Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

For

From Light to Heavy Alkali Metal Tetraphosphonates (M = Li, Na, K, Rb, Cs): Cation Size-Induced Structural Diversity and Water-Facilitated Proton Conductivity

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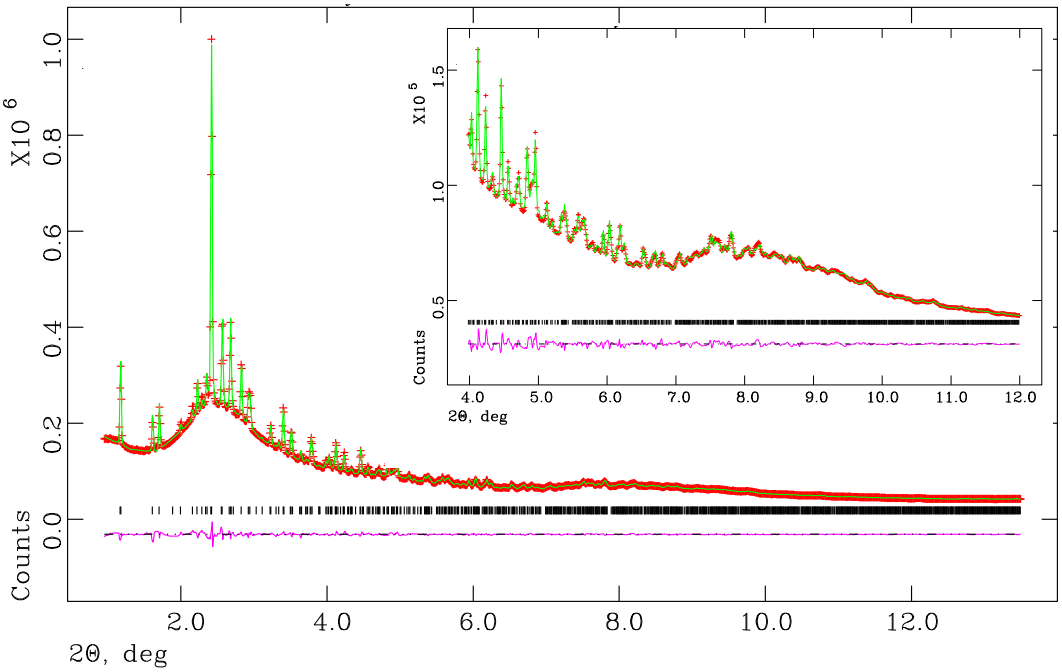
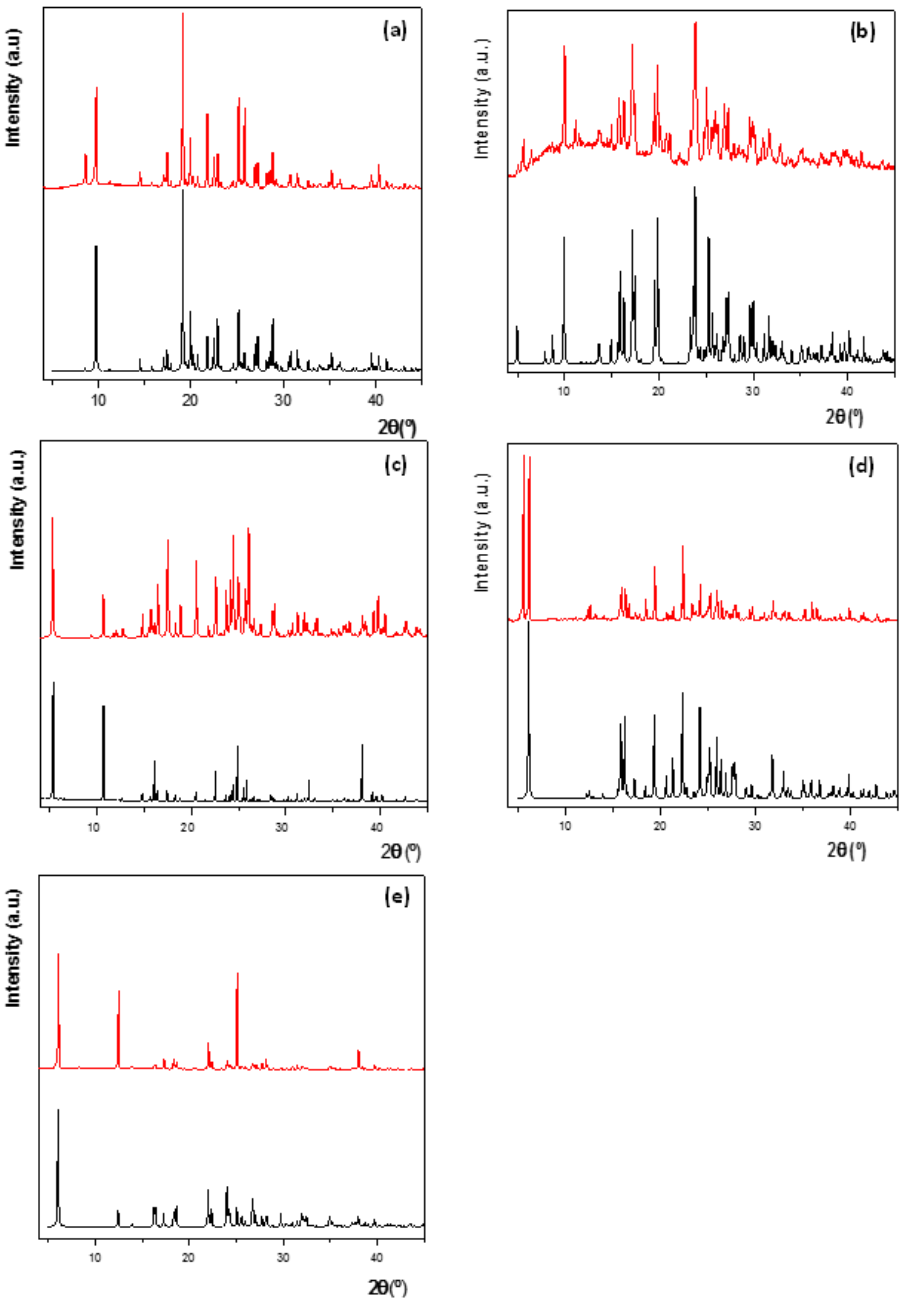


