Supporting Information

Alkylimidazolium Based Ionic Liquids: Impact of Cation Symmetry on the Nanoscale Structural Organization

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TABLES

Table 1S. Experimental density results at 0.1 MPa, ρ, for the $[C_{N-1}C_1im][NTf_2]$ ionic liquid series as a function of temperature.

T / K	ρ / (kg·m^{-3})								
	$[C_2C_1im][NTf_2]$	$[C_3C_1im][NTf_2]$	$[C_4C_1im][NTf_2]$	$[C_5C_1im][NTf_2]$	$[C_7C_1im][NTf_2]$	$[C_9C_1im][NTf_2]$	$[C_{11}C_1im][NTf_2]$	$[C_{14}C_1im][NTf_2]$	$[C_{16}C_1im][NTf_2]$
278.15	1539.8	1495.3	1452.0	1422.5	1363.0	1316.4	1279.1		
283.15	1534.6	1490.3	1447.0	1417.6	1358.2	1311.8	1274.5		
288.15	1529.5	1485.3	1442.2	1412.9	1353.6	1307.3	1270.1		
293.15	1524.4	1480.3	1437.4	1408.1	1349.1	1302.8	1265.7		
298.15	1519.3	1475.3	1432.5	1403.4	1344.6	1298.4	1261.4		
303.15	1514.2	1470.4	1427.8	1398.7	1340.1	1294.1	1257.1		
308.15	1509.1	1465.4	1423.0	1394.0	1335.6	1289.7	1252.9		
313.15	1504.1	1460.5	1418.3	1389.3	1331.1	1285.4	1248.6		
318.15	1499.0	1455.6	1413.5	1384.7	1326.7	1281.1	1244.4		
323.15	1494.0	1450.7	1408.8	1380.1	1322.3	1276.8	1240.2	1192.2	1170.0
328.15	1489.0	1445.8	1404.1	1375.5	1317.8	1272.5	1236.0	1188.1	1165.9
333.15	1484.1	1441.0	1399.4	1370.9	1313.4	1268.3	1231.8	1184.1	1161.9
338.15	1479.1	1436.2	1394.8	1366.4	1309.0	1264.0	1227.6	1180.0	1157.9
343.15	1474.2	1431.4	1390.2	1361.8	1304.6	1259.8	1223.5	1176.0	1153.9
348.15	1469.3	1426.6	1385.5	1357.3	1300.2	1255.6	1219.4	1172.0	1149.9
353.15	1464.4	1421.9	1381.0	1352.8	1295.9	1251.4	1215.3	1168.0	1146.0
358.15	1459.6	1417.2	1376.4	1348.4	1291.5	1247.3	1211.2	1164.1	1142.1
363.15				1344.0	1287.2	1243.1	1207.2	1160.2	1138.2

Table 2S. Experimental density results at 0.1 MPa, ρ, for the $[C_{N/2}C_{N/2}im][NTf_2]$ ionic liquid series as a function of temperature.

