Supporting Information for:

Ionic liquid-functionalized LDH as catalytic-initiating nanoparticles for microwave-activated ring opening polymerization of ε-caprolactone

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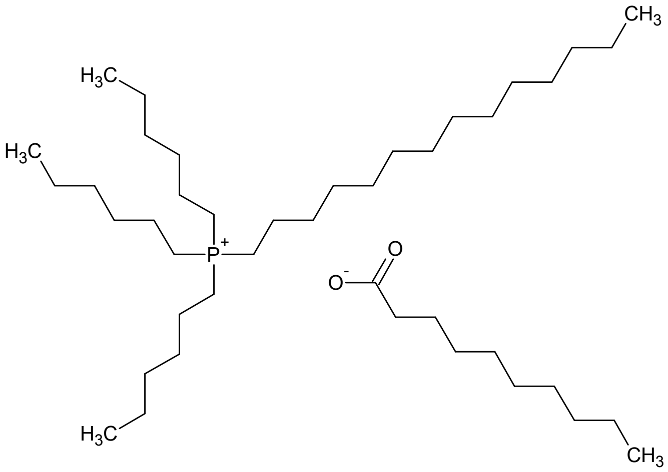

Figure S1. Structure of trihexyl(tetradecyl)phosphonium decanoate ionic liquid (IL-D) used for LDH modification.

Table S1. Basal spacing extension Δd_{hkl} of modified LDH.

Sample	Ca/Al LDH			Ca/Al-D LDH		
Plane (hkl)	(002)	(004)	(006)	(002)	(004)	(006)
2θ [°]	10.3	20.6	31.1	3.0	6.0	8.9
d_{hkl} [nm]	0.859	0.862	0.863	2.945	2.946	2.981
Δd_{hkl} [nm]	-			2.086	2.084	2.118
Intercalated anion size [nm]	0.243 (CO_3^{2-}), 0.230 (NO_3^-)			0.243 (CO_3^{2-}), 0.230 (NO_3^-), 1.33 (decanoate)		

Basal spacing d_{hkl} was calculated using Bragg's law $2d_{hkl} \cdot \sin\theta = n\lambda$, where θ is scattering angle, $n=1,2,3$ is positive integer (order) for (002), (004) and (006) reflection, respectively, λ is wavelength of incident X-ray wave (0.15418 nm).

Basal spacing extension Δd_{hkl} of each Ca/Al-D hkl plane was calculated as difference of Ca/Al-D d_{hkl} and corresponding Ca/Al d_{hkl}:

- $\Delta d_{002} = d_{002}(Ca/Al\text{-}D) - d_{002}(Ca/Al)$
- $\Delta d_{004} = d_{004}(Ca/Al\text{-}D) - d_{004}(Ca/Al)$
- $\Delta d_{006} = d_{006}(Ca/Al\text{-}D) - d_{006}(Ca/Al)$

Intercalated anions sizes were estimated using ACD/ChemSketch 3D Viewer. Size of decanoate anion was determined for extended hydrocarbon chain. All bond lengths and bond angles were normalized using 3D optimalization.

Table S2. Water content in vacuum dried LDH samples determined from TGA.

Sample	H_2O $_{adsorbed}$ [wt %][a]	H_2O $_{intercalated}$ [wt %][b]	H_2O $_{total}$ [wt %][c]
Ca/Al	6.22	3.93	10.15
Ca/Al-D	2.87	8.02	10.89
C-Ca/Al	-	-	0.57[d]
C-Ca/Al-D	-	-	1.85[d]

[a] determined from TGA as the weight loss below 130 °C

[b] determined from TGA as the weight loss between 130 - 200 °C

[c] determined from TGA as the sum of weight losses below 200 °C

[d] adsorbed water determined from TGA as the sum of weight losses below 200 °C

Table S3. XRF, elemental analysis and TGA results of the pristine LDH (Ca/Al) and the LDH modified with decanoate anions (Ca/Al-D).