Figure S1. X-ray powder diffraction (XRPD) pattern Rietveld plot for **Li-HDTMP-0W**.



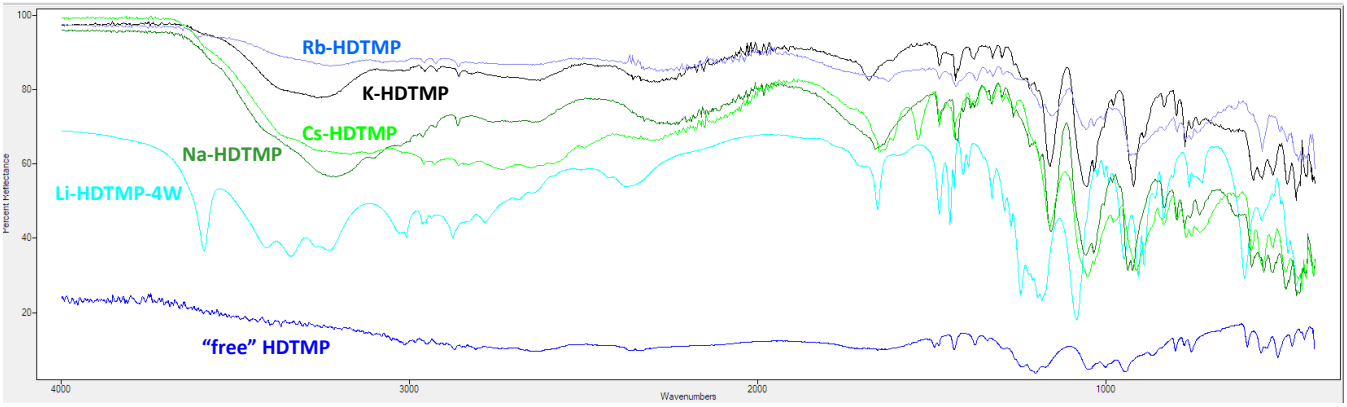


Figure S2. Upper: Simulated (black) and experimental X-ray powder diffraction patterns (red) for (a) Li-HDTMP-4W, (b) Na-HDTMP, (c) K-HDTMP, (d) Rb-HDTMP and (e) Cs-HDTMP. Lower: ATR-IR spectra of "free" HDTMP and all M-HDTMP compounds.

