Supplementary information

Local atomic and electronic structure in the $Li_xVPO_4(F,O)$ Tavorite-type materials from Solid State NMR combined with DFT calculations

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		Exp. Shift (ppm)	Calculated Fermi contact Shift (ppm)	
			GGA	GGA+U (4eV)
$LiVPO_4F$	^{7}Li	115	130	116
	^{31}P	3871	6900	3450
	^{19}F	-1500	-630	-140
$LiVPO_4O$	$^{7}Li(1)$	79	110	44
	$^{7}Li(2)$		105	40
	$^{31}P(1)$	1613	2815	1834
	$^{31}P(2)$	1441	2600	1577

Figure S1: Calculated Fermi contact shifts for ^{7}Li, ^{31}P and ^{19}F in $LiVPO_4F$ and ^{7}Li and ^{31}P in $LiVPO_4O$ compared to experimental ones while spinning at 30 kHz (T~320 K). Calculations were done using GGA and GGA+U approaches. In our previous study on $LiVPO_4F$, several values were used for the U term: as 4eV led to good agreement between calculated and experimental shifts it has been chosen in the previous study ref [1]. Further details concerning the Fermi contact shifts calculations using this method can be found in ref [1-2]. Overall, a localization of the electron on the Vanadium d orbital generated by the U term, induces a weaker spin transfer on the adjacent nuclei and thus a weaker computed Fermi contact shift. It was already discussed in our previous studies [3-4].

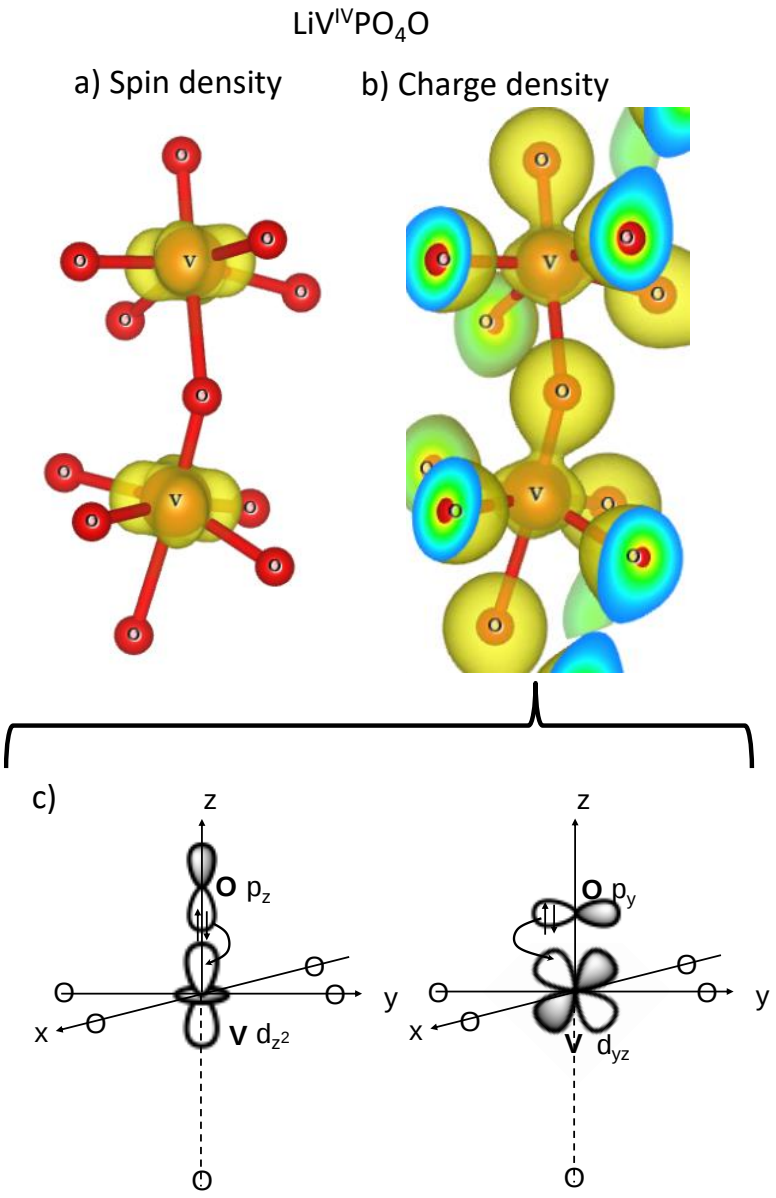

Figure S2: The peculiar electronic structure of V^{4+} ions involved in the vanadyl (V=O) bonds in $LiVPO_4O$. (a) 3D spin density map showing that the d_{xy} orbital perpendicular to the short V=O bond is carrying the spin. (b) 3D charge density map showing the strong covalency of the V=O bond and (c) the theoretical formation of this double bond involving the d_{z2} and the d_{yz} (or d_{xz}) orbitals.