	ρ / (kg·m^{-3})										
	$[C_1C_1im]$	$[C_2C_2im]$	$[C_3C_3im]$	$[C_4C_4im]$	$[C_5C_5im]$	$[C_6C_6im]$	$[C_7C_7im]$	$[C_8C_8im]$	$[C_9C_9im]$	$[C_{10}C_{10}im]$	$[C_{12}C_{12}im]$
T / K	$[NTf_2]$	$[NTf_2]$	$[NTf_2]$	$[NTf_2]$	$[NTf_2]$	$[NTf_2]$	$[NTf_2]$	$[NTf_2]$	$[NTf_2]$	$[NTf_2]$	$[NTf_2]$
278.15		1495.1	1418.3	1361.2	1310.3	1272.6	1242.4	1211.8	1185.9	1168.6	
283.15		1489.6	1413.4	1356.5	1305.7	1268.1	1237.9	1207.4	1181.5	1164.3	
288.15		1484.9	1408.6	1351.9	1301.2	1263.7	1233.6	1203.1	1177.4	1160.3	
293.15	1574.5	1479.9	1403.8	1347.3	1296.8	1259.3	1229.4	1198.9	1173.2	1156.2	
298.15	1569.2	1474.9	1399.0	1342.8	1292.4	1255.0	1225.2	1194.8	1169.2	1152.2	
303.15	1564.0	1469.9	1394.2	1338.2	1288.0	1250.7	1221.0	1190.7	1165.2	1148.2	
308.15	1558.8	1465.0	1389.5	1333.7	1283.7	1246.5	1216.9	1186.6	1161.2	1144.2	
313.15	1553.6	1460.0	1384.8	1329.3	1279.3	1242.2	1212.8	1182.6	1157.3	1140.3	
318.15	1548.5	1455.1	1380.2	1324.8	1275.0	1238.0	1208.7	1178.6	1153.4	1136.4	
323.15	1543.3	1450.2	1375.5	1320.3	1270.7	1233.8	1204.6	1174.5	1149.4	1132.5	1097.6
328.15	1538.2	1445.3	1370.9	1315.9	1266.4	1229.6	1200.6	1170.5	1145.5	1128.7	1093.9
333.15	1533.1	1440.5	1366.3	1311.5	1262.2	1225.5	1196.5	1166.5	1141.6	1124.8	1090.1
338.15	1528.1	1435.6	1361.7	1307.2	1257.9	1221.4	1192.5	1162.6	1137.7	1120.9	1086.4
343.15	1523.1	1430.8	1357.1	1302.8	1253.7	1217.2	1188.5	1158.6	1133.9	1117.1	1082.7
348.15	1518.1	1426.0	1352.6	1298.5	1249.5	1213.1	1184.4	1154.7	1130.0	1113.3	1079.0
353.15	1513.1	1421.2	1348.0	1294.2	1245.3	1209.0	1180.5	1150.7	1126.2	1109.5	1075.4
358.15	1508.1	1416.4	1343.6	1289.9	1241.2	1204.9	1176.5	1146.9	1122.3	1105.7	1071.7
363.15	1503.2	1411.7	1339.1	1285.6	1237.0	1200.9	1172.6	1143.0	1118.5	1102.0	1068.1

Table 3S. Experimental viscosity results at 0.1 MPa, η, for the $[C_{N-1}C_1im][NTf_2]$ ionic liquid series as a function of temperature.

T / K	η / (mPa·s)				
	$[C_5C_1im]$ $[NTf_2]$	$[C_9C_1im]$ $[NTf_2]$	$[C_{11}C_1im]$ $[NTf_2]$	$[C_{14}C_1im]$ $[NTf_2]$	$[C_{16}C_1im]$ $[NTf_2]$
278.15	181.43	354.64	475.42		
283.15	134.44	254.28	336.89		
288.15	101.97	187.03	244.85		
293.15	78.996	140.50	179.87		
298.15	62.384	107.90	138.02		
303.15	50.122	84.330	106.70		
308.15	40.871	67.020	83.910		
313.15	33.807	54.242	66.821		
318.15	28.317	44.260	54.337		
323.15	23.990	36.683	44.626	61.672	81.237
328.15	20.544	30.761	37.099	50.589	65.697
333.15	17.749	26.310	31.407	42.104	54.004
338.15	15.469	22.301	26.476	35.234	44.712
343.15	13.587	19.250	22.689	29.861	37.542
348.15	12.020	16.753	19.614	25.539	31.871
353.15	10.704			22.079	27.301
358.15	9.5897	12.970	14.999	19.137	23.480
363.15	8.6394	11.527	13.255	16.739	20.388

Table 4S. Experimental viscosity results at 0.1 MPa, η, for the $[C_{N/2}C_{N/2}im][NTf_2]$ ionic liquid series as a function of temperature.

