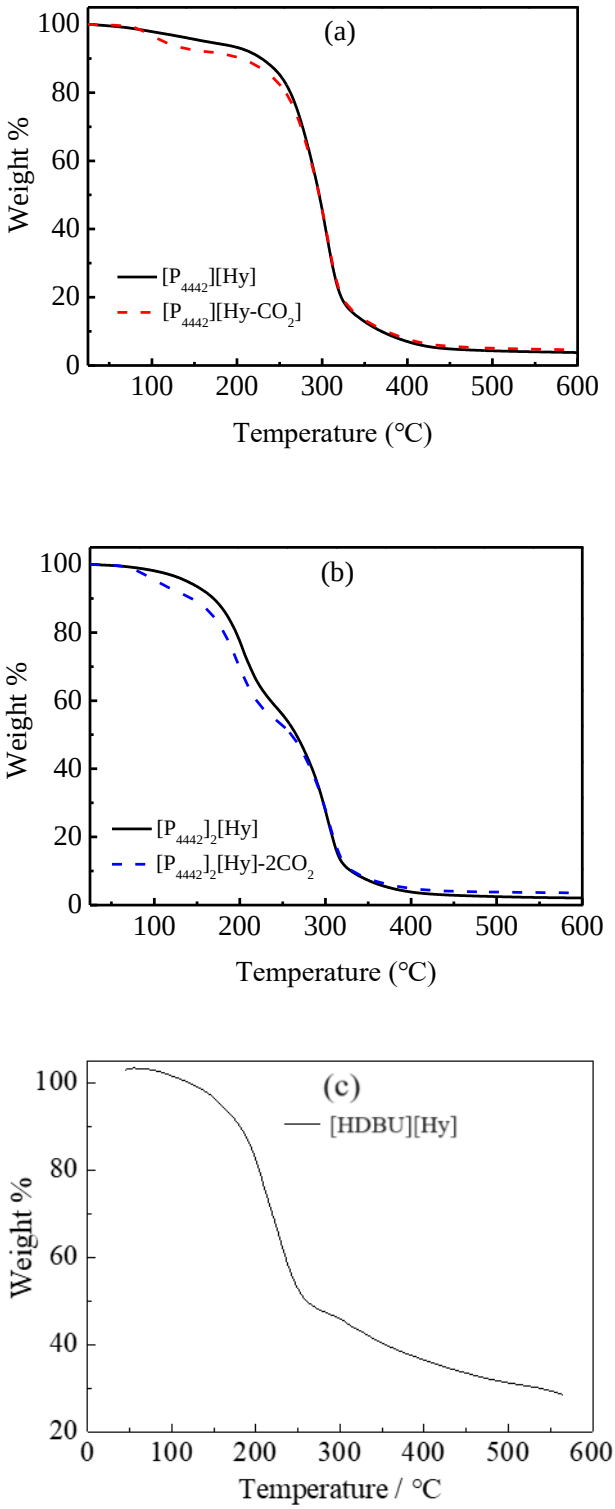


Fig. S3 Thermogravimetric curve of ILs and CO_2-absorbed ILs. (a), $[P_{4442}][Hy]$; (b), $[P_{4442}]_2[Hy]$; (c), [HDBU][Hy].

