

## Supplementary materials for

### Effect of cation and anion sizes of additive ionic liquid on the crystal structure of poly(vinylidene fluoride) nanofiber

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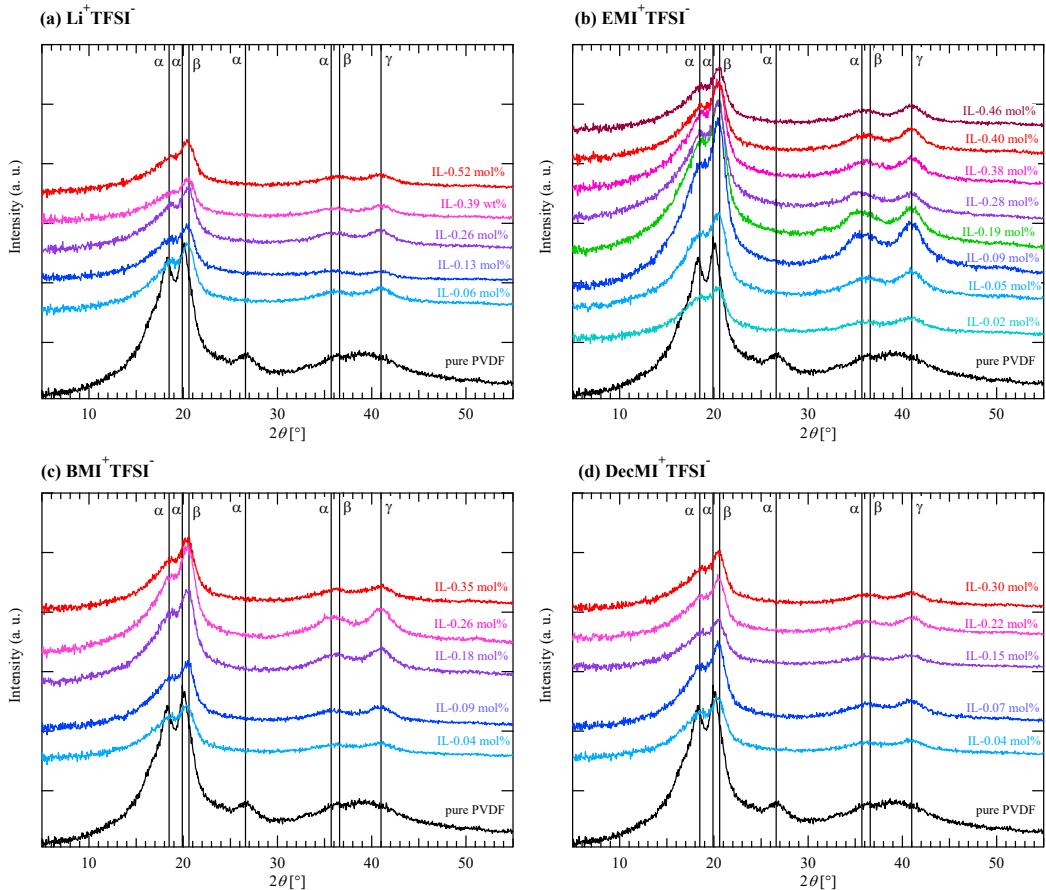
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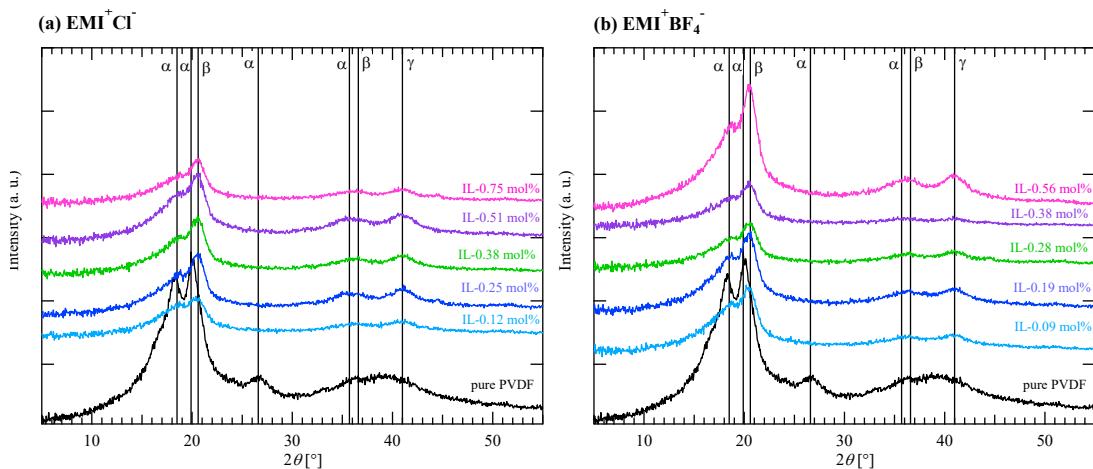
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**Table S1** Correspondence between mol% and wt% for each IL.

