Comparison of trifluoromethyl- and pentafluoroethyl-substituted dicyanoimidazolide lithium salts – their association and electrochemical properties in oligo(ethylene glycols) of different chain length

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Supplementary materials

FTIR band assignation description

For the diglyme solutions, in the 2200 cm^{-1} region, we can observe three signals. For LiTDI these signals are found at 2221.6 cm^{-1}, 2225.5 cm^{-1}, and 2244.5 cm^{-1}, while for LiPDI at 2222.2 cm^{-1}, 2227.1 cm^{-1}, and 2244.0 cm^{-1}. They are related to the nitrile moiety stretching vibration (ν C≡N) of "free" moiety, associated moiety, and higher associates, respectively.

In the 1250 cm^{-1} region, we can distinguish three pairs of signals. For LiTDI solutions, these signals can be seen at 1165.3 cm^{-1}, 1173.9 cm^{-1}, 1180.9 cm^{-1}, 1184.9 cm^{-1}, 1193.8 cm^{-1}, and 1200.5 cm^{-1}. The first pair is attributed to the in-plane $–CF_3$ stretching vibrations (ν C–F), while the second pair is attributed to the out-of-plane $–CF_3$ stretching vibrations. The last pair is related to the $–O–CH_3$ rocking vibrations (ρ O–C). The first signal of the pair (the one with the lower wavenumber) can be attributed to the "free" moiety, while the second to the associated moiety. For the LiPDI solutions, there seems to be a set of three pairs of signals at ca. 1200 cm^{-1}, 1215 cm^{-1}, and

1225 cm^{-1}. Due to the overlap with the signals related to –O–CH_3 rocking vibrations, deconvolution of this region was impossible.

In the 850 cm^{-1} region, we can see the set of four pairs of signals, with the additional ninth signal appearing for the pure diglyme. Signals are found at 789.0 cm^{-1}, 802.8 cm^{-1}, 824.1 cm^{-1}, 833.2 cm^{-1}, 842.5 cm^{-1}, 852.3 cm^{-1}, 860.7 cm^{-1}, 870.5 cm^{-1}, and 875.1 cm^{-1}. Signals at 789.0 cm^{-1}, 802.8 cm^{-1}, and 824.1 cm^{-1} are related to –CH_2–CH_2– stretching vibrations (ν C–C), and the signal at 789.0 cm^{-1} appears only for the pure diglyme. Apart from the first signal, the next two can be attributed to the rigid and free chain of diglyme. The next two pairs can be attributed to –CH_2– scissoring vibrations (δ –CH_2–) of different conformations of diglyme. The last pair can be attributed to the –CH_2–O–CH_2– stretching vibrations (ν C–O) of associated and free diglyme, respectively.

In the 750 cm^{-1} region, for the diglyme-LiTDI solutions, there are two pairs of signals at 751.5 cm^{-1} and 752.8 cm^{-1} as well as at 759.9 cm^{-1} and 763.3 cm^{-1}. Signals are related to different modes of –CF_3 deformation vibrations (δ –CF_3). The first signal in each pair can be attributed to "free" moiety, while the second is related to the associated moiety. For the LiPDI-based solutions, five signals are observed in that region at 744.6 cm^{-1}, 746.9 cm^{-1}, 750.4 cm^{-1}, 753.2 cm^{-1}, and 754.0 cm^{-1}. Based on the relative intensities of signals for LiTDI and LiPDI, which are greater for LiPDI, we assume that for LiPDI, there should be a sixth signal, which overlaps and cannot be distinguished during deconvolution.

In the 625 cm^{-1} region, signals are found only for the LiPDI solutions at 625.4 cm^{-1} and 627.2 cm^{-1}. These signals can be attributed to –CF_2– deformation vibrations (δ –CF_2–) of the free and associated moiety, respectively.

For the tetraglyme-based solutions in the 2200 cm^{-1} region, we can observe a similar set of three signals. For LiTDI solutions, they are found at 2221.6 cm^{-1}, 2226.2 cm^{-1}, and 2244.5 cm^{-1}, while for LiPDI solutions at 2222.0 cm^{-1}, 2226.9 cm^{-1}, and 2244.0 cm^{-1}. The first signal is related to "free" moiety, the second to an associated moiety, and the third to the higher associates.

