Supporting Information

A straightforward solvothermal synthesis towards phase pure Li_2CoPO_4F

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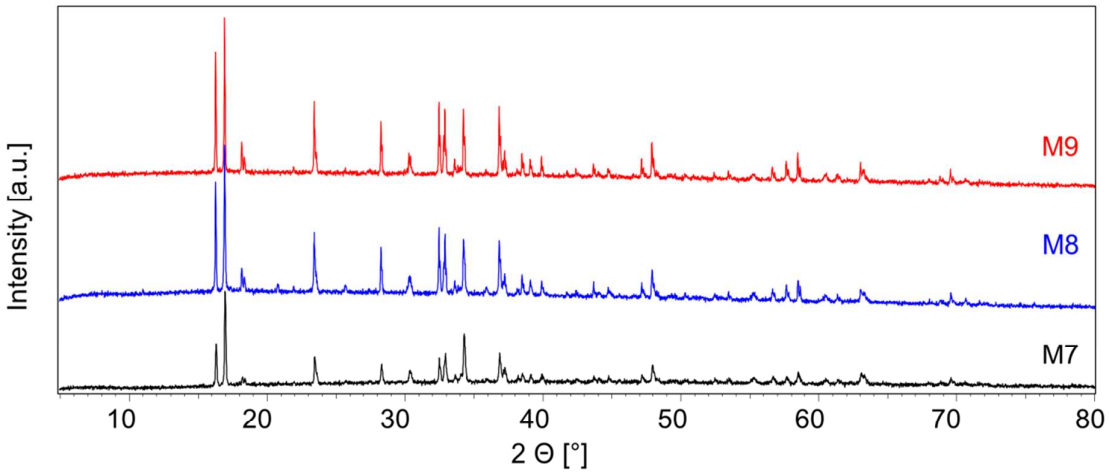

Figure S1. PXRD of Li_2CoPO_4F (M7 – M9) from different solvents (7 – 9) after 36 h reaction time.

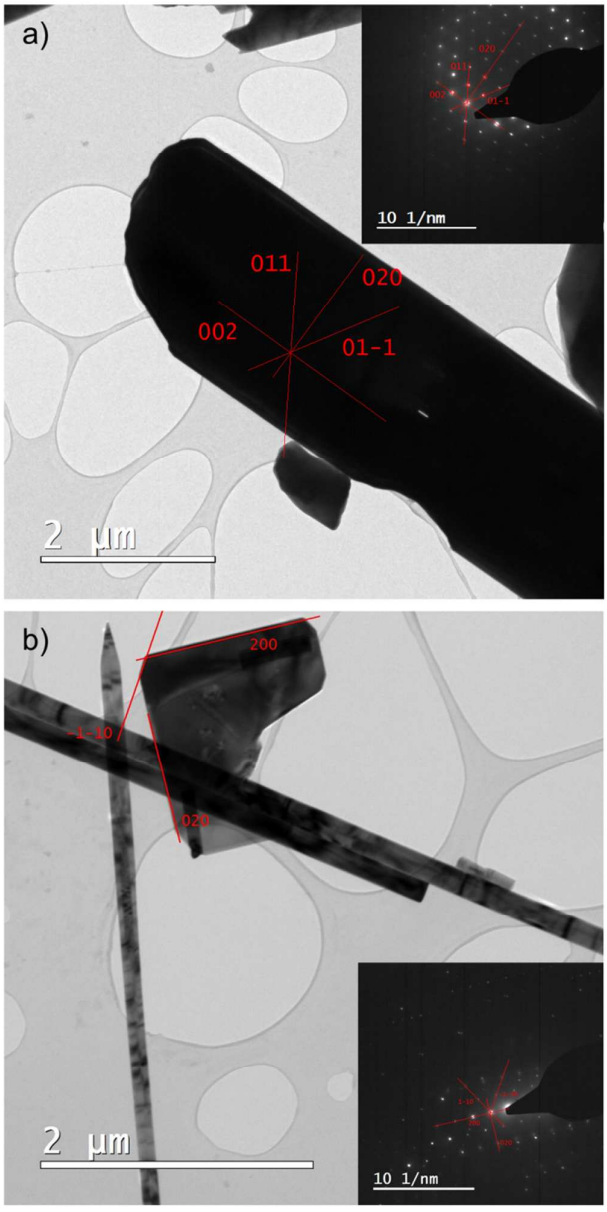

Figure S2. TEM images and electron diffraction pattern of Li_2CoPO_4F particles from different solvents a) M7 and b) M8. The scale bar corresponds to 2 µm for the TEM images and 10 nm^{-1} for the electron diffraction pattern. TEM image and electron diffraction pattern for a) and b) are 90° rotated to each other.