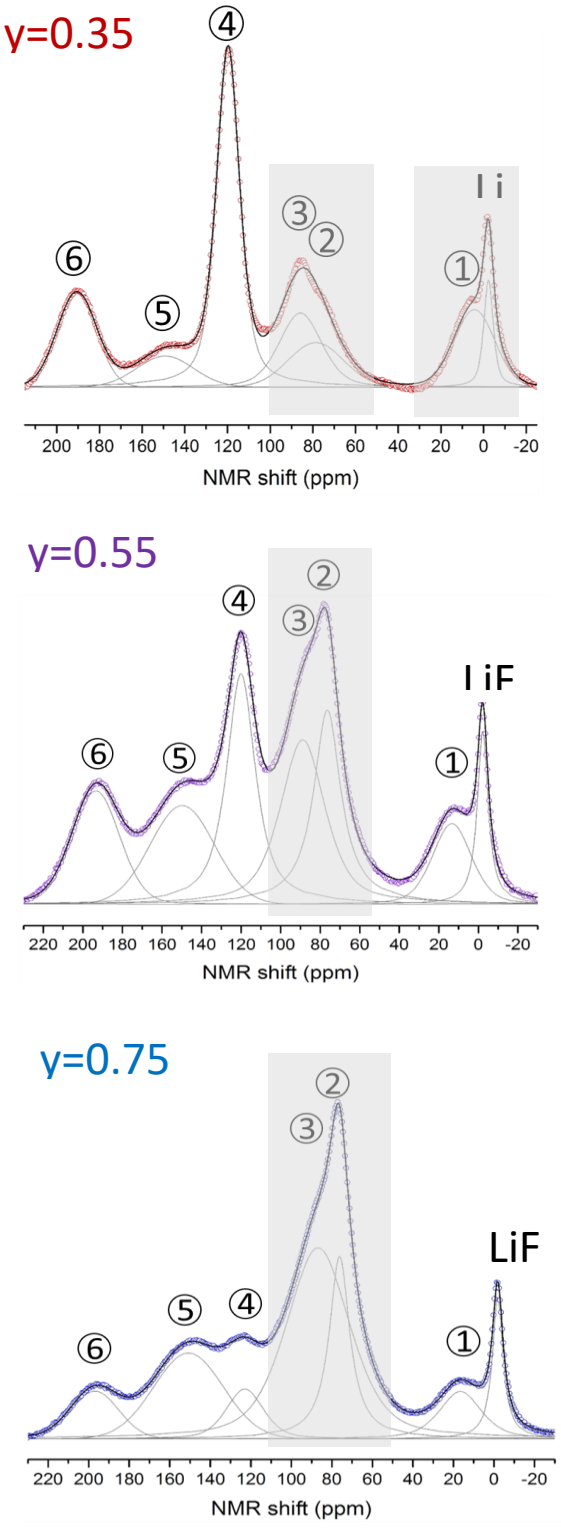

Figure S3: Tentative decomposition of the 1D ^{7}Li MAS NMR spectra of the three intermediate $LiVPO_4F_{1-y}O_y$ phases with y = 0.35, 0.55, 0.75 using 6 contributions with a pseudo voigt lineshape in addition to the LiF contribution around 0ppm. Note that especially in the grey regions with strong overlap, more contributions could have been considered.