	XRF		Elemental analysis		TGA	
Sample	Ca [wt %]	Al [wt %]	N [wt %]	C [wt %]	H_2O adsorbed [wt %]	H_2O intercalated [wt %]
Ca/Al	24.85	8.24	2.85	1.35	8.15	4.02
Ca/Al-D	23.28	7.96	0.33	10.33	3.18	9.03

Content of each element in sample differs from its content in formula due to presence of adsorbed and intercalated water. Number of moles of water *n* is related to content of crystalline water in LDH formula. Pristine Ca/Al LDH formula calculation procedure with reference to general LDH formula $[Ca^{2+}_{1-x}Al^{3+}_{x}(OH)_2][(NO_3^-)_m(CO_3^{2-})_{(x-m)/2}]\cdot nH_2O$ was determined as follows:

- number of Ca^{2+} and Al^{3+} moles <u>in whole sample</u> was calculated:

  $n_{Ca}=\mathbf{0.620\ mol}$, $n_{Al}=\mathbf{0.305\ mol}$;
- molar ratio of Ca^{2+}/Al^{3+} was calculated:

  $0.620/0.305=\mathbf{2.03}=1-x/x$;
- number of Al^{3+} moles <u>in formula</u> was calculated:

  $x=\mathbf{0.33}$;
- number of Ca^{2+} moles <u>in formula</u> was calculated:

  $1-x=\mathbf{0.67}$;
- number of NO_3^- moles <u>in whole sample</u> was calculated:

  $n_{NO3-}=\mathbf{0.203\ mol}$;
- number of NO_3^- moles <u>in formula</u> was calculated as a proportion keeping constant ratio between content of Al^{3+} in sample and NO_3^- in sample:

  $m=0.203\cdot 0.33/0.305=\mathbf{0.22}$;
- number of CO_3^{2-} moles <u>in formula</u> was calculated:

  $(x-m)/2=\mathbf{0.055}$;
- total water content w_{H2O} in sample was calculated as a complementary value to 100% sample weight:

Ions and water <u>in formula</u>	Ca^{2+}	Al^{3+}	OH^-	NO_3^-	CO_3^{2-}	H_2O
Number of moles <u>in formula</u>	0.67	0.33	2	0.22	0.055	*n*
Number of moles <u>in sample</u>	0.62	0.305	1.85	0.203	0.051	
Molecular weight [g/mol]	40.08	26.98	17.02	62.00	60.01	18.02
Content of species <u>in sample</u> [wt.%]	24.85	8.24	31.50	12.60	3.06	w_{H2O}

$w_{H2O}=100-24.85-8.24-31.5-12.6-3.06=\mathbf{19.75\%}$

- content of crystalline water w_{cryst} was calculated as:

  $w_{cryst}=w_{H2O}-w_{intercalated}-w_{adsorbed}=19.75-4.02-8.15=\mathbf{7.58\%}$
- as weight content of species is equal to mass of species per 100 g of whole sample, *n* mole content of crystalline water was calculated:

  $n=7.58/18.02=\mathbf{0.42\ mol}$

Content of <u>decanoate anions</u> in whole Ca/Al-D LDH sample was calculated analogically as a value complementary to 100% sample weight with some assumptions:

✓ content of CO_3^{2-} is constant for both samples;
✓ number of moles of crystalline water *n* is constant for both samples;
✓ only nitrate anions undergo anion exchange reaction with decanoate anions.