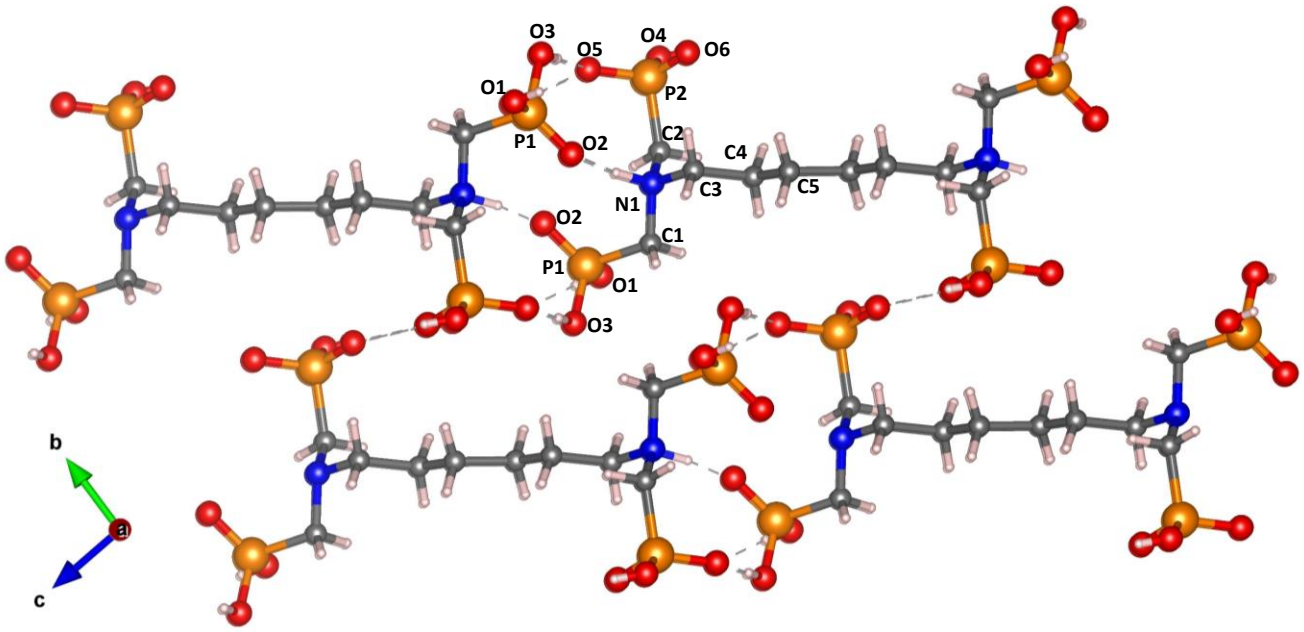


Figure S3. H-bond interactions for HDTMP acid.

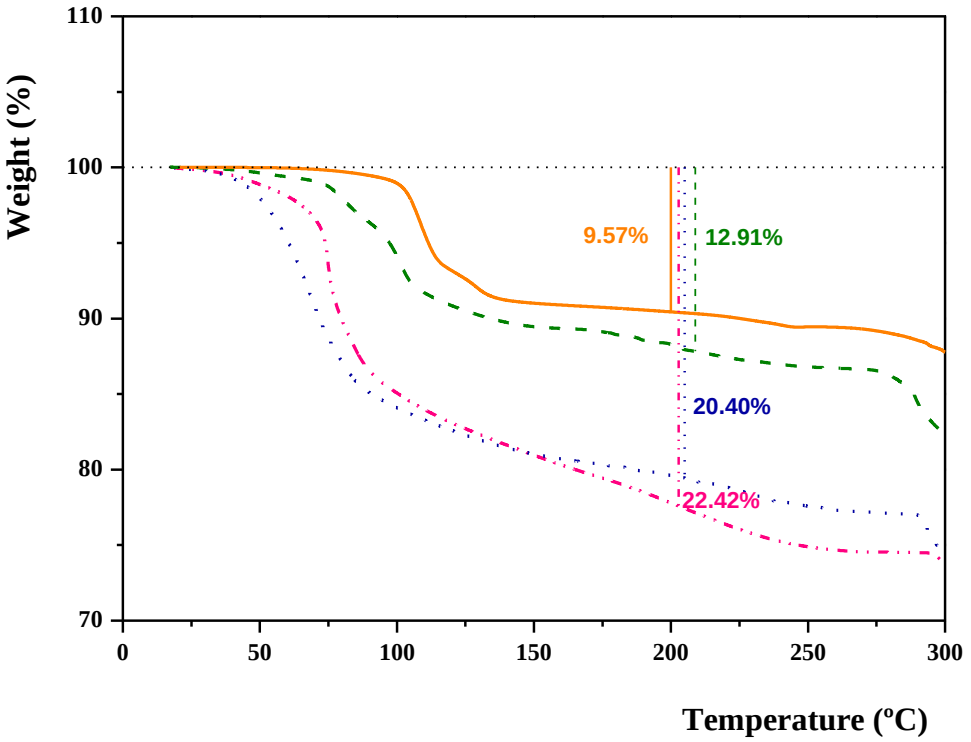


Figure S4. TGA curves for **M-HDTMP** derivatives [M=Na (pink), K (blue), Rb (green) and Cs (orange)].

