Supporting Information

Tuning environmental friendly chelate-based ionic liquids for highly efficient and reversible SO_2 chemisorption

Guokai Cui,* Yanan Li, Jiaxin Liu, Huiyong Wang, Zhiyong Li, and Jianji Wang*

Henan Key Laboratory of Green Chemistry, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China.

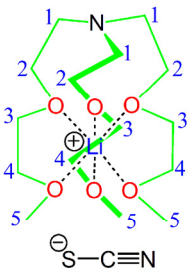
E-mail: chemcgk@163.com (G. Cui), jwang@htu.cn (J. Wang)

Number of pages: 7

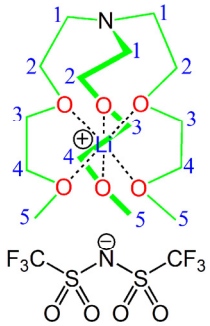
Number of figures: 3

Number of tables: 6

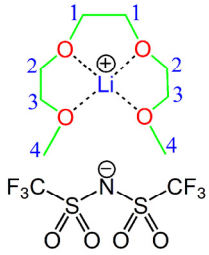
NMR and IR data of the chelate-based Ls



[Li(TDA-1)][SCN]



[Li(TDA-1)][TFSI]



[Li(G3)][TFSI]

[Li(TDA-1)][SCN]: ^{1}H NMR (DMSO-d$_6$): 2.65 (t, 6H, 3×C^{1}H$_2$), 3.23 (s, 9H, 3×C^{5}H$_3$), 3.39-3.44 (m, 12H, 3×C^{2}H$_2$+3×C^{4}H$_2$), 3.48 (t, 6H, 3×C^{3}H$_2$) ppm; ^{13}C NMR (DMSO-d$_6$): 54.2 (C^{1}), 58.1 (C^{5}), 69.2 (C^{2}), 69.5 (C^{4}), 71.4 (C^{3}), 129.9 (N≡C) ppm; IR: 2877, 2065, 1452, 1353, 1333, 1289, 1244, 1199, 1217, 1091, 1026, 984, 962, 927, 846 cm^{-1}.

After the absorption of SO_2: ^{1}H NMR (DMSO-d$_6$): 3.24 (s, 9H, 3×C^{5}H$_3$), 3.41 (t, 6H, 3×C^{1}H$_2$), 3.45 (t, 6H, 3×C^{4}H$_2$), 3.56 (t, 6H, 3×C^{3}H$_2$), 3.76 (t, 6H, 3×C^{2}H$_2$) ppm; ^{13}C NMR (DMSO-d$_6$): 53.1 (C^{1}), 58.1 (C^{5}), 64.6 (C^{2}), 69.5 (C^{4}), 71.1 (C^{3}), 124.3 (N≡C) ppm; IR: 2886, 2070, 1454, 1356, 1321, 1246, 1199, 1140, 1104, 1026, 970, 966, 946, 845 cm^{-1}.

[Li(TDA-1)][TFSI]: ^{1}H NMR (DMSO-d$_6$): 2.65 (t, 6H, 3×C^{1}H$_2$), 3.24 (s, 9H, 3×C^{5}H$_3$), 3.40-3.44 (m, 12H, 3×C^{2}H$_2$+3×C^{4}H$_2$), 3.48 (t, 6H, 3×C^{3}H$_2$) ppm; ^{13}C NMR (DMSO-d$_6$): 54.2 (C^{1}), 59.1 (C^{5}), 69.3 (C^{2}), 69.5 (C^{4}), 71.4 (C^{3}), 116.4 (-CF$_3$), 118.5 (-CF$_3$), 120.6 (-CF$_3$), 122.8 (-CF$_3$) ppm; IR: 2885, 2841, 1454, 1351, 1334, 1297, 1227, 1180, 1130, 1087, 1054, 1015, 965, 928, 844, 787, 761, 739 cm^{-1}.

After the absorption of SO_2: ^{1}H NMR (DMSO-d$_6$): 2.92 (t, 6H, 3×C^{1}H$_2$), 3.24 (s, 9H, 3×C^{5}H$_3$), 3.43 (t, 6H, 3×C^{4}H$_2$), 3.51 (t, 6H, 3×C^{3}H$_2$), 3.57 (t, 6H, 3×C^{2}H$_2$) ppm; ^{13}C NMR (DMSO-d$_6$): 53.2 (C^{1}), 58.1 (C^{5}), 67.2 (C^{2}), 69.6 (C^{4}), 71.3 (C^{3}), 116.4 (-CF$_3$), 118.5 (-CF$_3$), 120.7 (-CF$_3$), 122.8 (-CF$_3$) ppm; IR: 2890, 2834, 1455, 1350, 1330, 1227, 1185, 1134, 1107, 1083, 1055, 971, 899, 845, 789, 762, 740 cm^{-1}.