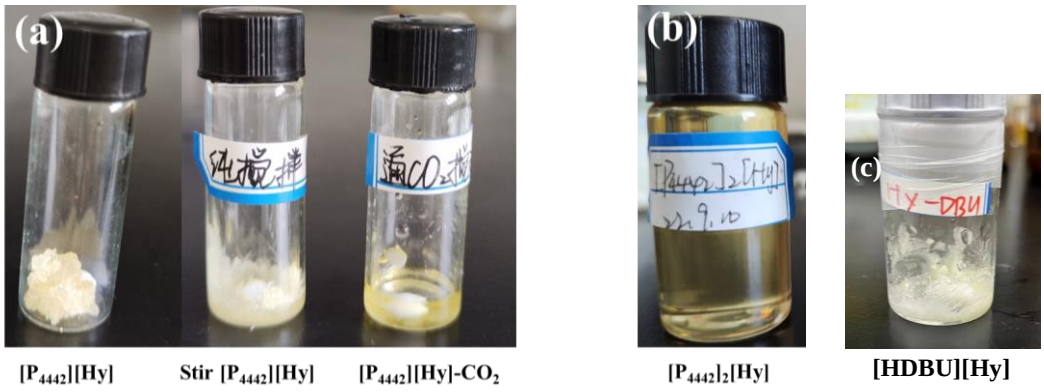
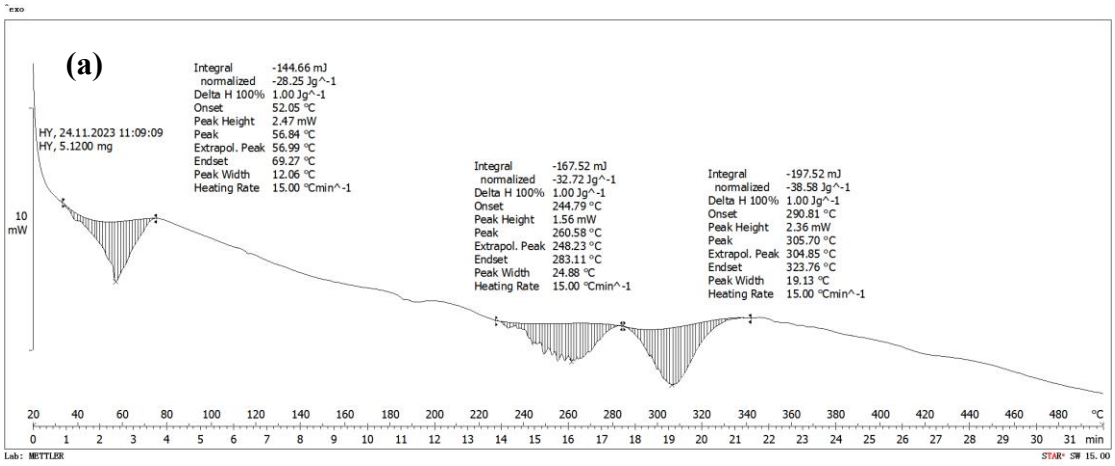


Fig. S4 The states of ILs at room temperature (~298 K). (a), $[P_{4442}][Hy]$ before CO_2 absorption, after stirring and absorbing CO_2; (b), $[P_{4442}]_2[Hy]$; (c), [HDBU][Hy].



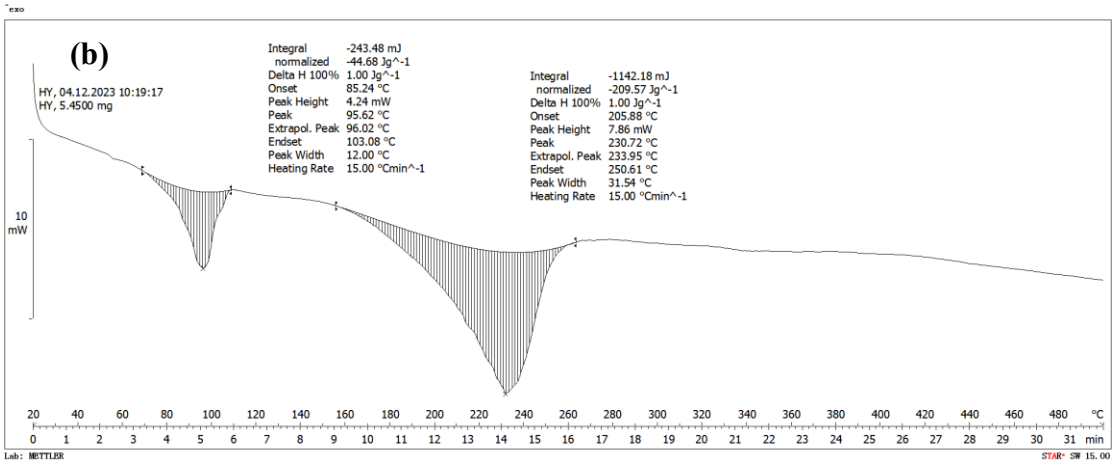


Fig. S5 DSC curve of ILs. (a), $[P_{4442}][Hy]$; (b), [HDBU][Hy].