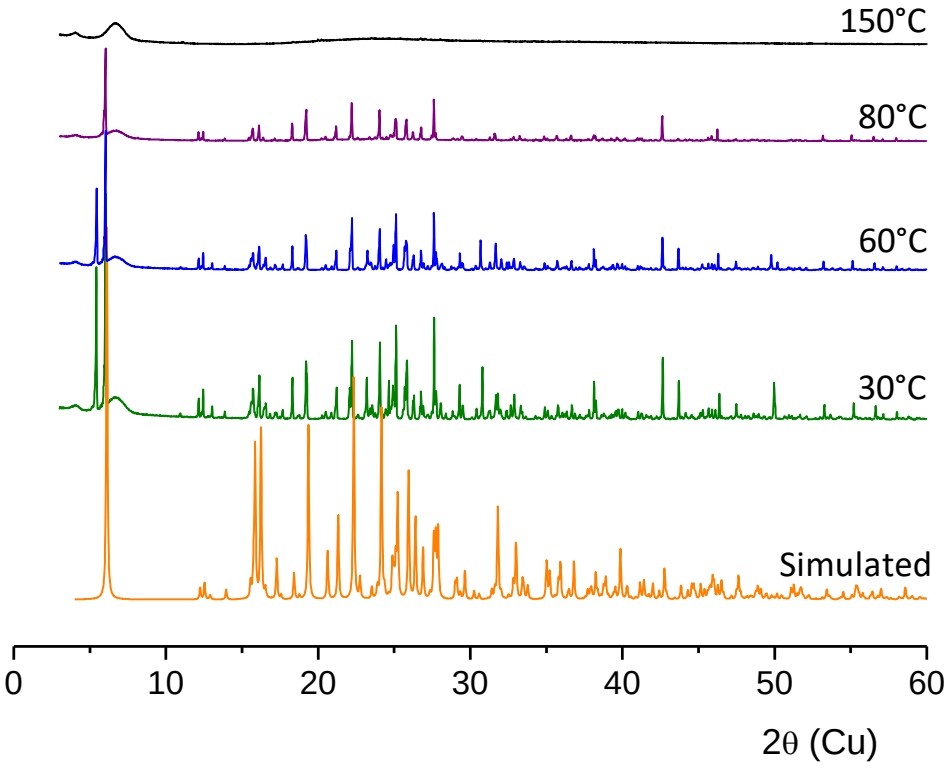


Figure S5. Thermodiffraction patterns for the **Rb-HDTMP** compound.