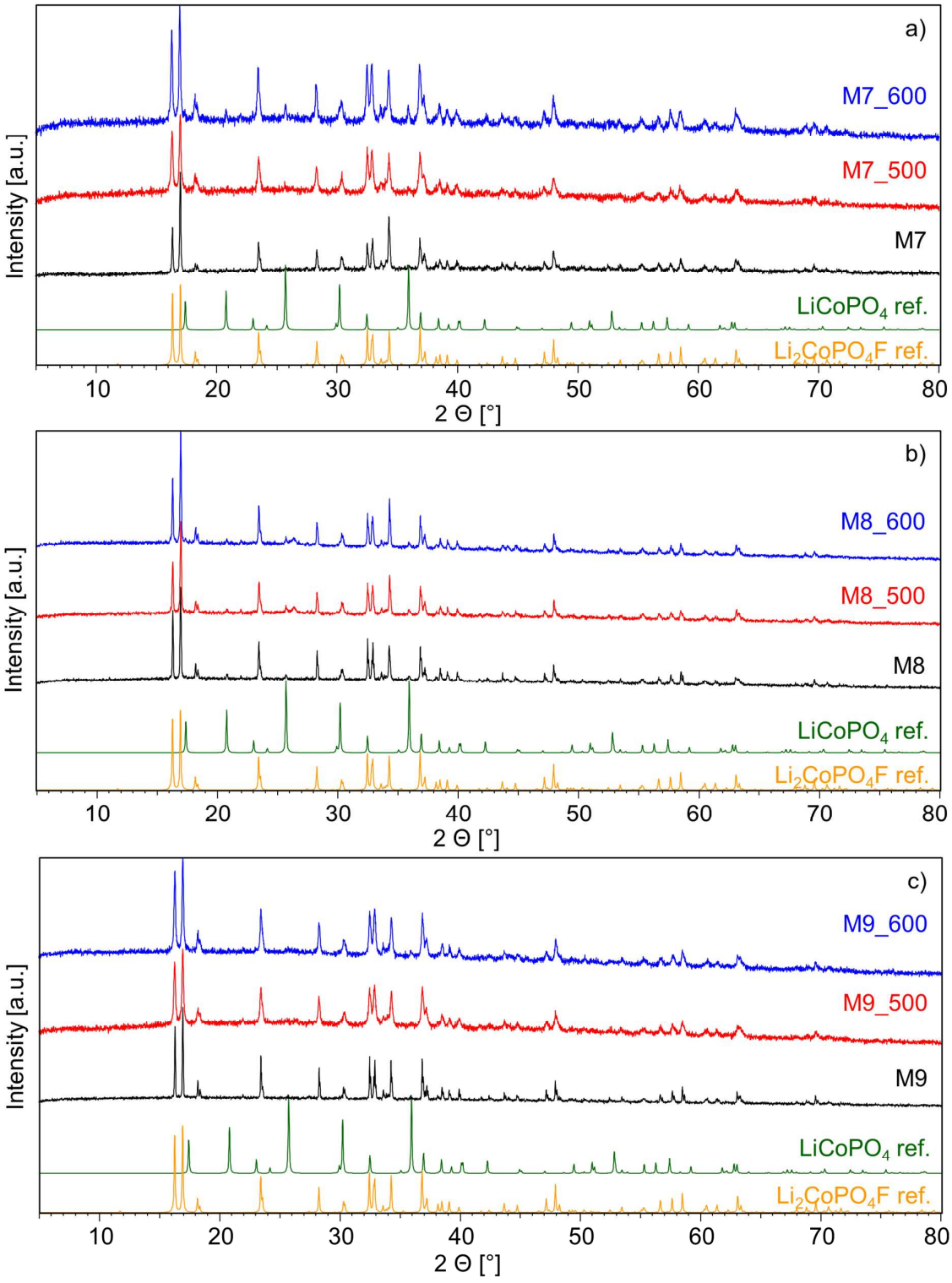

Figure S3. PXRD pattern of Li_2CoPO_4F synthesized from different solvents a) M7, b) M8 and c) M9 and carbon coated compounds annealed at different temperatures a) M7_500 and

M7_600; b) M8_500 and M8_600; c) M9_500 and M9_600; Including reference plots (ref.) of Li_2CoPO_4F and $LiCoPO_4$.