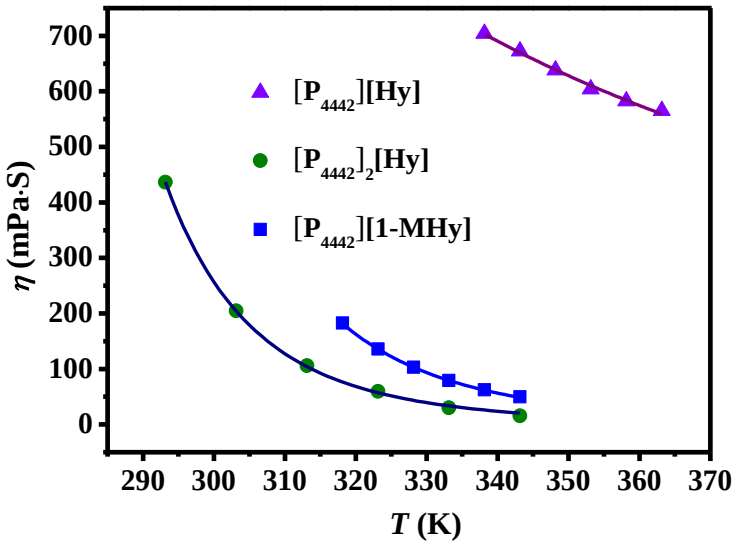


Fig. S6 Experimental viscosity of $[P_{4442}][Hy]$ and $[P_{4442}]_2[Hy]$ at different temperatures, compared with $[P_{4442}][1\text{-MHy}]$ from our previous work.[2] –, fitted by VFT equation.[3]