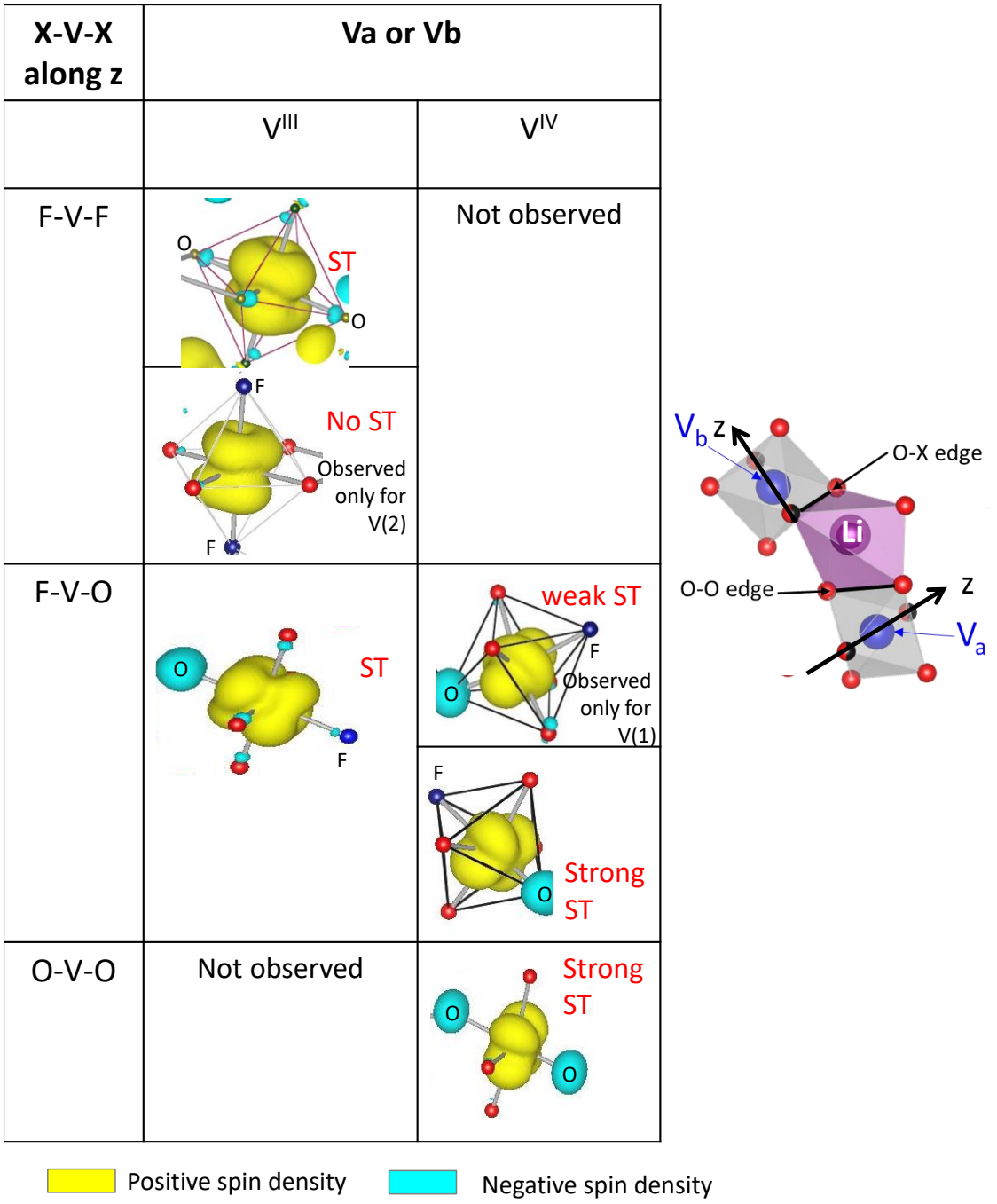

Figure S4: Spin density maps around V ions depending on their VO_4X_2 environment typically calculated for $LiVPO_4(O,F)$ model phases and their corresponding oxidation states V^{III} or V^{IV}. From the Li environment on the left, the expected magnitude of spin transfer from V to Li, relative to the spin transfer observed in $LiV^{III}PO_4F$, is deduced. ST = similar spin transfer, weak ST = weaker spin transfer, strong ST = larger spin transfer and no ST = almost no spin transfer.