[Li(G3)][TFSI]: ^{1}H NMR (DMSO-d$_6$): 3.24 (s, 6H, 2×C^{4}H$_3$), 3.43 (t, 4H, 2×C^{3}H$_2$), 3.48-3.52 (m, 8H, 2×C^{2}H$_2$+2×C^{1}H$_2$) ppm; ^{13}C NMR (DMSO-d$_6$): 58.1 (C^{4}), 69.7 (C^{2}), 69.9 (C^{1}), 71.4 (C^{3}), 116.4 (-CF$_3$), 118.5 (-CF$_3$), 120.6 (-CF$_3$), 122.8 (-CF$_3$) ppm; IR: 2938, 2888, 1477, 1460,

1350, 1332, 1291, 1276, 1230, 1184, 1135, 1090, 1057, 1024, 983, 939, 870, 844, 793, 765 cm^{-1}.

After the absorption of SO_2: ^1H NMR (DMSO-d_6): 3.24 (s, 6H, 2×C^4H_3), 3.43 (t, 4H, 2×C^3H_2), 3.48-3.52 (m, 8H, 2×C^2H_2+2×C^1H_2) ppm; ^{13}C NMR (DMSO-d_6): 58.1 (C^4), 69.7 (C^2), 69.9 (C^1), 71.4 (C^3), 112.8 (-CF_3), 116.4 (-CF_3), 118.5 (-CF_3), 120.6 (-CF_3) ppm; IR: 2939, 2889, 2844, 1637, 1461, 1333, 1327, 1230, 1186, 1134, 1091, 1024, 1057, 939, 870, 844, 792, 764, 742 cm^{-1}.

Table S1. The temperature dependent of density (g cm^{-3}) over the range of 20~80 °C at atmospheric pressure for these chelate-based ionic liquids

Temperature (°C)	[Li(TDA-1)][SCN]	[Li(TDA-1)][TFSI]	[Li(G3)][TFSI]
20	1.0812	1.3228	1.4597
30	1.0737	1.3138	1.4494
40	1.0663	1.3048	1.4391
50	1.0588	1.2959	1.4288
60	1.0513	1.2871	1.4186
70	1.0439	1.2783	1.4085
80	1.0365	1.2695	1.3985

Table S2. The temperature dependent of viscosity (mPa s) over the range of 20~80 °C at atmospheric pressure for these chelate-based ionic liquids

Temperature (°C)	[Li(TDA-1)][SCN]	[Li(TDA-1)][TFSI]	[Li(G3)][TFSI]
20	80.58	124.47	215.20
30	44.06	72.82	113.30
40	27.24	43.99	62.93
50	17.96	27.62	40.23
60	12.42	18.77	26.9
70	8.54	13.56	18.85
80	6.02	8.72	13.11

Table S3. The parameters for the equation ln ρ = a + b T

IL	Parameter		
	a	b [×10^4]	r^2
[Li(TDA-1)][SCN]	0.2847	-7.043	0.99998
[Li(TDA-1)][TFSI]	0.4806	-6.850	1.00000
[Li(G3)][TFSI]	0.5878	-7.146	1.00000

Table S4. The parameters at 20°C for the equation $V_M = V_m/N = M/\rho/N$

IL	Parameter			
	V_M (nm^3)	V_m (cm^3 mol^{-1})	M (g mol^{-1})	ρ (g cm^{-3})
[Li(TDA-1)][SCN]	0.5967	359.2445	388.45	1.0813
[Li(TDA-1)][TFSI]	0.7666	461.5087	610.52	1.3229
[Li(G3)][TFSI]	0.5295	318.7604	465.32	1.4598

Table S5. The parameters of the equation $\ln \eta = \ln A + E_{vis}/(RT)$

IL	Parameter		
	A[×10^{-5}]	E_{vis} (kJ mol^{-1})	r^2
[Li(TDA-1)][SCN]	2.2767	36.5	0.99723
[Li(TDA-1)][TFSI]	2.4320	37.6	0.99873
[Li(G3)][TFSI]	1.6726	39.6	0.99422