T / K	η / (mPa·s)										
	$[C_1C_1im]$ $[NTf_2]$	$[C_2C_2im]$ $[NTf_2]$	$[C_3C_3im]$ $[NTf_2]$	$[C_4C_4im]$ $[NTf_2]$	$[C_5C_5im]$ $[NTf_2]$	$[C_6C_6im]$ $[NTf_2]$	$[C_7C_7im]$ $[NTf_2]$	$[C_8C_8im]$ $[NTf_2]$	$[C_9C_9im]$ $[NTf_2]$	$[C_{10}C_{10}im]$ $[NTf_2]$	$[C_{12}C_{12}im]$ $[NTf_2]$
278.15			157.39	204.75	305.55	372.75	465.71	575.61	684.41		
283.15			117.13	150.67	220.39	266.69	330.56	404.83	475.01		
288.15		44.808	89.324	113.75	163.09	195.54	240.46	292.06	339.25		
293.15	46.228	36.890	69.517	87.625	123.25	146.49	176.75	212.10	249.93		
298.15	38.058	30.784	55.111	68.739	94.970	111.92	135.49	161.77	185.49	211.59	
303.15	31.807	26.020	44.429	54.845	74.473	87.049	104.62	123.87	141.54	160.75	
308.15	26.902	22.207	36.364	44.435	59.352	68.762	82.094	96.548	109.70	124.24	
313.15	23.016	19.149	30.173	36.506	48.011	55.214	65.265	75.967	86.875	96.836	
318.15	19.891	16.654	25.348	30.374	39.369	44.973	52.931	61.309	69.230	77.761	
323.15	17.343	14.611	21.534	25.569	32.685	37.099	43.372	49.891	56.164	62.827	87.146
328.15	15.233	12.896	18.484	21.748	27.450	30.960	35.959	41.083	46.106	51.416	70.405
333.15	13.490	11.460	16.008	18.679	23.293	26.111	30.387	34.460	38.392	42.767	57.594
338.15	12.025	10.246	13.981	16.183	19.951	22.258	25.543	28.836	32.134	35.628	47.655
343.15	10.785	9.2098	12.304	14.135	17.242	19.136	21.840	24.529	27.245	30.114	39.842
348.15	9.7307	8.3154	10.903	12.440	15.021	16.582	18.834	21.057	23.278	25.687	33.629
353.15	8.8211	7.5397	9.7271	11.025	13.184	14.481	16.721		20.116	22.485	28.637
358.15	8.0304	6.8706	8.7290	9.8310	11.653	12.733	14.359	15.879	17.418	19.150	24.584
363.15	7.3432	6.2895	7.8756	8.8163	10.369	11.270	12.638	13.939	15.227	16.718	21.269