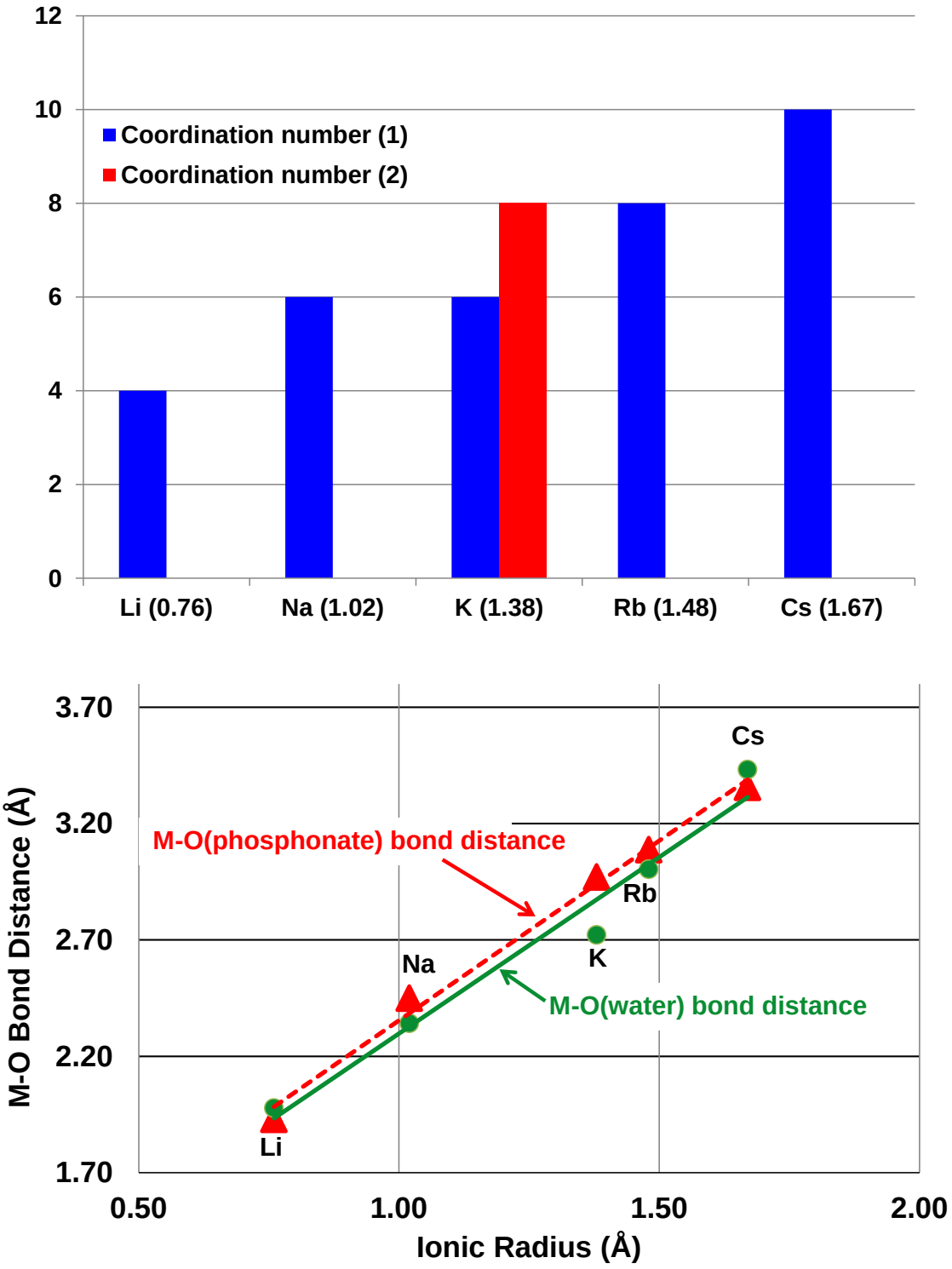


Figure S6. Number coordination vs cation size.

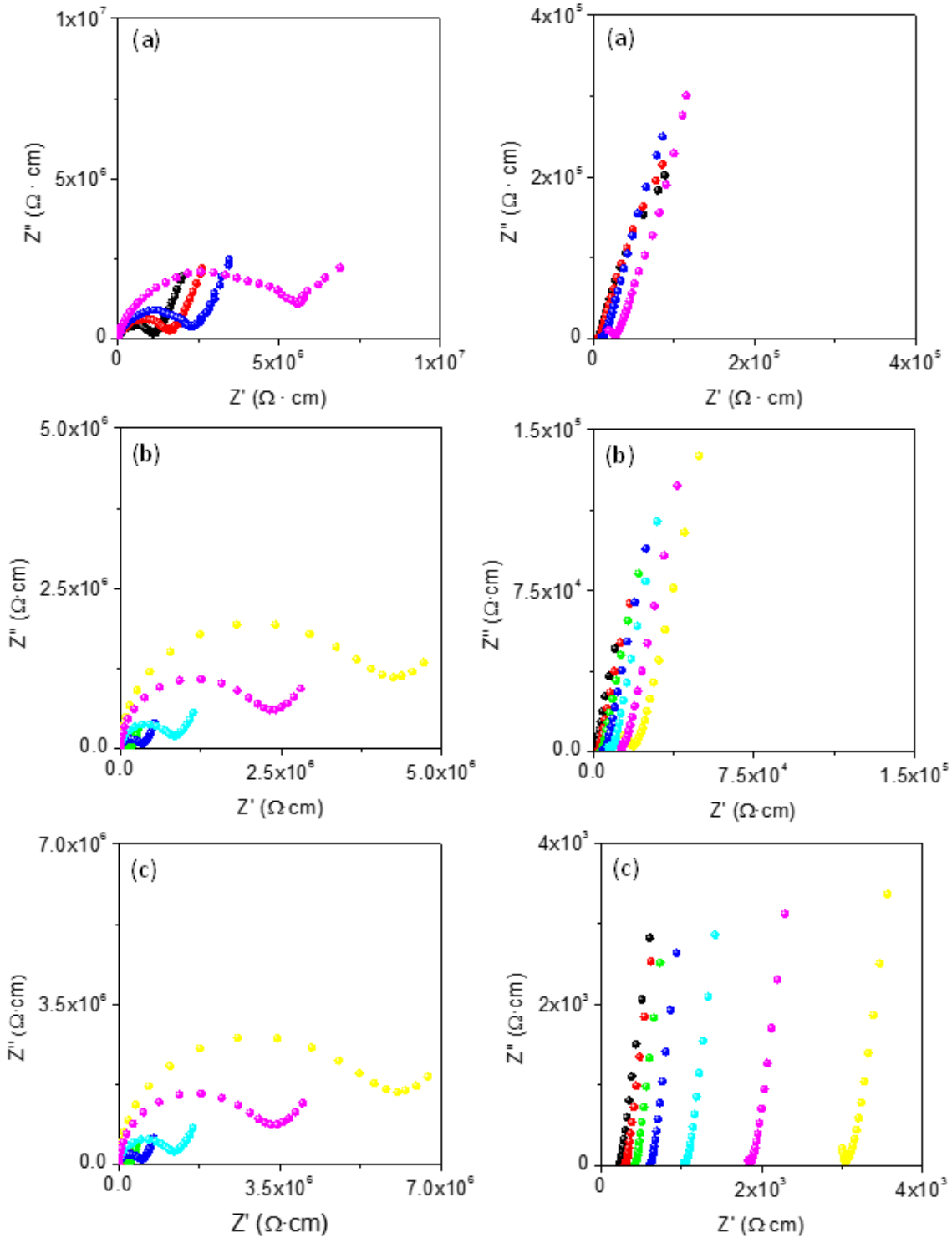


Figure S7. Plot of the complex impedance plane for (a) **HDTMP**, (b)) **Li-HDTMP-4W** and (c) **Li-HDTMP rehydrated** at 60% (left column) and 95% RH (right column) and temperatures: 80 (black), 70 (red), 60 (green), 50 (blue), 40 (cyan), 30 (magenta) and 25 °C (yellow).