Table S6. The effect of water constituent on SO_2 capture by these chelate-based ILs.[a]

Ionic liquid	Time [b] (min)	Water loading [b]		SO_2 dry (mol mol^{-1} IL)	SO_2 wet [b,c] (mol mol^{-1} IL)
		(mol mol^{-1} IL)	(g g^{-1} IL)		
[Li(TDA-1)][SCN]	95	6.92	0.32	5.50	4.75
[Li(TDA-1)][TFSI]	93	5.49	0.16	4.00	4.71
[Li(G3)][TFSI]	39	3.46	0.13	1.50	0.96

[a] Performed at 20 °C and 1.0 bar. [b] Absorption time from Figure 4(a). [c] Relative humidity is 100%. [d] Does not include mass of loaded water.

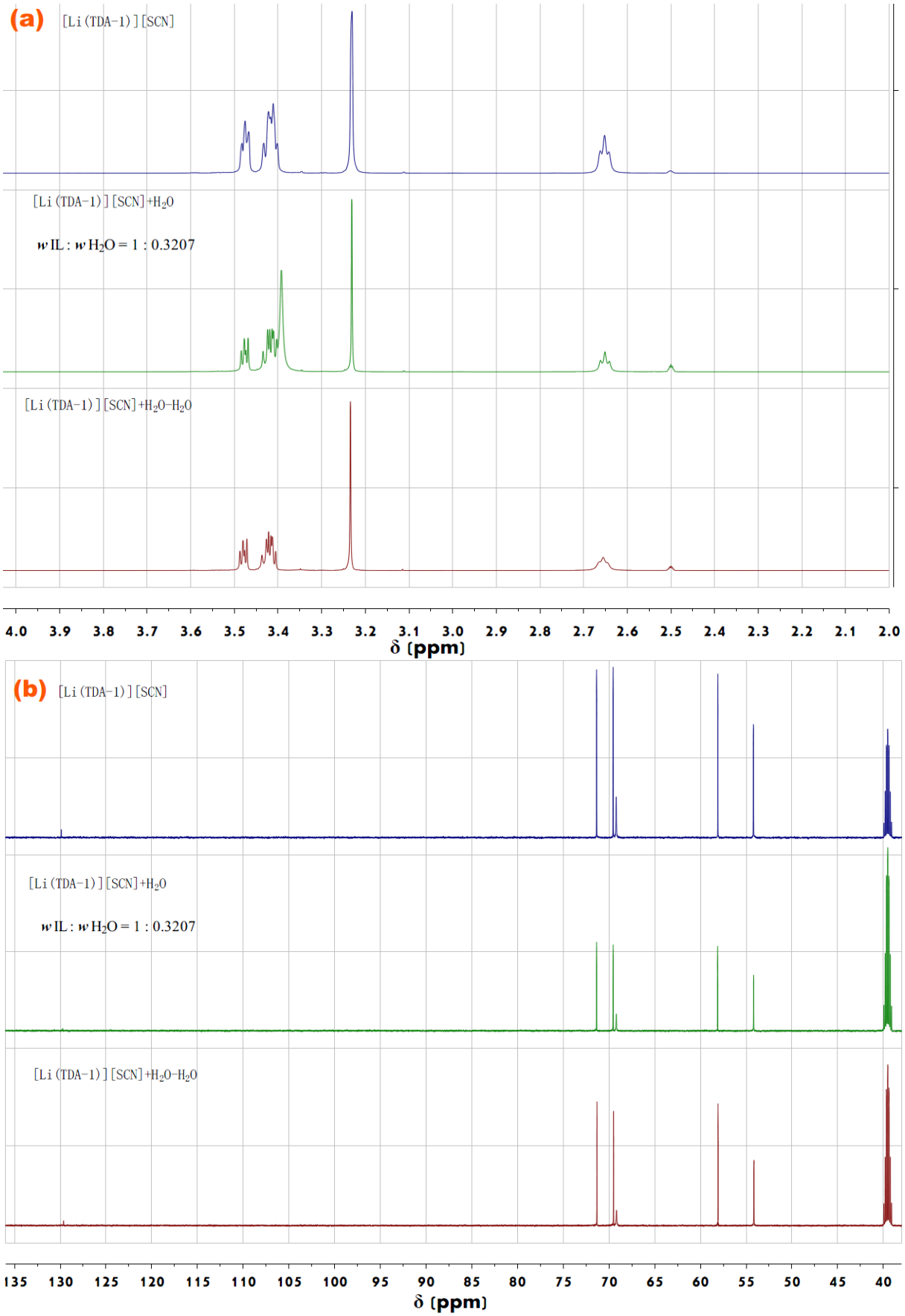


Figure S1 Comparative ^{1}H NMR (a) and ^{13}C NMR (b) spectra of [Li(TDA-1)][SCN] (blue), [Li(TDA-1)][SCN] with water (green) and regenerated [Li(TDA-1)][SCN] (red).