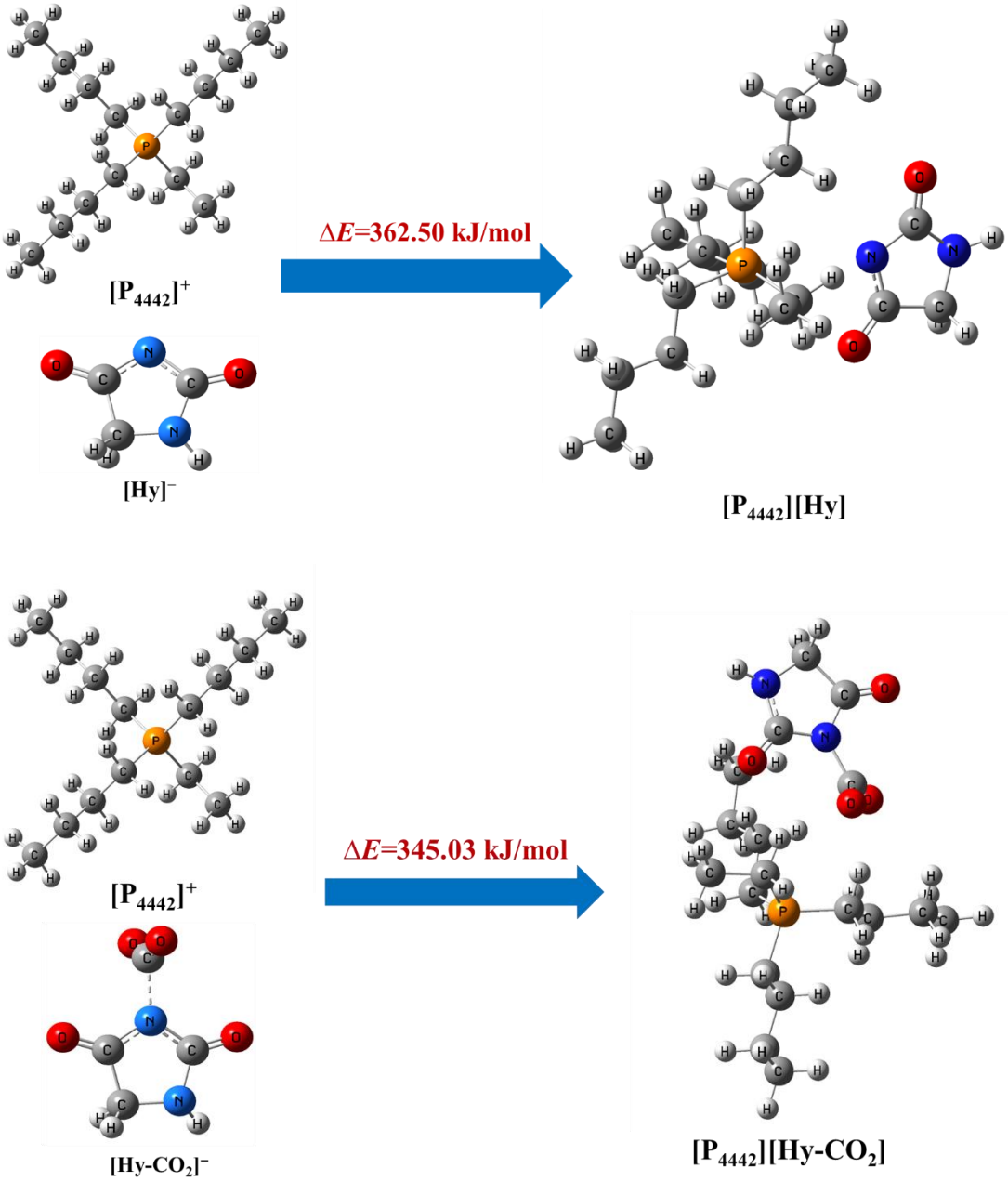


Fig. S7 The interaction energies of $[P_{4442}][Hy]$ and $[P_{4442}][Hy\text{-}CO_2]$ ion pairs at the B3LYP-D3/6-311++G (d, p) level.