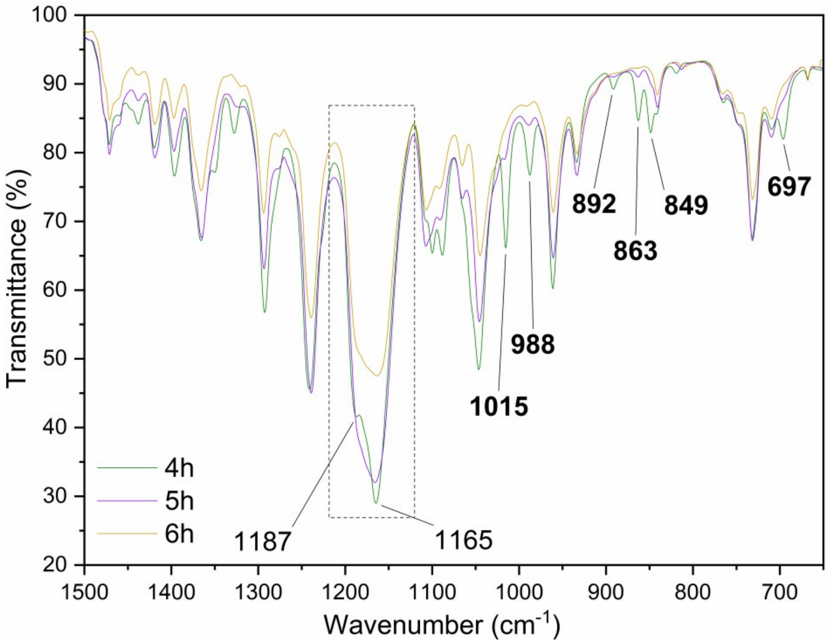

Figure S2. ATR-FTIR spectra of samples containing 0.5 wt.% Ca/Al-D after 240 min, 300 min and 360 min (reaction 6). Peaks marked in bold wavenumber are related to monomer. Intensity of them decreases with time what corresponds to increasing monomer conversion reaching 98.9% after 6 hours of reaction time. Peak at 1165 cm^{-1} related to ester bond in lactones confirms presence of cyclic structures in final reaction mixture. However, regarding to original position of this peak for monomer (1164 cm^{-1}), it is slightly shifted to higher wavenumber values.

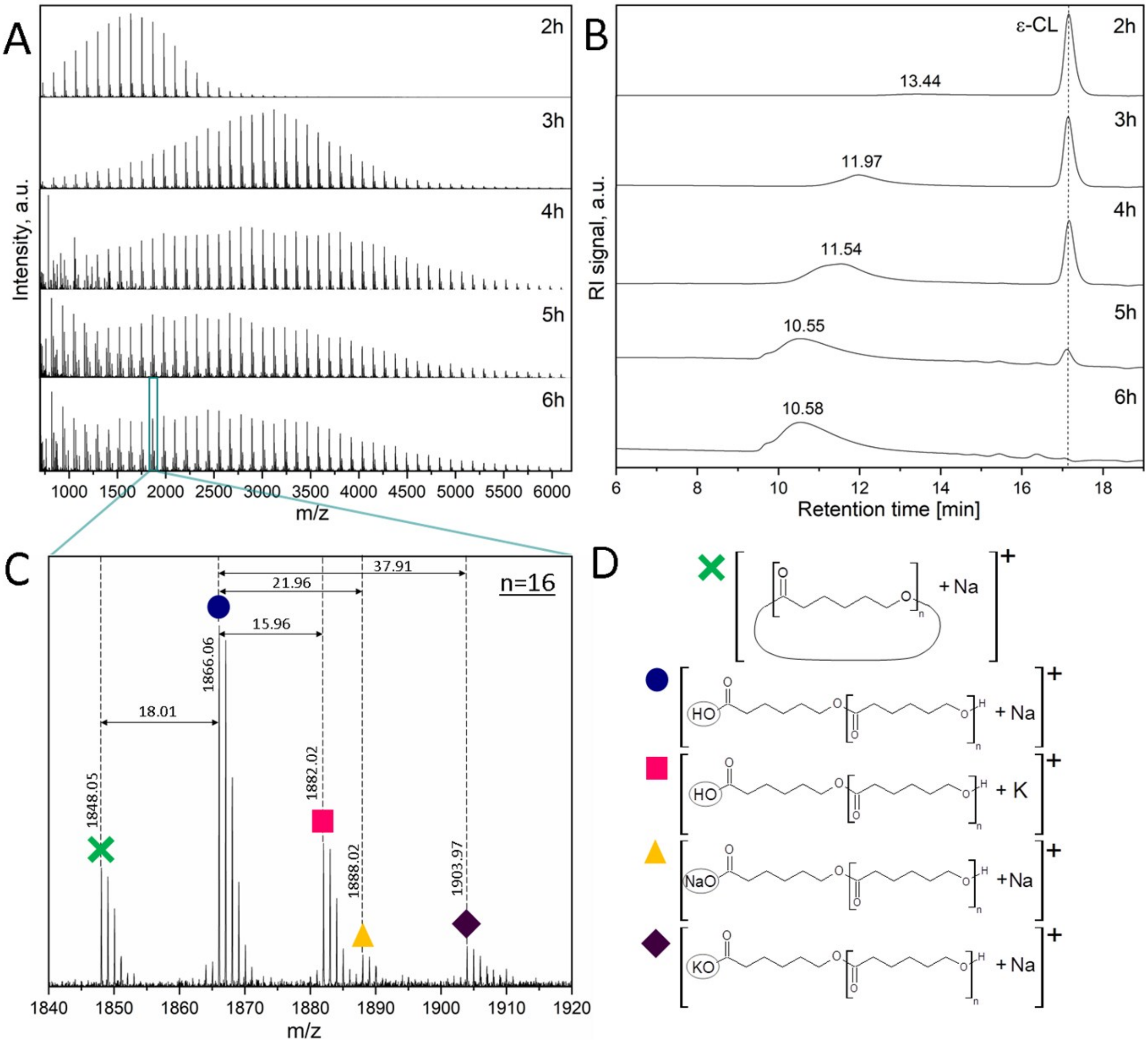

Figure S3. MALDI-TOF mass spectra (A and C) with corresponding polymer structures (D) and GPC traces (B) during the microwave-assisted ring opening polymerization of ε-caprolactone after 2 h, 3 h, 4 h, 5 h and 6 h at 170 °C in the presence of 0.5 wt% LDH modified with decanoate anions (Ca/Al-D, reaction 6)