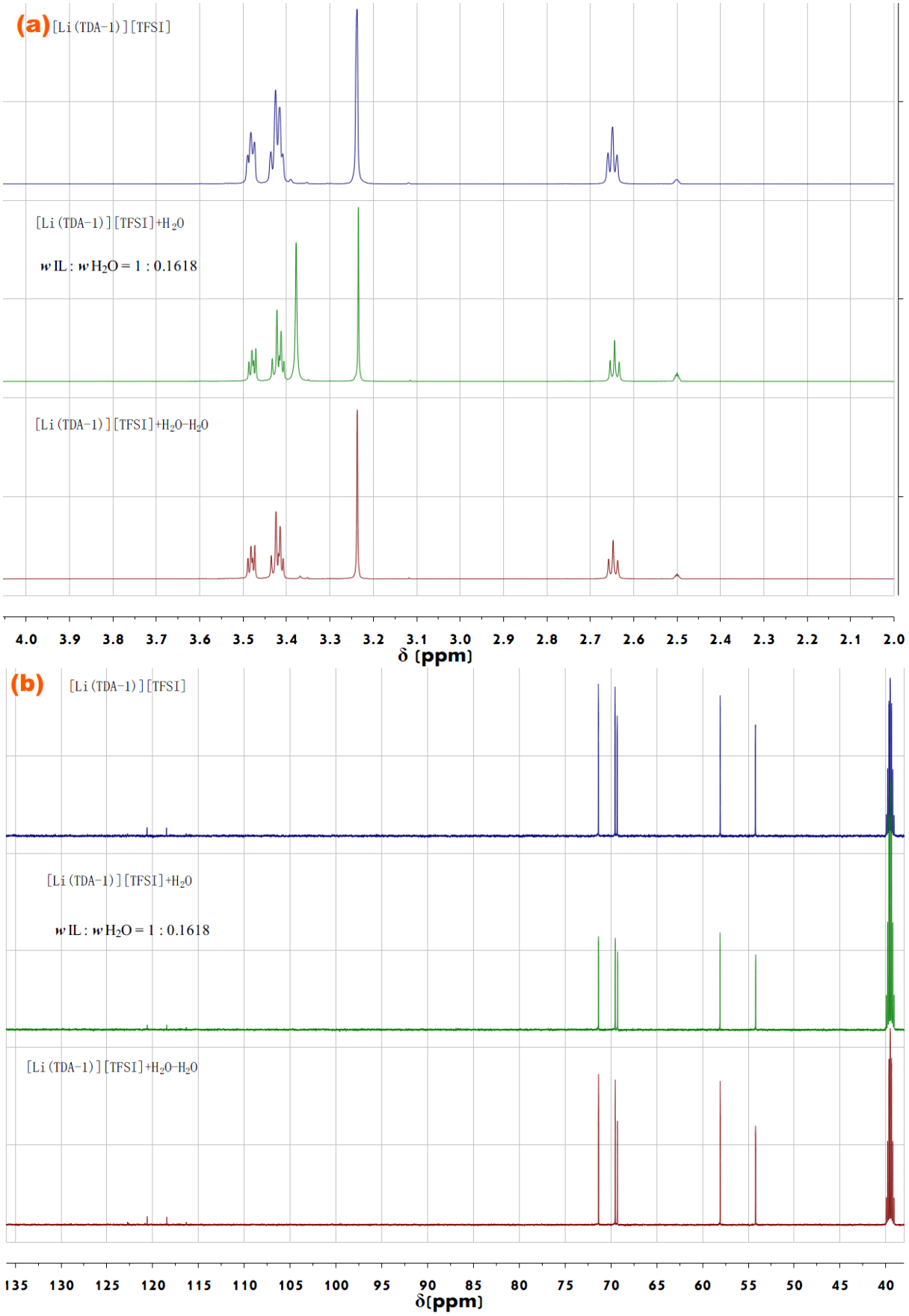


Figure S2 Comparative ^{1}H NMR (a) and ^{13}C NMR (b) spectra of [Li(TDA-1)][TFSI] (blue), [Li(TDA-1)][TFSI] with water (green) and regenerated [Li(TDA-1)][TFSI] (red).

