Electronic Supplementary Information

Magnesium Bis(trifluoromethanesulfonyl)amide Complexes with Triglyme and Asymmetric Homologues: Phase Behavior, Coordination Structures and Melting Point Reduction

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Table S1 Crystallographic data of $[Mg(G3)][TFSA]_2$, $[Mg(G3Et)][TFSA]_2$ and $[Mg(G4Et)][TFSA]_2$.

	$[Mg(G3)][TFSA]_2$	$[Mg(G3Et)][TFSA]_2$	$[Mg(G4Et)][TFSA]_2$
Reference	[S1]	This study	This study
Chemical formula	$C_{12}H_{18}F_{12}MgN_2O_{12}S_4$	$C_{13}H_{20}F_{12}MgN_2O_{12}S_4$	$C_{15}H_{24}F_{12}MgN_2O_{12}S_4$
Formula weight	762.83	776.86	820.91
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group	*P*1 (no. 1)	*Pca*2$_1$ (no. 29)	*Pca*2$_1$ (no. 29)
a / Å	8.7021(4)	14.1667(11)	18.8845(18)
b / Å	9.1183(6)	12.2367(11)	13.5041(14)
c / Å	9.2356(5)	17.2204(15)	25.530(2)
α / °	97.006(5)	90	90
β / °	95.727(4)	90	90
γ / °	100.012(5)	90	90
V / Å^3	710.77(7)	2985.2(4)	6510.6(10)
Z	1	4	8
D_{calc} / g cm^{-3}	1.782	1.729	1.675
μ / mm^{-1}	0.491	0.469	0.437
Temp. / °C	−50	−50	−50
Reflections collected	8422	8939	19393
Independent reflection, R_{int}	3659, 0.0376	3127, 0.1030	4911, 0.1664
R_1 [$I > 2\sigma(I)$]	0.0473	0.0767	0.1036
wR_2 (all data)	0.1294	0.2162	0.2925
GooF	0.891	1.003	1.029
Largest residual density / e Å^{-3}	0.409, −0.410	0.721, −0.500	0.990, −0.520

*The precision of the analyses is not good enough to be registered with Cambridge Structural Database (CSD), thus, the $[Mg(G3Et)][TFSA]_2$ and $[Mg(G4Et)][TFSA]_2$ crystals have no CCDC number. $[Mg(G3)][TFSA]_2$: CCDC 1541951.

Table S2 Decomposition temperatures (T_d) of $Mg[TFSA]_2$ and G3 binary mixtures estimated by TG measurements.

Composition ($Mg[TFSA]_2$: G3)	T_d / °C
Pure G3	98
1:5	104
1:2	151
1:1	241
$Mg[TFSA]_2$ salt	342

* T_d was defined as the temperature at 5% mass loss.

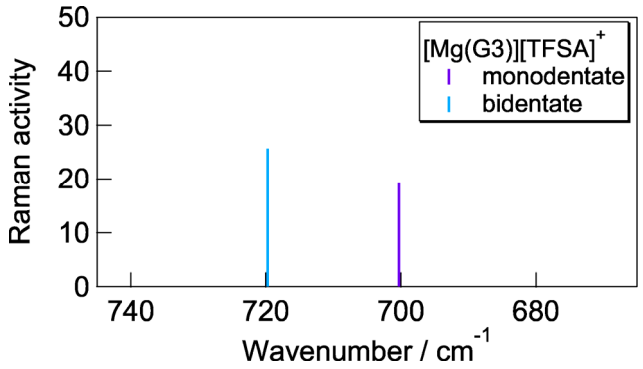

Fig. S1 Calculated Raman bands for $[Mg(G3)][TFSA]^+$ with bidentate and monodentate anions. The optimized structure is shown in **Fig. 5c** and **d**.

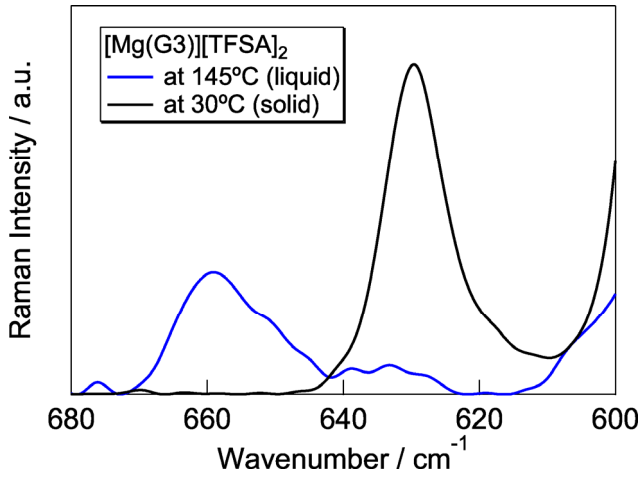

Fig. S2 Raman spectra in the crystalline and the molten states of $[Mg(G3)][TFSA]_2$, in the range of 680–600 cm^{-1}.