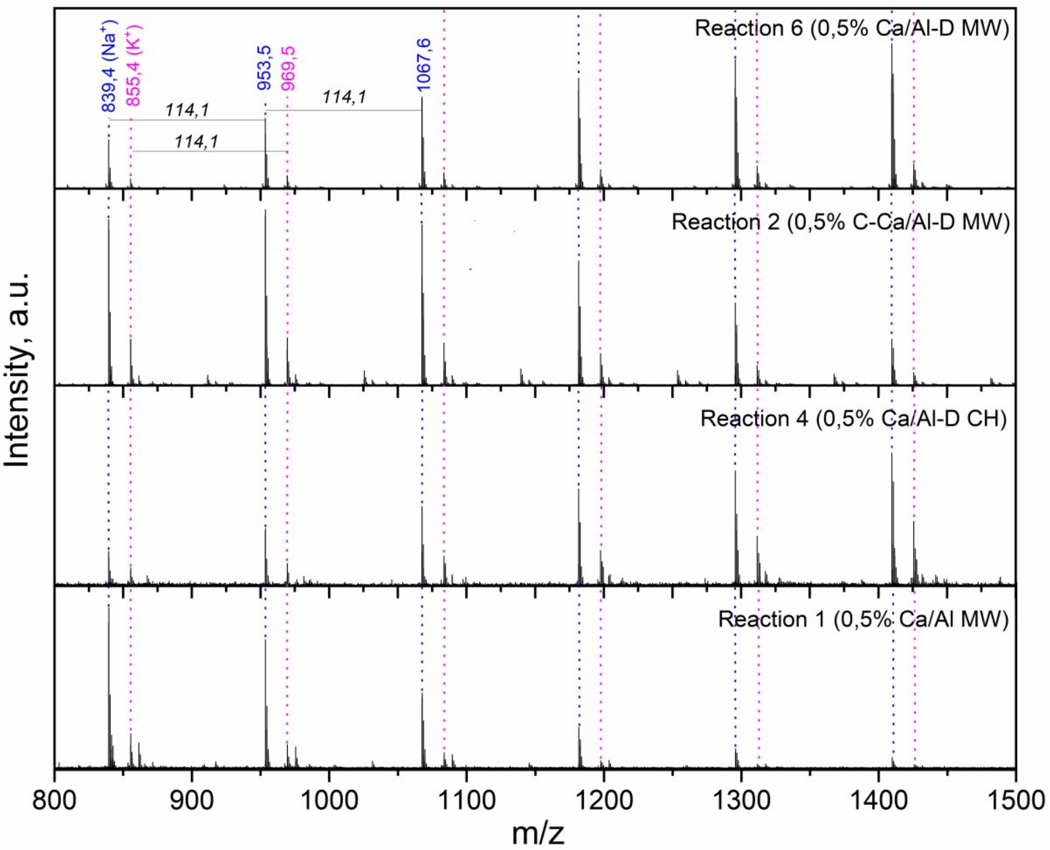

Figure S4. MALDI-TOF mass spectra of samples after 2h in m/z range of 800 -1500 Da (reaction 6, 2, 4 and 1).