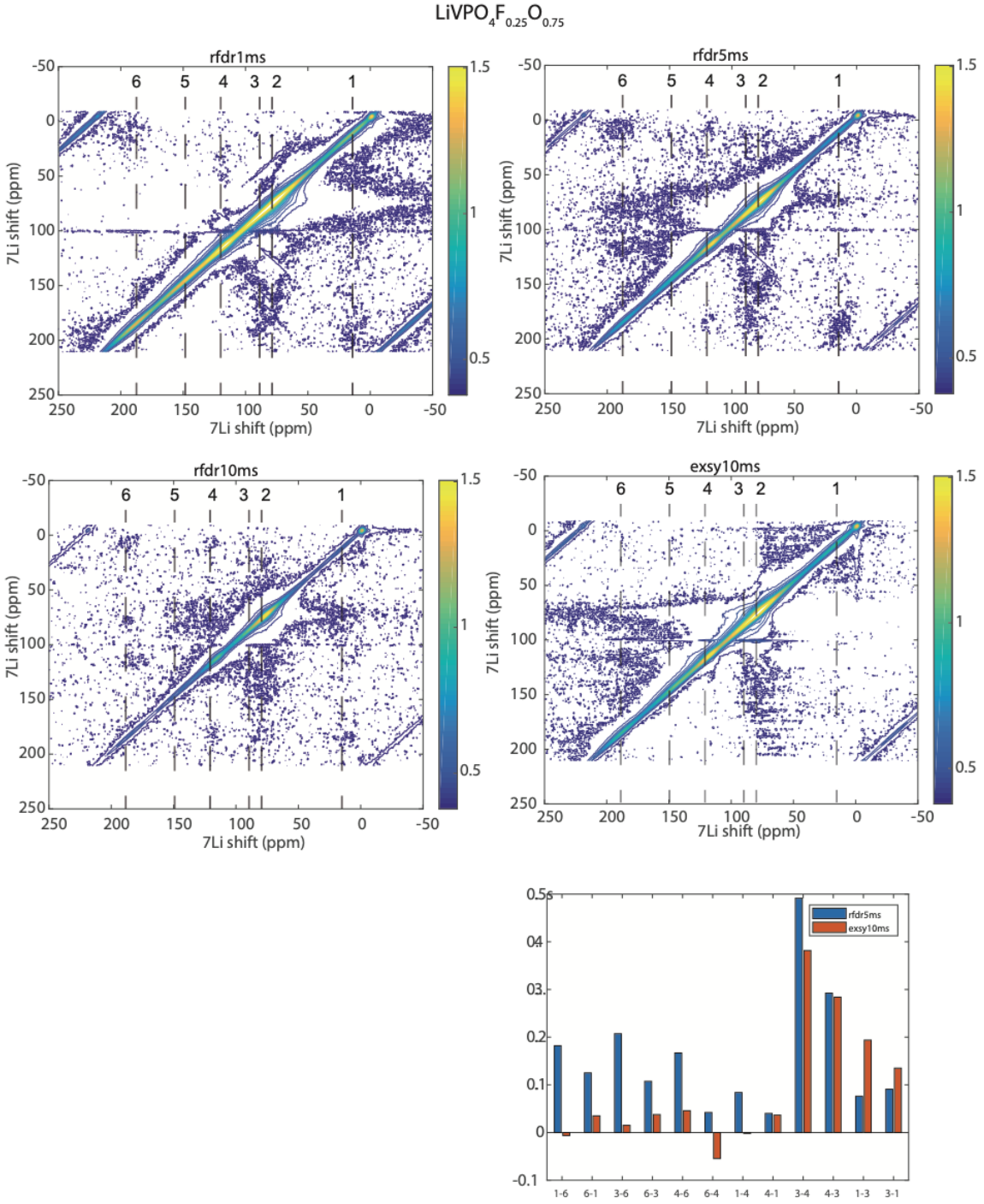

Figure S5: ^{7}Li-^{7}Li fp-RFDR correlation spectra with a mixing time of 1, 5 and 10 ms for $LiVPO_4F_{0.25}O_{0.75}$, with the ^{7}Li-^{7}Li EXSY correlation spectrum acquired in the same conditions with a mixing time of 10 ms. The cross peak areas are compared for the RFDR (5ms) and the EXSY at the bottom tight.