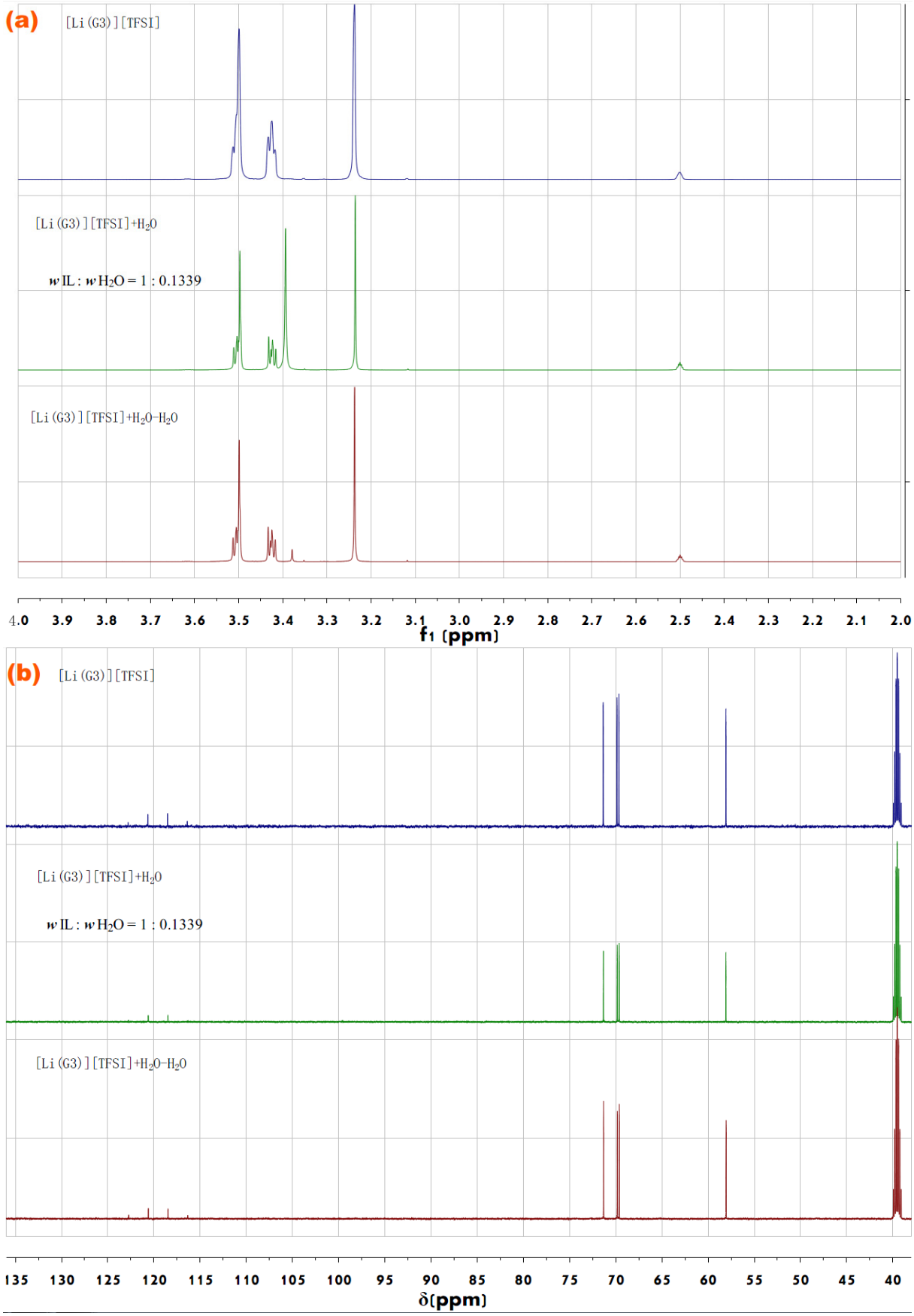


Figure S3. Comparative ^{1}H NMR (a) and ^{13}C NMR (b) spectra of [Li(G3)][TFSI] (blue), [Li(G3)][TFSI] with water (green) and regenerated [Li(G3)][TFSI] (red).