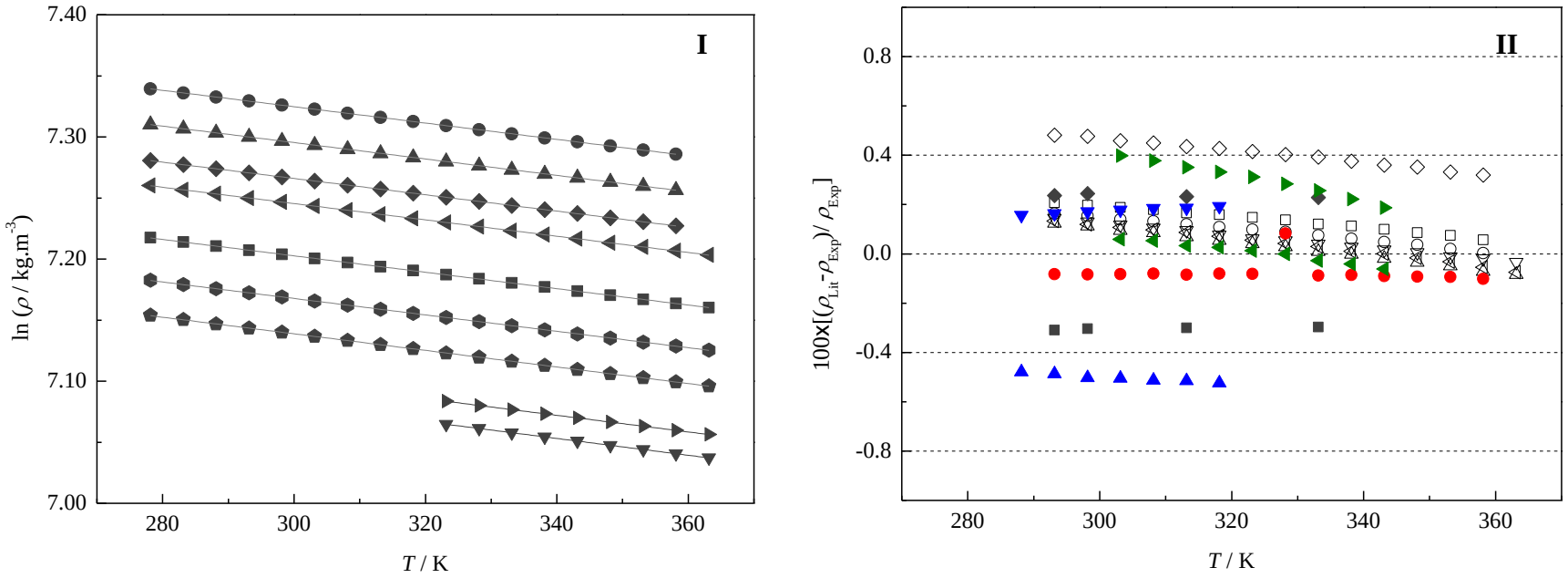

Figure 1S. (I) Logarithm of density as a function of temperature for the $[C_{N\text{-}1}C_1im][NTf_2]$ ionic liquid series: ● - $[C_2C_1im][NTf_2]$; ▲- $[C_3C_1im][NTf_2]$; ◆ - $[C_4C_1im][NTf_2]$; ◀ - $[C_5C_1im][NTf_2]$; ■ - $[C_7C_1im][NTf_2]$; ⬢ - $[C_9C_1im][NTf_2]$; ⬟ - $[C_{11}C_1im][NTf_2]$; ▶ - $[C_{14}C_1im][NTf_2]$; ▼ - $[C_{16}C_1im][NTf_2]$. The thin lines represent from the linear fitting of the experimental results by eq 1. **(II)** Relative deviations between the experimental density measured in this work (ρ_{exp}) and those reported in the literature (ρ_{exp}) as a function of temperature for the $[C_{N\text{-}1}C_1im][NTf_2]$ ionic liquid series. Tariq *et al.*[21] : □ - $[C_2C_1im][NTf_2]$; ○ - $[C_3C_1im][NTf_2]$; ◇ - $[C_4C_1im][NTf_2]$; ◁ - $[C_5C_1im][NTf_2]$; ▽ - $[C_7C_1im][NTf_2]$; △ - $[C_9C_1im][NTf_2]$; ▷ - $[C_{14}C_1im][NTf_2]$. Tariq *et al.* [18]: ■ - $[C_2C_1im][NTf_2]$; ◆ - $[C_4C_1im][NTf_2]$; Jacquemin *et al.*[22] : ● - $[C_2C_1im][NTf_2]$. Tokuda *et al.*[23] : ▼- $[C_2C_1im][NTf_2]$; ▲ - $[C_4C_1im][NTf_2]$. M.F. Costa Gomes *et al.*[24] ◀ - $[C_2C_1im][NTf_2]$, ▶ - $[C_4C_1im][NTf_2]$.