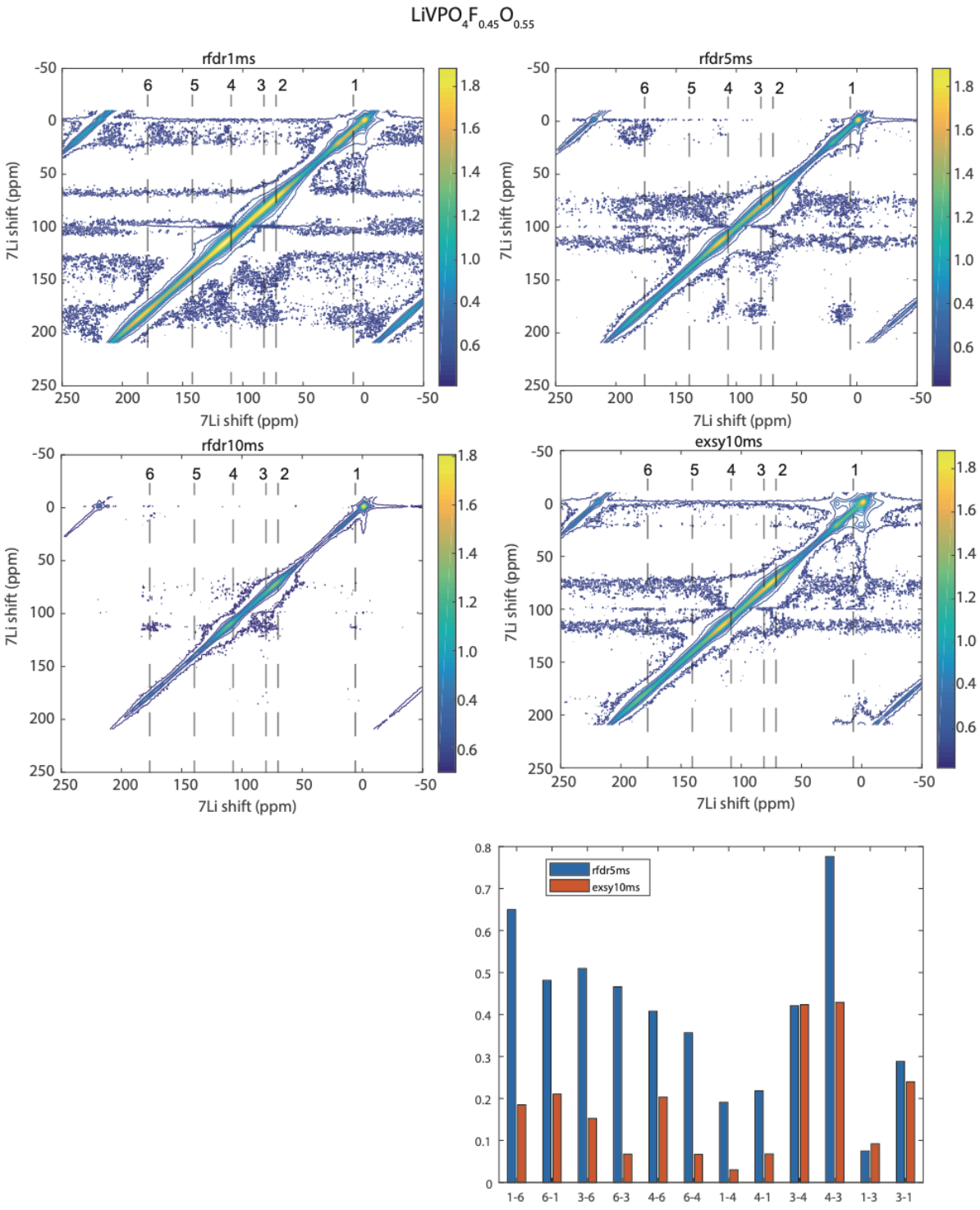

Figure S6: ^{7}Li-^{7}Li fp-RFDR correlation spectra with a mixing time of 1, 5 and 10 ms for $LiVPO_4F_{0.45}O_{0.55}$, with the 7Li-7Li EXSY correlation spectrum acquired in the same conditions with a mixing time of 10 ms. The cross peak areas are compared for the RFDR (5ms) and the EXSY at the bottom tight.