In the 1250 cm^{-1} region, we can see three pairs of signals. The first and second pairs at 1165.5 cm^{-1}, 1174.0 cm^{-1}, 1180.9 cm^{-1}, and 1184.9 cm^{-1} are attributed to in-plane and out-of-plane $–CF_3$ stretching vibrations (ν C–F), of which the signal of lower wavenumber in each pair is related to a "free" moiety and the signal of higher wavenumber is related to an associated moiety. The last pair at 1192.0 cm^{-1} and 1198.9 cm^{-1} can be attributed to the $–O–CH_3$ rocking vibrations (ρ O–C). The first signal of the pair can be attributed to the "free" moiety, while the second is related to the associated moiety. Similarly to diglyme solutions, this region for LiPDI was not deconvoluted.

In the 850 cm^{-1} region, there are three pairs of signals. The first pair at 807.7 cm^{-1} and 825.5 cm^{-1} is related to $–CH_2–CH_2–$ stretching vibrations (ν C–C) of a rigid and free moiety, respectively. The second pair at 840.9 cm^{-1} and 850.2 cm^{-1} is related to $–CH_2–$ scissoring vibrations (δ $–CH_2–$) of the rigid and free chains, respectively. The last pair at 865.4 cm^{-1} and 878.2 cm^{-1} is related to the $–CH_2–O–CH_2–$ stretching vibrations (ν C–O) of associated and free tetraglyme, respectively. The positions and assignments of signals for LiPDI solutions are the same.

In the 750 cm^{-1} region, we can see two pairs of signals at 751.4 cm^{-1}, 752.8 cm^{-1} and 759.8 cm^{-1}, 763.3 cm^{-1}. Signals are related to different modes of $–CF_3$ deformation vibrations (δ $–CF_3$). The first signal in each pair can be attributed to "free" moiety, while the second is related to the associated moiety. Similarly to diglyme-based solutions, for LiPDI, we can observe five signals, which are likely the effect of six overlapping signals. Signals are observed at 744.4 cm^{-1}, 747.3 cm^{-1}, 750.5 cm^{-1}, 753.0 cm^{-1}, and 754.0 cm^{-1}.

In the 625 cm^{-1} region, we can observe only one signal at 625.9 cm^{-1}, which can be attributed to the $–CF_2–$ deformation vibrations (δ $–CF_2–$).

Table S1: FTIR band assignation.

Band position / cm^{-1}	Band assignation
2221-2223	ν C≡N (-C≡N)
2225-2228	ν C≡N (-C≡N$\cdots Li^+$)
2244-2245	ν C≡N (triplets)
1165-1166	ν C-F (-CF_3) in plane
1173-1174	ν C-F (-$CF_3\cdots Li^+$) in plane
1180-1181	ν C-F (-CF_3) out of plane
1198-1199	ν C-F (-$CF_3\cdots Li^+$) out of plane

1192-1194	ρ CH_3-O- (CH_3-O-)
1198-1201	ρ CH_3-O- (CH_3-O$\cdots Li^+$)
789-790	ν C-C (-CH_2-CH_2-)
802-808	ν C-C (-CH_2-CH_2-) free
824-826	ν C-C (-CH_2-CH_2-) rigid
825-834	δ -CH_2 (-CH_2-) free
833-841	δ -CH_2 (-CH_2-) rigid
850-853	δ -CH_2 (-CH_2-) free
860-861	δ -CH_2 (-CH_2-) rigid
865-872	ν C-O-C (-CH_2-O$\cdots Li^+$)
876-879	ν C-O-C (-CH_2-O-)
751-752	δ -CF_3 (-CF_3) $_{LiTDI}$
752-753	δ -CF_3 (-$CF_3\cdots Li^+$) $_{LiTDI}$
759-760	δ -CF_3 (-CF_3) $_{LiTDI}$
763-764	δ -CF_3 (-$CF_3\cdots Li^+$) $_{LiTDI}$
744-745	δ -CF_3 (-CF_3) $_{LiPDI}$
746-748	δ -CF_3 (-$CF_3\cdots Li^+$) $_{LiPDI}$
750-751	δ -CF_3 $_{LiPDI}$
753-754	δ -CF_3 (-CF_3) $_{LiPDI}$
754-755	δ -CF_3 (-$CF_3\cdots Li^+$) $_{LiPDI}$
625-626	δ -CF_2 (-CF_2-)
627-628	δ -CF_2 (-$CF_2\cdots Li^+$)