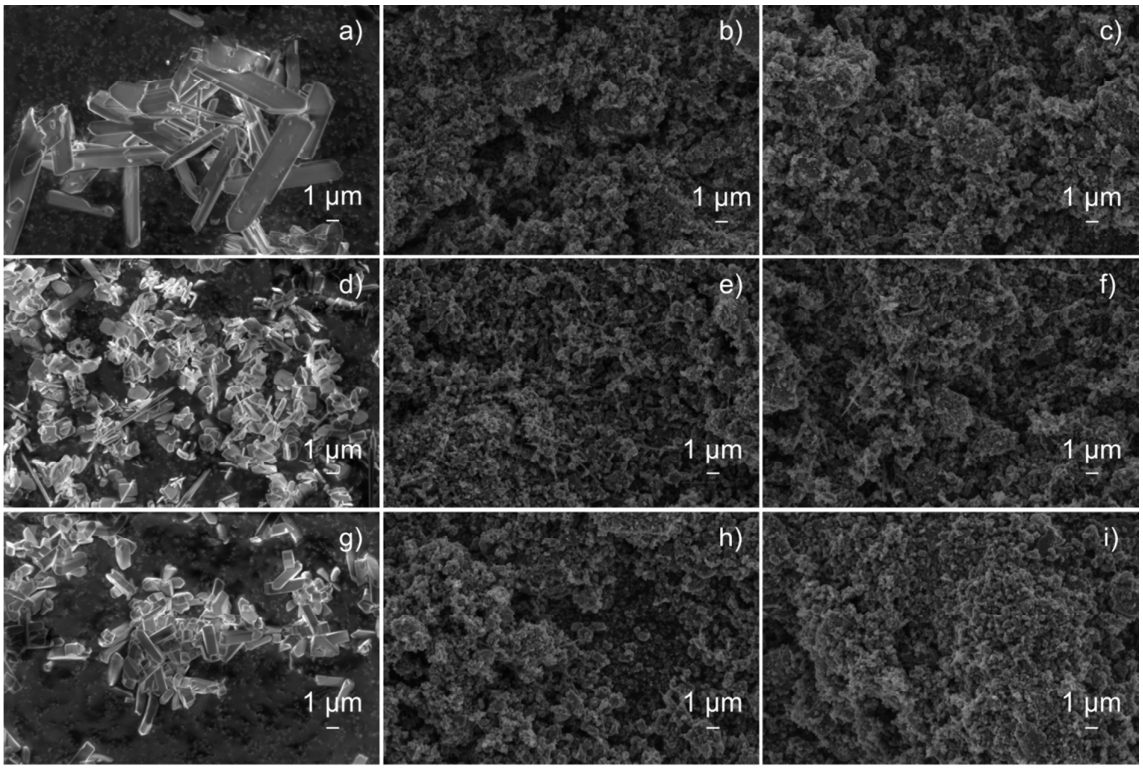

Figure S4. SEM of as-synthesized and carbon coated Li_2CoPO_4F particles obtained from the different solvents (a) M7, d) M8 and g) M9; annealed at different temperatures (b) M7_500 and c) M7_600; e) M8_500 and f) M8_600; h) M9_500 and i) M9_600).

To identify the product after the solvothermal reaction with solvent 7, ^{1}H NMR investigations were carried out.

For 1,5-pentane diol the following signals were obtained:

^{1}H NMR (300 MHz, DMSO-d_6, δ): 3.34 (t, 2H, OH), 3.37 (q, 4H; CH_2), 1.40 (q, 4H; CH_2), 1.29 (q, 2H, CH_2);

For the supernatant of solvent 7 after the reaction following signals were obtained additionally to the signals for 1,5-pentane diol:

^{1}H NMR (600 MHz, DMSO-d_6, δ): 3.52 (t, 4H, CH_2), 3.44 (s, 2H; H_2O), 1.57 (q, 2H; CH_2), 1.46 (q, 4H, CH_2);

These observations lead to the conclusion of a ring closing reaction of 1,5-pentane diol to tetrahydropyrane as condensation product as well as H_2O.