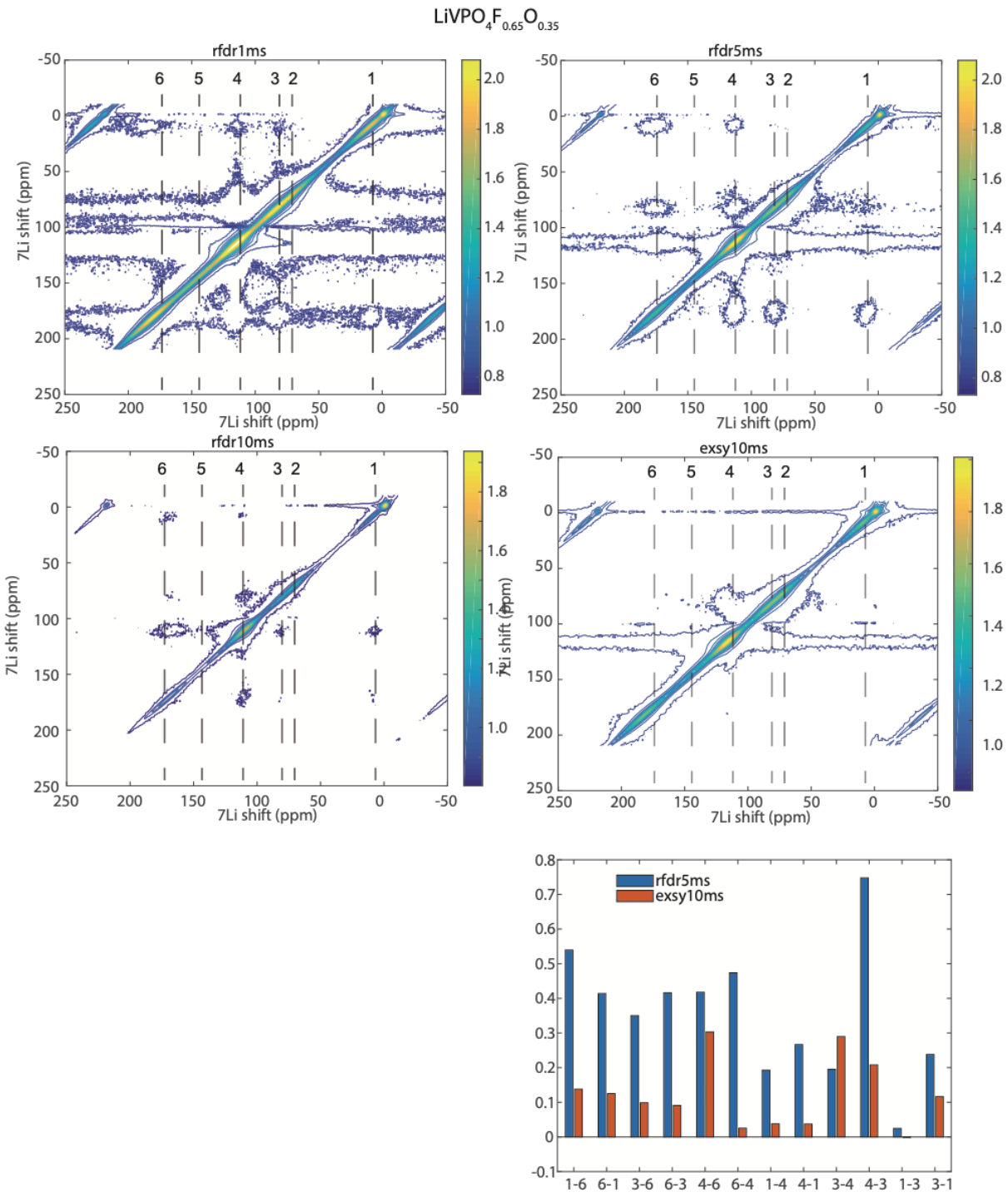

Figure S7: ^{7}Li-^{7}Li fp-RFDR correlation spectra with a mixing time of 1, 5 and 10 ms for)) $LiVPO_4F_{0.65}O_{0.35}$, with the ^{7}Li-^{7}Li EXSY correlation spectrum acquired in the same conditions with a mixing time of 10 ms. The cross peak areas are compared for the RFDR (5ms) and the EXSY at the bottom tight.

References

[1] T. Bamine, T. E. Boivin, F. Boucher, R. Messinger, E. Salager, M. Deschamps, C. Masquelier, L. Croguennec, M. Ménétrier, D. Carlier, *J. Phys. Chem. C* **2017**, *121 (6)*, 3219−3227.

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