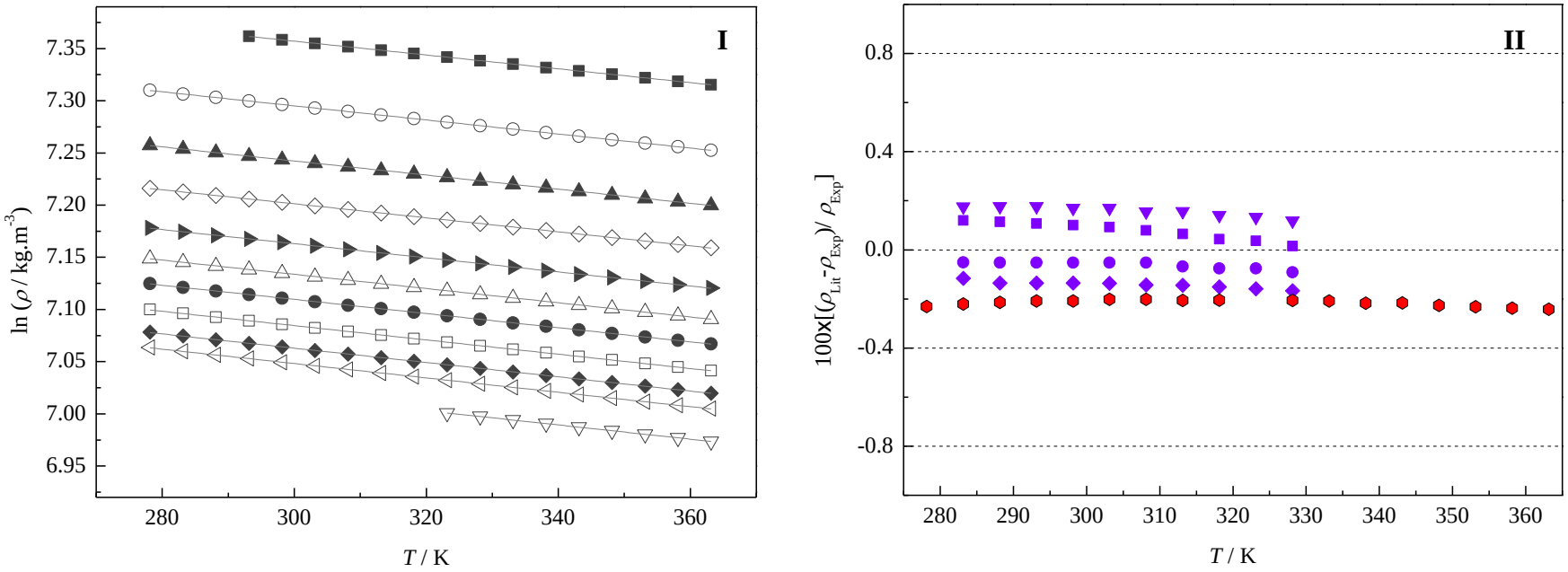

Figure 2S. (I) Logarithm of density as a function of temperature for the $[C_{N/2}C_{N/2}im][NTf_2]$ ionic liquid series: ■ - $[C_1C_1im][NTf_2]$; ○ - $[C_2C_2im][NTf_2]$; ▲- $[C_3C_3im][NTf_2]$; ◇ - $[C_4C_4im][NTf_2]$; ▶ - $[C_5C_5im][NTf_2]$; △ - $[C_6C_6im][NTf_2]$; ● - $[C_7C_7im][NTf_2]$; □ - $[C_8C_8im][NTf_2]$; ◆ - $[C_9C_9im][NTf_2]$; ◁ - $[C_{10}C_{10}im][NTf_2]$; ▽ - $[C_{12}C_{12}im][NTf_2]$. The thin lines results from the linear fitting of the experimental results. **(II)** Relative deviations between the experimental density measured in this work (ρ_{exp}) and those reported in the literature (ρ_{exp}) as a function of temperature for $[C_{N/2}C_{N/2}im][NTf_2]$ ionic liquid series. Zheng *et al.* [14]: ◆- $[C_2C_2im][NTf_2]$; ●- $[C_3C_3im][NTf_2]$; ■ - $[C_4C_4im][NTf_2]$; ▼ - $[C_5C_5im][NTf_2]$. Hasse *et al.* [25]: ⬢ - $[C_4C_4im][NTf_2]$.