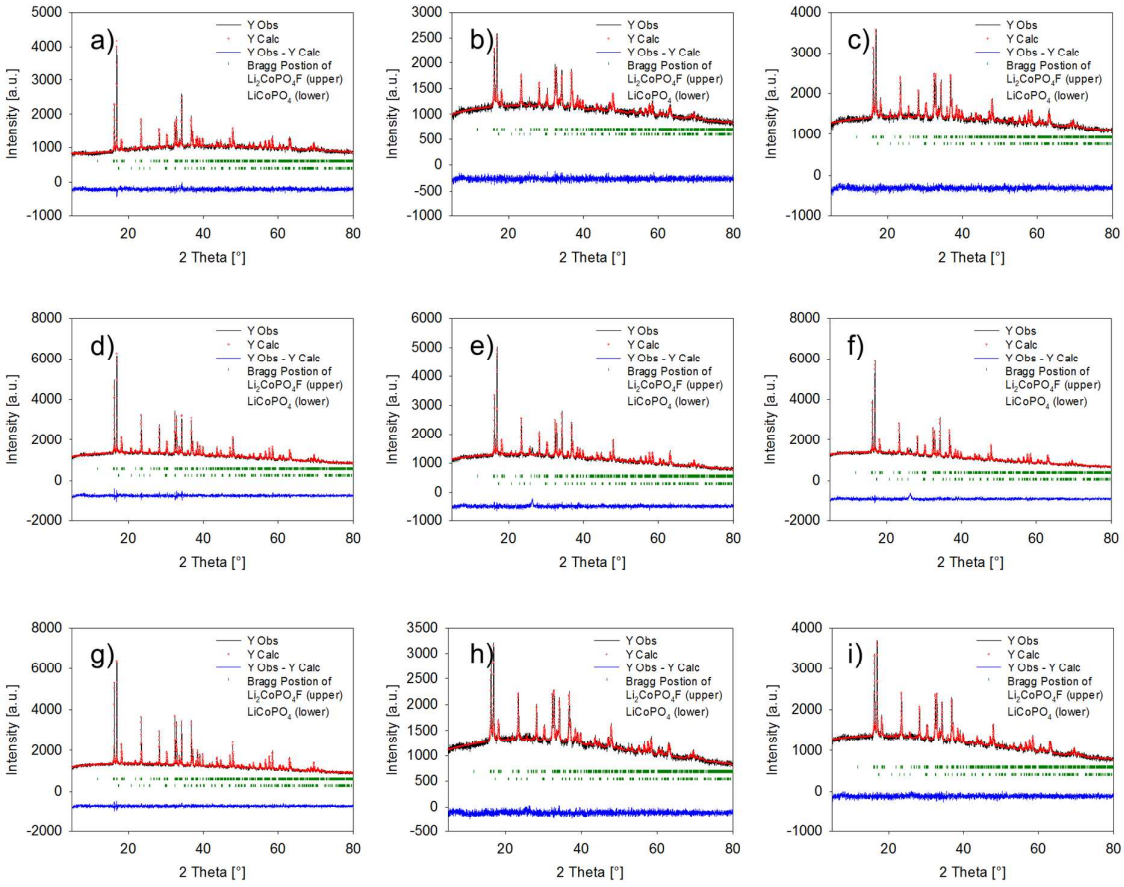

Figure S5. PXRD pattern of as-synthesized Li_2CoPO_4F particles from solvents 7 – 9 after 36 h reaction time a), d) and g), respectively; PXRD pattern of carbon coated and annealed at 500 °C Li2CoPO4F particles from solvents 7 – 9 after 36 h reaction time b), e) and h), respectively; PXRD pattern of carbon coated and annealed at 600 °C Li_2CoPO_4F particles from solvents 7 – 9 after 36 h reaction time c), f) and i), respectively;

Table S1. Refined unit cell parameters and compound content from Rietveld refinement from PXRD measurements (LCPF = Li_2CoPO_4F, LCP = $LiCoPO_4$).

Compound	Phase	a [Å]	b [Å]	c [Å]	V [Å^3]	Amount [%]	Crystallinity [%]	Crystallite size [nm]
7	LCPF	10.465	6.395	10.882	728.29	93.42	62.1	x
	LCP	10.208	5.924	4.705	284.51	6.58	x	x
7_500	LCPF	10.464	6.392	10.894	728.75	93.53	73.7	63
	LCP	10.239	5.929	4.693	284.91	6.47	x	x
7_600	LCPF	10.456	6.389	10.884	727.13	91.46	33.3	91
	LCP	10.206	5.923	4.702	284.22	8.54	x	x
8	LCPF	10.459	6.389	10.874	726.67	92.87	78.9	x
	LCP	10.206	5.923	4.702	284.21	7.13	x	x
8_500	LCPF	10.449	6.389	10.877	726.19	89.46	90.2	216
	LCP	10,211	5.918	4.703	284.21	10.54	x	x
8_600	LCPF	10.449	6.388	10.876	726.08	90.35	80.1	225
	LCP	10.211	5.918	4.703	284.21	9.65	x	x
9	LCPF	10.466	6.392	10.879	727.77	97.05	83.2	x
	LCP	10.211	5.918	4.703	284.21	2.95	x	x
9_500	LCPF	10.456	6.389	10.881	726.86	97.75	65.0	68
	LCP	10.231	5.928	4.694	284.69	2.25	x	x
9_600	LCPF	10.455	6.389	10.879	726.67	96.7	53.4	97
	LCP	10.231	5.928	4.694	284.69	3.3	x	x