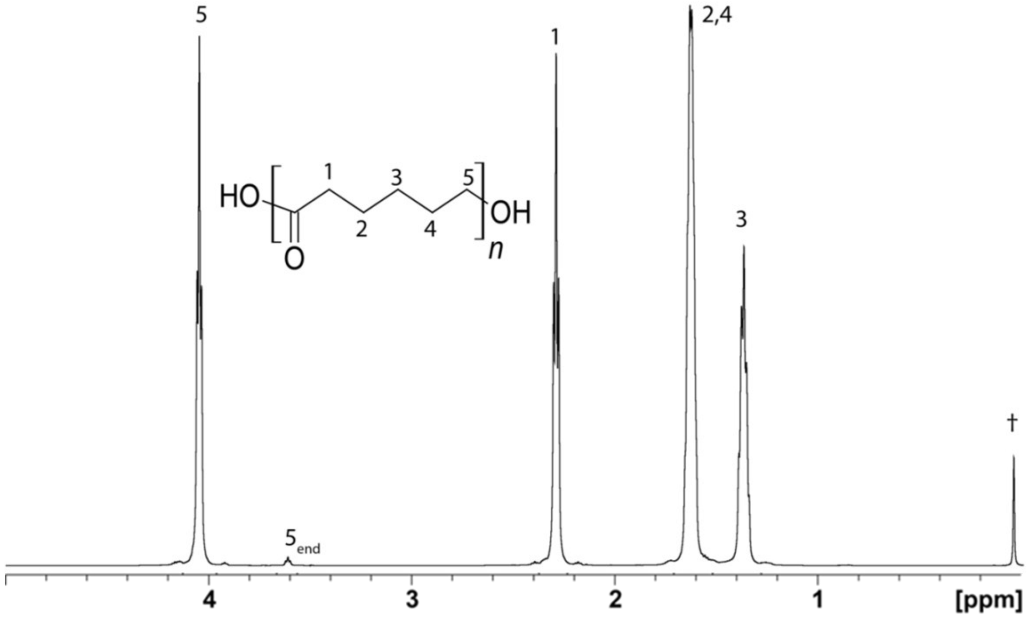

Figure S5. ^{1}H NMR spectrum of the reaction 6 (R6) product after 6h showing the structure of the prepared polymer with the peak at 3.6 ppm (5_{end} marked) corresponding to the end-group. The cross corresponds to the standard HMDS, its peak is set to 0.05 ppm.

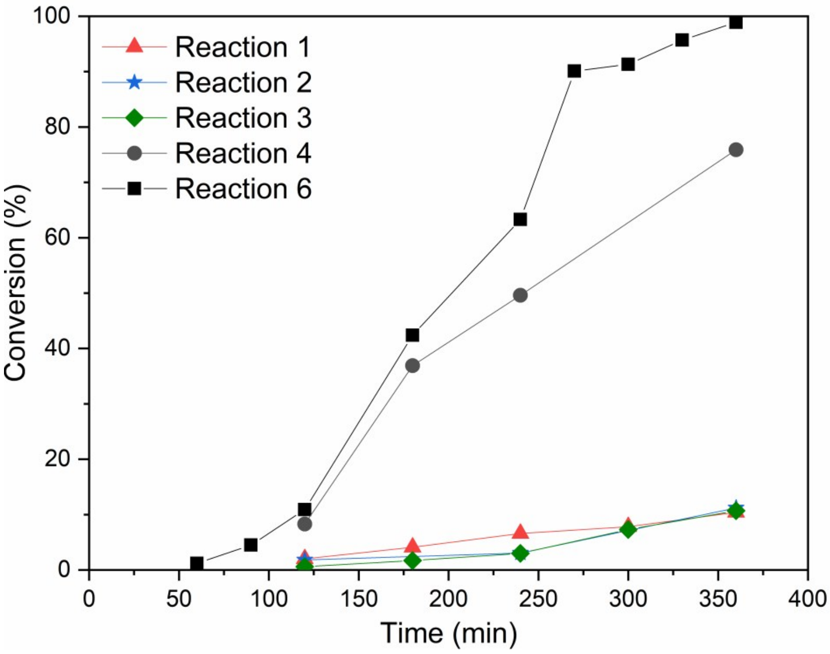

Figure S6. Conversion-time plots of microwave-assisted ROP of ε-caprolactone conducted in the presence of different type of LDH. For reaction conditions – see Table 1.