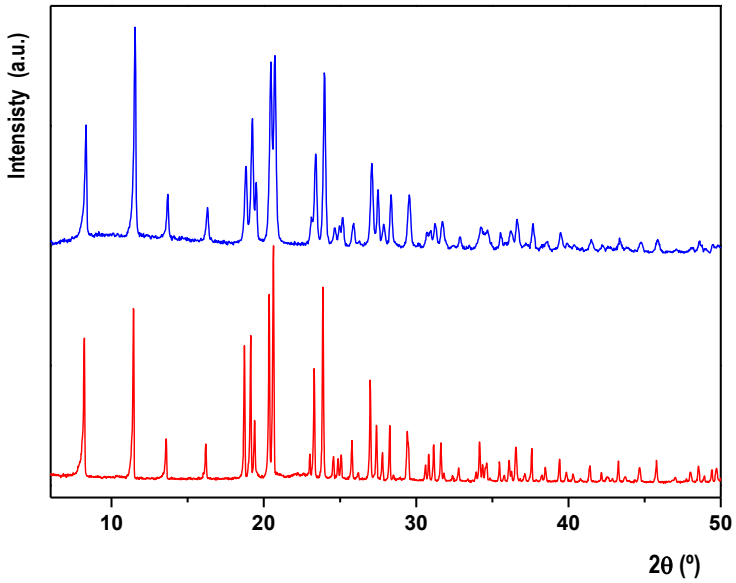


Figure S8. Powder X ray diffraction pattern for **HDTMP** as synthesized (red) and after impedance measurement (blue) at 95% of relative humidity (RH).

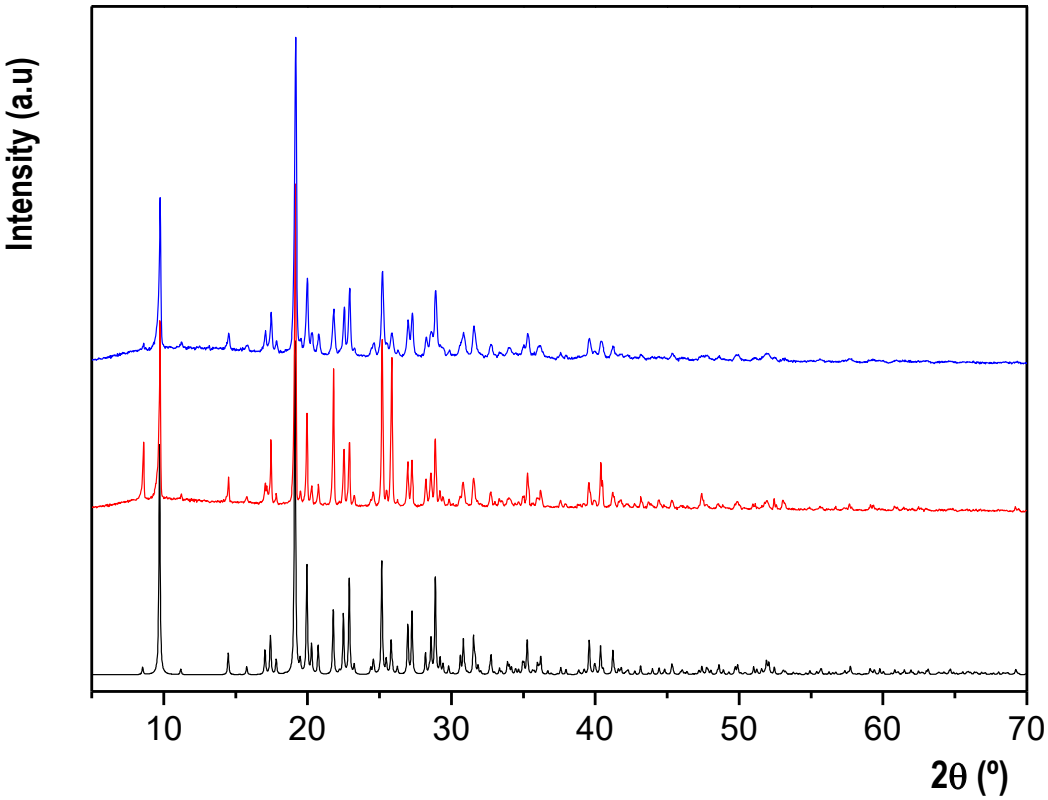


Figure S9. Powder X ray diffraction patterns for: (a) simulated for Li-HDTMP-4W (black), (b) as synthesized **Li-HDTMP-4W** (red) and (c) **Li-HDTMP-0W** (blue) fully rehydrated upon accomplishing impedance measurements at 95% RH.

Table S1. Summary of the hydrogen bonding data for the reported materials.