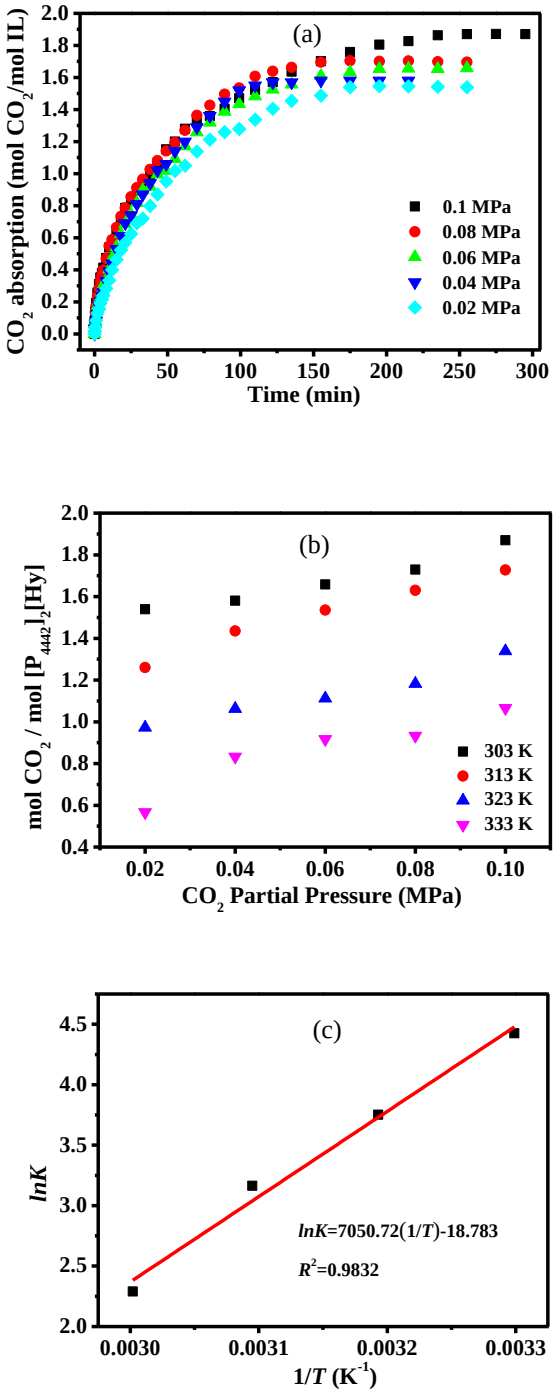


Fig. S8 (a) CO_2 absorption behavior of $[P_{4442}]_2[Hy]$ under different pressures; (b) CO_2 saturation absorption of $[P_{4442}]_2[Hy]$ at different temperatures and partial pressure; (c) The relationship between ln$K$ and 1/T of $[P_{4442}]_2[Hy]$.

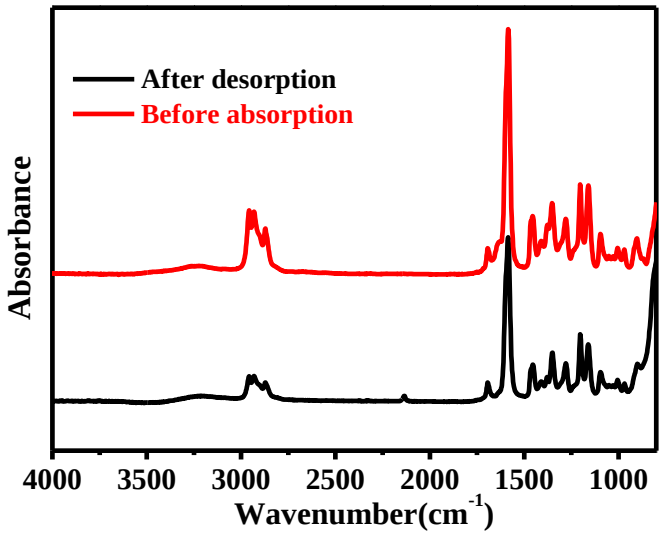


Fig. S9 FT-IR spectra of pure and received $[P_{4442}]_2[Hy]$ after CO_2 five cycles of CO_2 absorption/desorption.

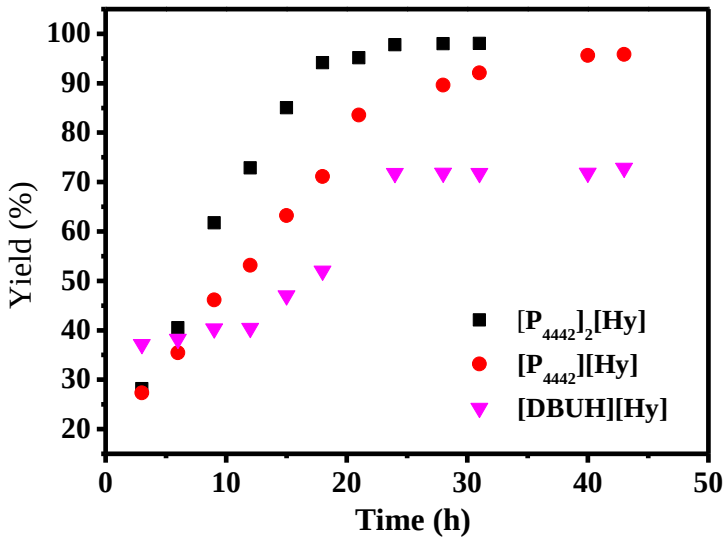


Fig. S10 Reaction of CO_2 with 2-aminobenzonitrile catalyzed by ILs as a function of time. Reaction condition: 20 mol% of IL to 2-aminobenzonitrile, 353.15 K, without solvent, HPLC yield.

References

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2. T. Chen, Y. Zhang and Y. Xu, *ACS Sustainable Chem. Eng.*, 2022, **10**, 10699.

3. (a) X. Wang, Y. Chi and T Mu. *J. Mol. Liq.*, 2014, **193**, 262. (b), T. Chen, T. Chen, X. Wu and Y. Xu, *J. Mol. Liq.*, 2022, **362**, 119743.