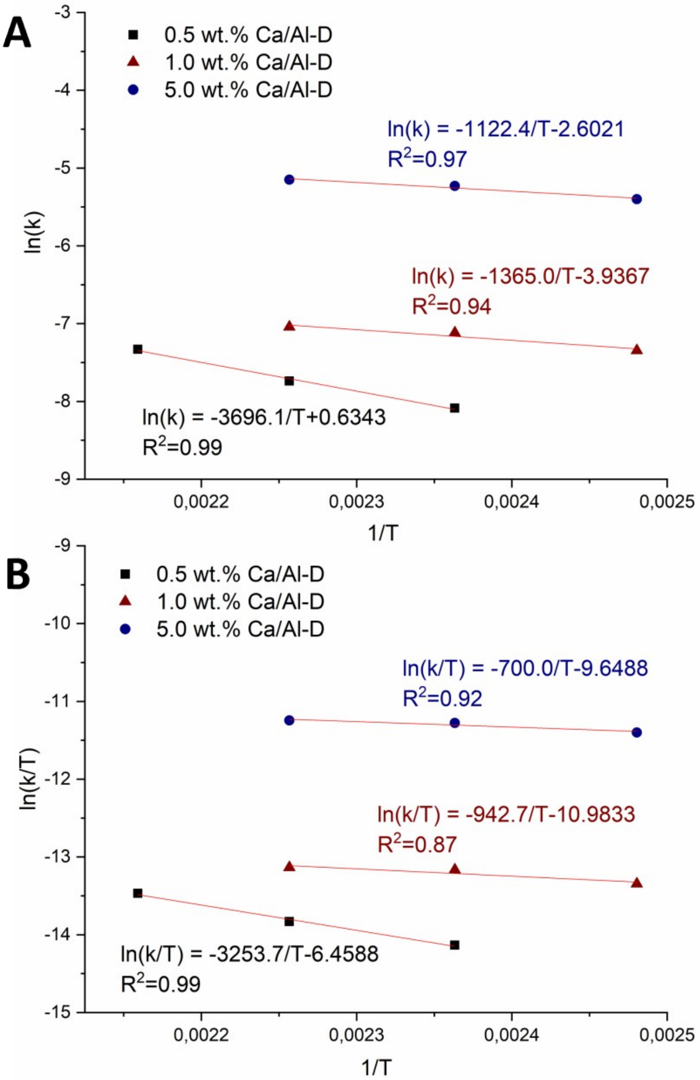

Figure S7. Arrhenius (A) and Eyring (B) plots microwave-assisted ROP of ε-caprolactone conducted in the presence of 0.5, 1.0 and 5.0 wt % LDH modified with decanoate anion (Ca/Al-D).

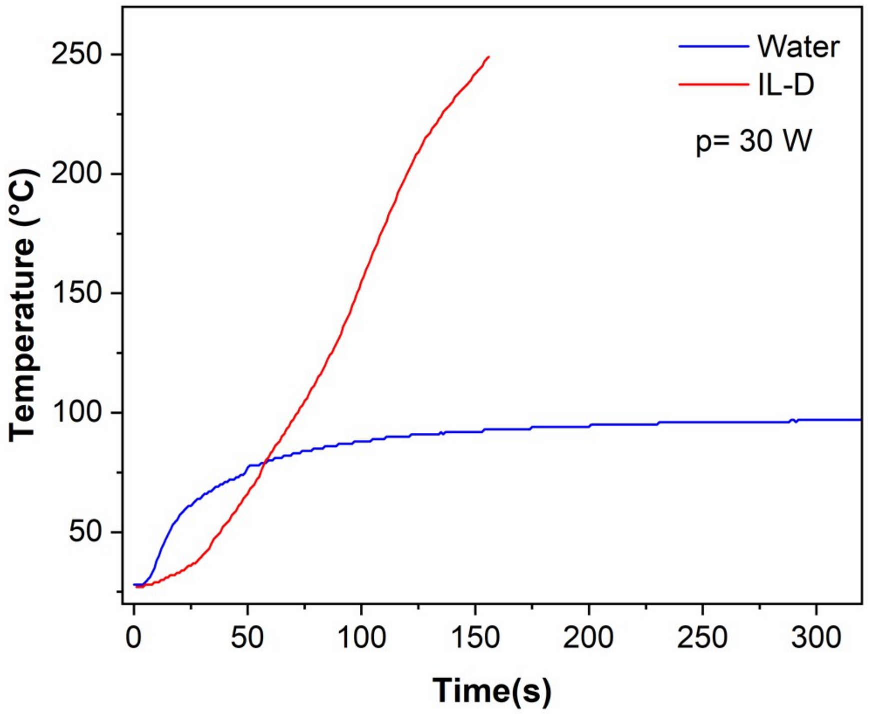

Figure S8. Temperature profiles of trihexyl(tetradecyl)phosphonium decanoate ionic liquid (IL-D) and water under microwave irradiation at constant power of 30 W. This comparison demonstrates much stronger ability of IL-D to absorb microwave energy than that of water. At a relatively low level of microwave power, IL-D reached 200 °C within 2 min.