Compound	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H–A (°)	Symmetry operator for A
HDTMP	O1–H1···O5#	0.785(16)	1.748(16)	2.5326(18)	176(2)	−x+1, −y+1, −z+1
	O3–H3···O5#	0.810(16)	1.755(16)	2.565(2)	177(3)	−x+1, −y+1, −z+1
	O4–H4···O6#	0.789(16)	1.764(16)	2.552(2)	177(3)	−x+1, −y+1, −z+2
	N1–H10···O2#	0.98	1.85	2.7390(19)	150.1	−x+1, −y+1, −z+1
Li-HDTMP	O1–H1o···O2#	0.827(19)	1.77(2)	2.593(4)	178(5)	−x+1, −y+1, −z
	O5–H5o···O4#	0.819(19)	1.81(2)	2.624(4)	175(5)	−x+2, −y+1, −z+1
	O7–H7a···O2#	0.815(19)	1.91(2)	2.727(4)	178(5)	−x+1, −y+1, −z
	O7–H7b···O3#	0.828(19)	2.01(2)	2.806(4)	162(4)	−x+2, −y+1, −z
	O8–H8a···O7#	0.831(19)	2.03(3)	2.827(5)	161(6)	−x+1, −y+2, −z
	O8–H8b···O5#	0.81(2)	2.19(2)	2.996(4)	170(5)	x−1, y, z
	N1–H1n···O4#	0.861(18)	2.05(3)	2.794(4)	145(4)	−x+1, −y+1, −z+1
Na-HDTMP	O3–H3o···O4#	0.793(16)	1.697(16)	2.4870(16)	174(3)	x+1, y, z
	O5–H5o···O21	0.805(15)	1.732(16)	2.5189(17)	165(2)	
	O8–H8o···O10#	0.797(15)	1.754(16)	2.5399(16)	169(2)	x−1, y, z
	O11–H11o···O20#	0.800(15)	1.745(16)	2.5233(17)	164(2)	x, y−1, z
	O13–H13a···O23#	0.804(16)	2.007(17)	2.7857(17)	163(2)	x+1, y, z
	O13–H13b···O18#	0.827(16)	1.984(16)	2.7974(18)	168(2)	−x+1, −y+1, −z+2
	O14–H14a···O9	0.822(16)	1.908(17)	2.7267(17)	174(2)	
	O14–H14b···O16#	0.820(16)	2.025(17)	2.8357(19)	170(2)	x−1, y, z
	O15–H15b···O9#	0.802(16)	2.070(17)	2.8363(16)	160(2)	−x−1, −y, −z+2
	O16–H16a···O1#	0.805(16)	1.948(16)	2.7524(17)	179(3)	x, y, z+1
	O16–H16b···O22#	0.824(16)	2.014(16)	2.8273(19)	169(2)	−x+1, −y+1, −z+1
	O17–H17a···O9#	0.815(16)	2.087(17)	2.8906(17)	169(3)	x+1, y, z
	O17–H17b···O4#	0.829(16)	2.104(17)	2.9166(18)	167(2)	−x+1, −y+1, −z+1
	O18–H18a···O2#	0.805(16)	1.882(16)	2.6854(17)	175(2)	−x+1, −y+1, -z+1
	O18–H18b···O19#	0.828(16)	2.015(17)	2.8179(18)	163(2)	x+1, y, z
	O19–H19a···O1#	0.801(16)	2.015(17)	2.7921(17)	164(2)	−x+1, −y+1, −z+1
	O19–H19b···O7#	0.798(16)	2.283(16)	3.0780(17)	175(2)	x, y+1, z
	O20–H20a···O6#	0.802(16)	1.978(16)	2.7717(17)	170(2)	−x, −y+1, −z+1
	O20–H20b···O6	0.816(16)	1.902(16)	2.7088(17)	170(2)	
	O21–H21a···O12#	0.824(16)	1.878(17)	2.6839(17)	166(2)	x, y+1, z
	O21–H21b···O12#	0.807(16)	1.953(16)	2.7548(16)	172(2)	−x+1, −y+1, −z+1
	O22–H22a···O17#	0.828(16)	2.516(19)	3.249(2)	148(2)	−x+2, −y+1, −z+1
	O22–H22a···O18#	0.828(16)	2.59(2)	3.2063(18)	132(2)	x, y, z−1
	O22–H22b···O2	0.825(16)	1.837(17)	2.6509(17)	169(2)	
	O23–H23b···O1#	0.809(16)	1.882(16)	2.6870(16)	173(2)	x−1, y, z+1
	N1–H1···O19#	0.849(15)	2.196(17)	2.9357(18)	146(2)	−x, −y+1, −z+1
	N2–H2···O15#	0.845(15)	1.935(15)	2.7504(17)	162(2)	−x, −y, -z+2