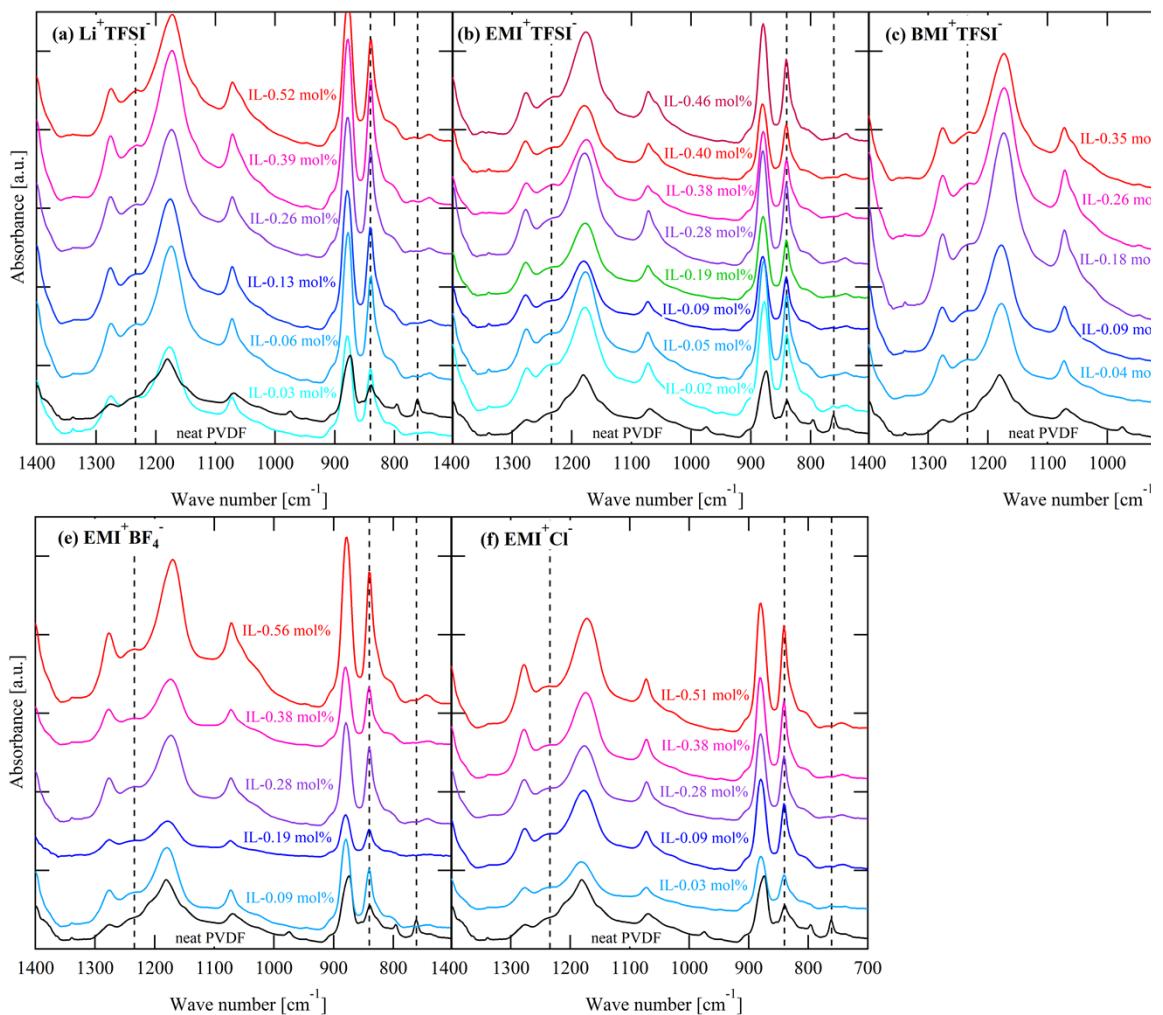
Li <sup>+</sup> TFSI <sup>-</sup>		EMI <sup>+</sup> TFSI <sup>-</sup>		BMI <sup>+</sup> TFSI <sup>-</sup>		DecMI <sup>+</sup> TFSI <sup>-</sup>		EMI <sup>+</sup> Cl <sup>-</sup>		EMI <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	
mol %	wt %	mol %	wt %	mol %	wt %	mol %	wt %	mol %	wt %	mol %	wt %
0.03	0.10	0.05	0.25	0.04	0.25	0.04	0.25	0.03	0.07	0.04	0.10
0.06	0.25	0.09	0.50	0.09	0.50	0.07	0.50	0.09	0.18	0.09	0.25
0.13	0.50	0.19	1.00	0.18	1.00	0.15	1.00	0.19	0.38	0.19	0.50
0.26	1.00	0.28	1.50	0.26	1.50	0.22	1.50	0.28	0.55	0.28	0.75
0.39	1.50	0.38	2.00	0.35	2.00	0.30	2.00	0.38	0.75	0.38	1.01
0.52	2.00	0.46	2.40					0.51	1.01	0.56	1.50