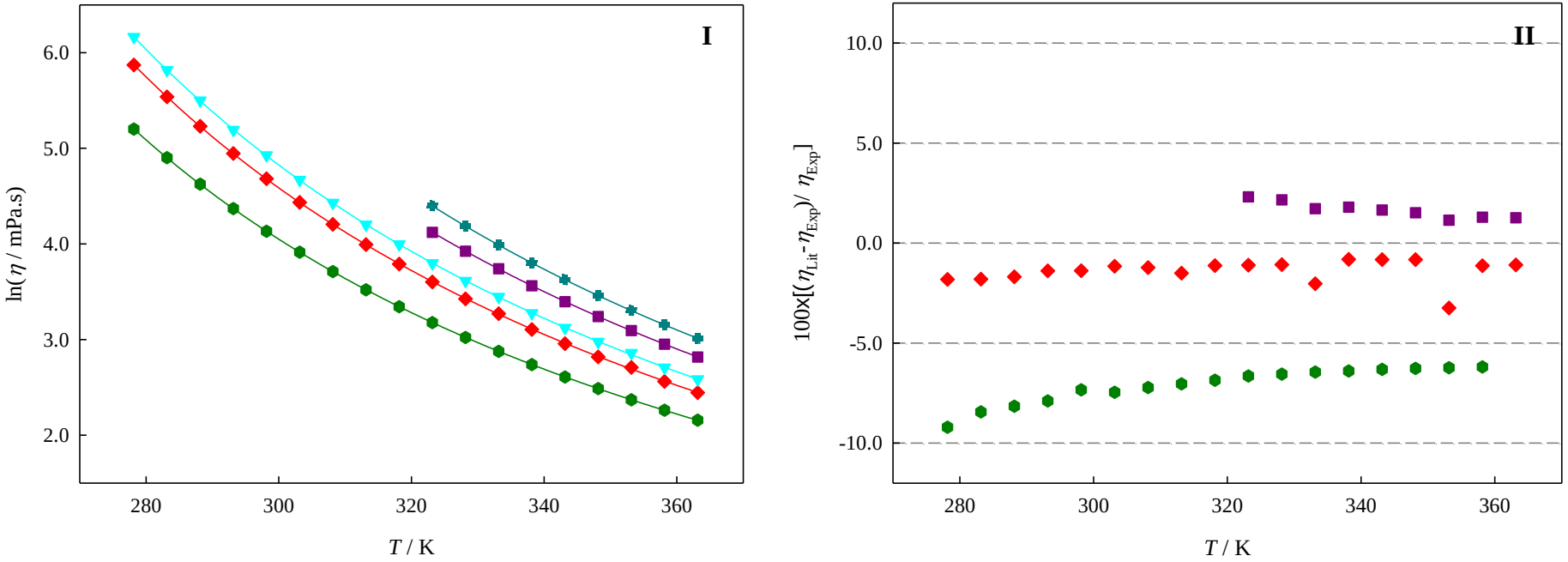

Figure 3S. (I) Graphic representation of ln(η / mPa·s) = f(T) for [$C_{N-1}C_1$im][NTf_2] ionic liquid family: ⬢ - [C_5C_1im][NTf_2]; ◆ - [C_9C_1im][NTf_2]; ▼ - [$C_{11}C_1$im][NTf_2]; ■ - [$C_{14}C_1$im][NTf_2]; ✚ - [$C_{16}C_1$im][NTf_2]. . The solid lines represent the Vogel-Tammann-Fulcher fitting (equation 5). **(II)** Relative deviations between the experimental viscosity measured in this work (η_{exp}) and those reported in the literature (η_{exp}) as a function of temperature. Tariq *et al.*[19]: ⬢ - [C_5C_1im][NTf_2]; ◆ - [C_9C_1im][NTf_2]; ■ - [$C_{14}C_1$im][NTf_2].