K-HDTMP	O3–H3o···O10#	0.804(14)	1.773(14)	2.5738(13)	174(2)	−x+1, −y+1, −z+1
	O5–H5o···O20#	0.817(14)	1.735(14)	2.5413(14)	169(2)	−x, y−1/2, −z+1/2
	O7–H7o···O4#	0.797(14)	1.749(14)	2.5411(13)	172(2)	−x, −y+1, −z+2
	O11–H11o···O19#	0.795(14)	1.747(14)	2.5314(14)	169(2)	x+1, y, z+1
	O13–H13a···O9#	0.833(14)	1.901(15)	2.7249(14)	170(2)	−x+1, −y+1, −z+2
	O15–H15b···O1#	0.790(14)	2.053(15)	2.8215(13)	164(2)	x, −y+1/2, z+1/2
	O16–H16b···O2#	0.822(14)	1.959(15)	2.7763(14)	173(2)	x, −y+1/2, z+1/2
	O17–H17b···O1#	0.829(15)	1.937(15)	2.7411(13)	164(2)	x-1, y, z
	O18–H18a···O9#	0.814(14)	2.288(15)	3.0754(15)	163(2)	−x+1, −y+1, −z+2
	O19–H19a···O12#	0.802(15)	1.917(15)	2.7101(14)	170(2)	−x+1, −y+1, −z+1
	O19–H19b···O6#	0.829(15)	1.931(15)	2.7511(14)	170(2)	−x, -y+1, −z+1
	O20–H20a···O6#	0.825(14)	1.883(15)	2.7008(14)	171(2)	x+1, −y+3/2, z-1/2
	O20–H20b···O12#	0.823(14)	1.919(15)	2.7391(14)	174(2)	x, −y+3/2, z-1/2
	N1–H1n···O18	0.860(13)	2.025(14)	2.8325(15)	156(2)	
	N2–H2n···O15#	0.854(13)	1.886(14)	2.7105(15)	162(2)	−x+1, y+1/2, −z+3/2
Rb-HDTMP	O2–H2o···O8#	0.810(15)	1.749(17)	2.5383(18)	164(2)	x-1, y, z
	O5–H5o···O5#	0.788(18)	1.68(2)	2.439(2)	161(5)	-x+1, y, -z+1/2
	O6–H6o···O1#	0.812(16)	1.686(16)	2.4924(16)	172(2)	x-1/2, y+1/2, z
	O7a–H7a2···O4#	0.817(19)	2.24(3)	2.987(3)	153(5)	x+1, y, z
	O7b–H7b1···O4#	0.812(19)	2.24(3)	2.958(3)	148(5)	x+1, y, z
	O8–H8a···O3	0.805(17)	1.912(17)	2.7176(19)	179(3)	
	O8–H8b···O3#	0.812(17)	1.952(18)	2.752(2)	168(3)	-x+3/2, -y+1/2, -z+1
	N1–H1n···O7a	0.860(14)	1.996(15)	2.767(3)	149(2)	
	N1–H1n···O7b	0.860(14)	2.139(15)	2.903(3)	148(2)	
Cs-HDTMP	O2–H2o···O8#	0.827(17)	1.720(19)	2.530(3)	166(3)	x, y+1, z
	O4–H4o···O4#	0.816(19)	1.71(2)	2.525(3)	174(7)	-x+2, -y+1, -z+1
	O6–H6o···O1#	0.825(17)	1.656(19)	2.464(2)	166(3)	x+1, y-1, z
	O8–H8a···O3	0.827(18)	1.911(19)	2.725(3)	168(3)	x+1, y-1, z
	O8–H8b···O3#	0.815(18)	1.97(2)	2.743(3)	158(3)	-x+1, -y+1, -z+2
	N1–H1n···O7	0.863(16)	1.891(18)	2.718(3)	160(2)	

S2 ^{1}H-SS-NMR data and band assignments for ligand HDTMP and Li-HDTMP samples.

Compound	δ (ppm)	Calculated integral (%)*	Assignment
HDTMP	13.22	7.31	P-$(OH)_2$
	12.11	5.48	P-$(OH)_2$
	11.11	6.84	N-H^+
	9.54	12.58	P-OH
	5.61	20.84	CH_2
	2.39	38.18	CH_2
	0.2	8.76	CH_2
Li-HDTMP-0W	11.44	4.92	N-H^+
	10.00	16.65	P-OH
	5.97	16.66	CH_2
	4.80	3.61	H_2O
	2.56	51.08	CH_2
	0.25	7.07	CH_2
Rehydrated Li-HDTMP-0W	11.08	6.29	N-H^+
	9.12	14.37	P-OH
	6.23	17.53	CH_2
	4.73	5.76	H_2O
	2.67	39.81	CH_2
	0.27	16.21	CH_2
Li-HDTMP-4W	11.14	6.67	N-H^+
	9.11	13.82	P-OH
	5.95	15.73	CH_2
	4.73	6.59	H_2O
	2.76	40.43	CH_2
	0.14	16.76	CH_2

*Renormalized without the signal probe