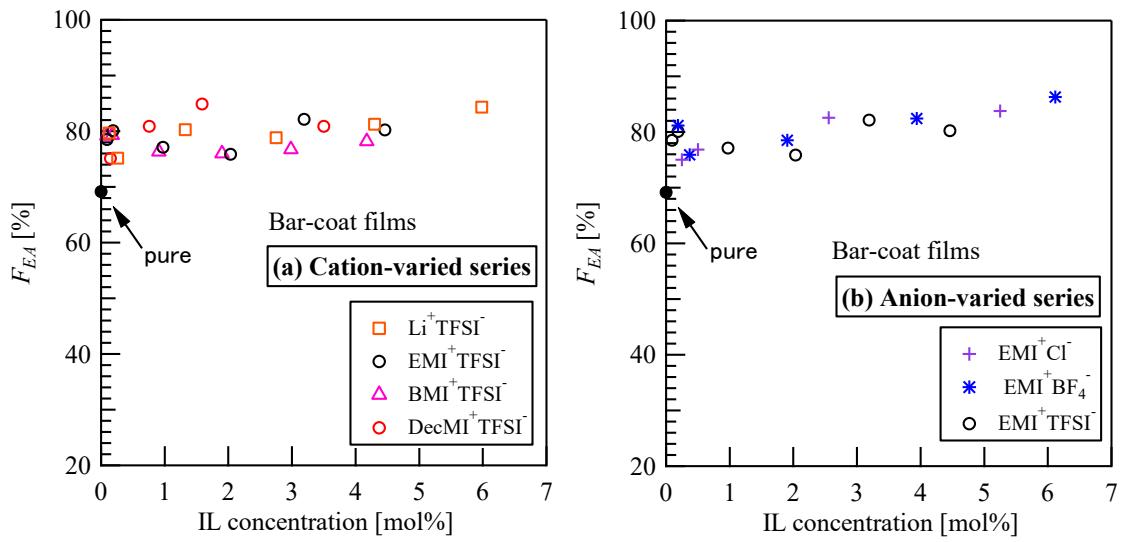
**Figure S1** XRD for cation-varied series. The broken and dotted lines indicate the  $\alpha$ - and  $\beta$ -phases, respectively. The dotted line at  $41.7^\circ$  indicates the  $\gamma$ -phase.



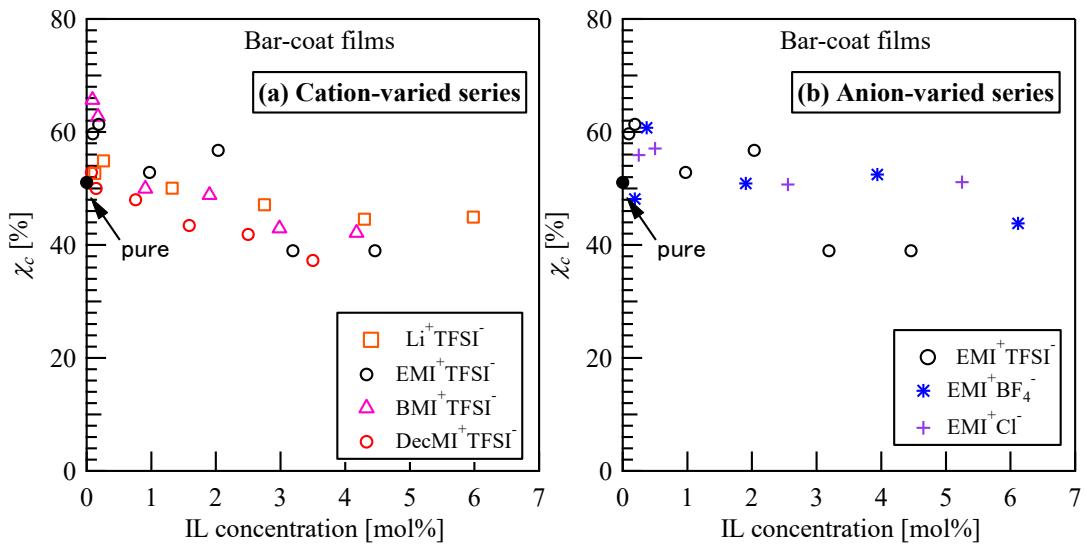
**Figure S2** XRD for anion-varied series. The thin and thick broken lines indicate the  $\alpha$ - and  $\beta$ -phases, respectively. The dotted line at  $41.7^\circ$  indicates the  $\gamma$ -phase.