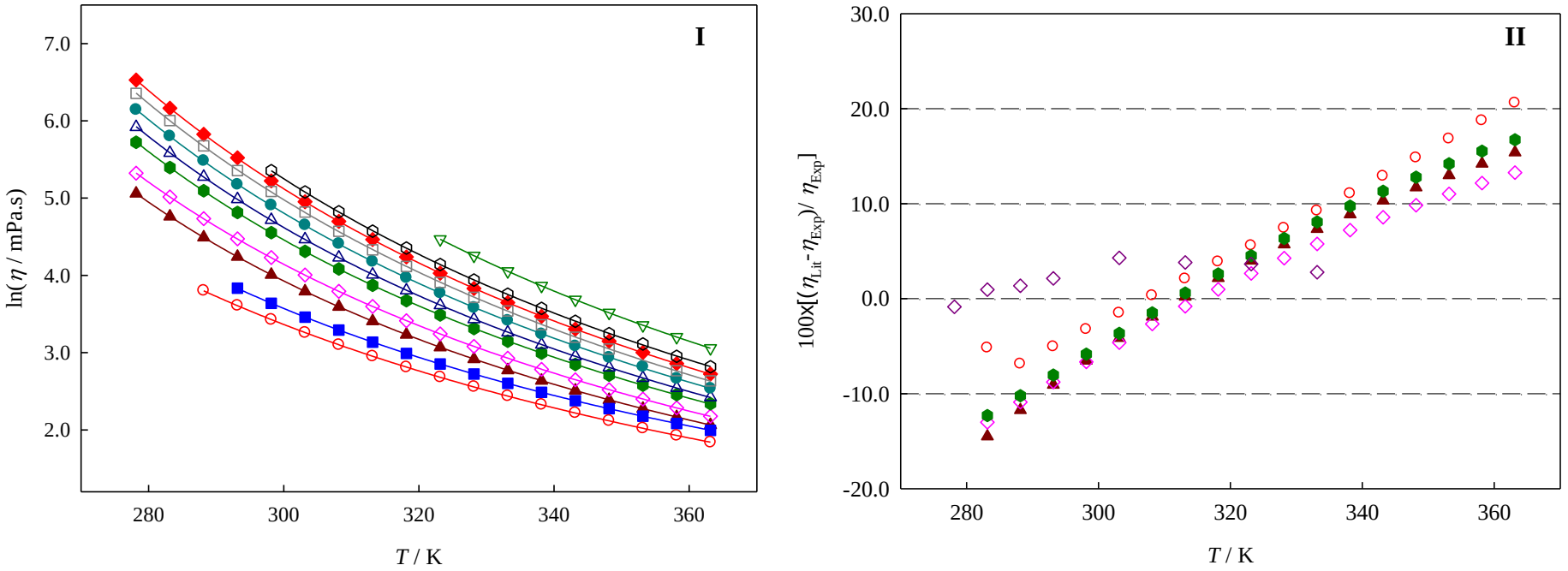

Figure 4S. (I) Graphic representation of ln(η / mPa·s) = f(T) for the [$C_{N/2}C_{N/2}$im][NTf_2] ionic liquid series: ■ - [C_1C_1im][NTf_2]; ○ - [C_2C_2im][NTf_2]; ▲- [C_3C_3im][NTf_2]; ◇ - [C_4C_4im][NTf_2]; ⬢ - [C_5C_5im][NTf_2]; △ - [C_6C_6im][NTf_2]; ● - [C_7C_7im][NTf_2]; □ - [C_8C_8im][NTf_2]; ◆ - [C_9C_9im][NTf_2]; ⬡ - [$C_{10}C_{10}$im][NTf_2]; ▽ - [$C_{12}C_{12}$im][NTf_2]. The solid lines represent the Vogel-Tammann-Fulcher fittings (equation 5). **(II)** Relative deviations between the experimental viscosity measured in this work (η_{exp}) and those reported in the literature (η_{exp}) as a function of temperature, for [$C_{N/2}C_{N/2}$im][NTf_2] ionic liquid series. Zheng *et al.* [14]: ○- [C_2C_2im][NTf_2]; ▲- [C_3C_3im][NTf_2]; ◇ - [C_4C_4im][NTf_2]; ⬢ - [C_5C_5im][NTf_2]. Hasse *et al.* [25]: ◇ - [C_4C_4im][NTf_2].

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