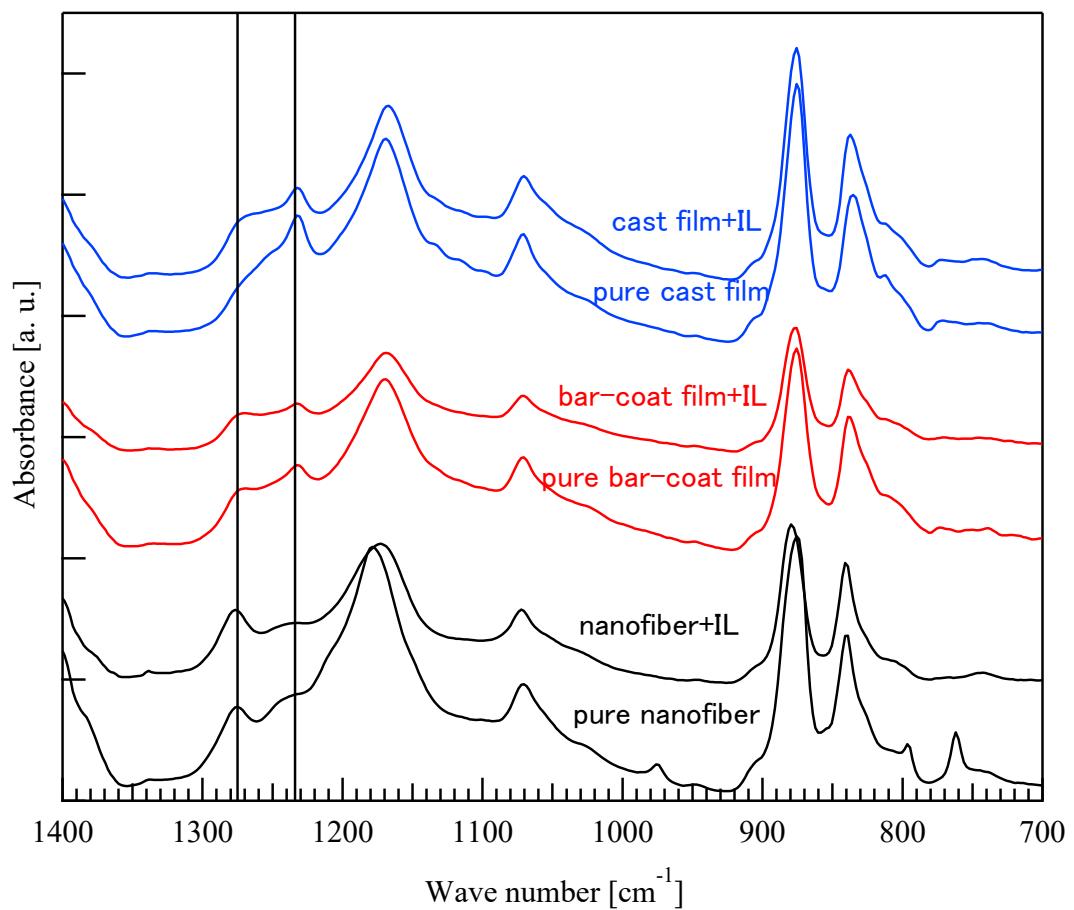
**Figure S3** FT-IR spectra for nanofiber samples containing each IL with various concentrations.



**Figure S4**  $F_{EA}$  values of the bar-coat film samples evaluated from FT-IR measurements. (a) Cation-varied series, (b) anion-varied series. The film samples were washed by ethanol before the measurements, because the spectrum from the IL around  $761\text{ cm}^{-1}$  overlapped with those from the sample (the added IL amount is much larger than the case of nanofiber samples).



**Figure S5** Additive IL concentration dependences on the crystallinity,  $\chi_c$  of the bar-coat film samples. (a) Cation-varied series and (b) anion-varied series.



**Figure S6** FT-IR spectra for cast films, bar-coat films and nanofibers with and without IL. The added IL was EMI<sup>+</sup>BF<sub>4</sub><sup>-</sup>, and the IL concentration was 0.28 mol%.