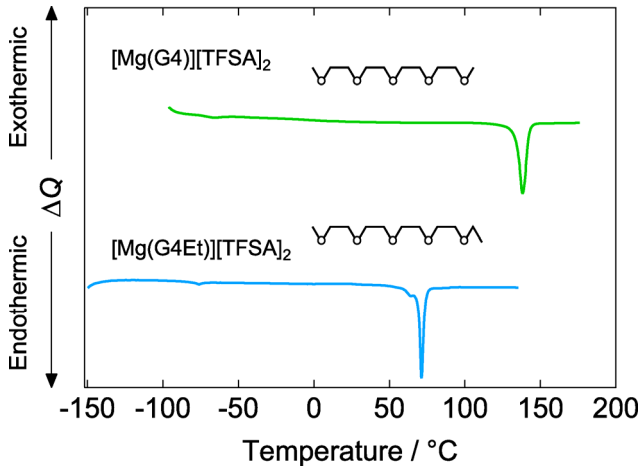

Fig. S3 DSC thermogram of equimolar mixture of $Mg[TFSA]_2$ and G4 together with the corresponding one for G4Et.

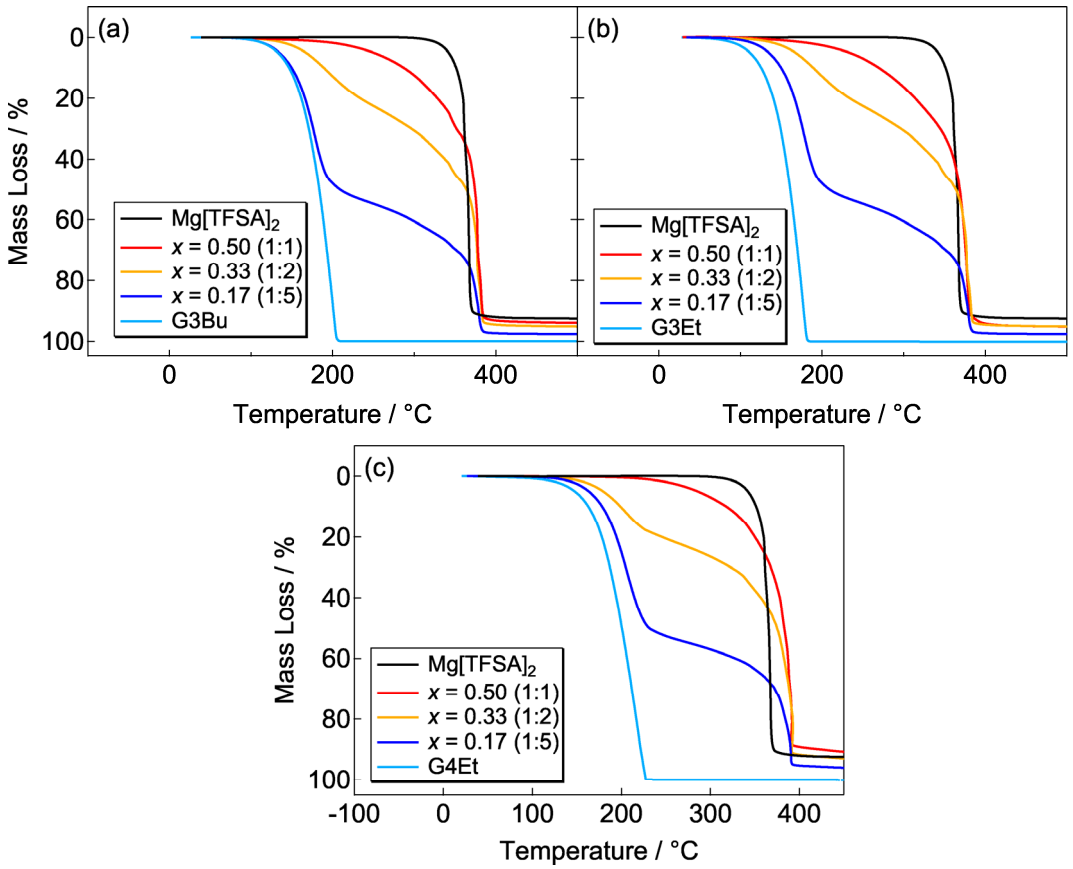

Fig. S4 TG curves of $Mg[TFSA]_2$/G3Bu, $Mg[TFSA]_2$/G3Et and $Mg[TFSA]_2$/G4Et binary mixtures with different $Mg[TFSA]_2$ concentrations. T_ds of $[Mg(G3Bu)][TFSA]_2$, $[Mg(G3Et)][TFSA]_2$ and $[Mg(G4Et)][TFSA]_2$ were estimated to be 251, 234 and 287 °C, respectively.

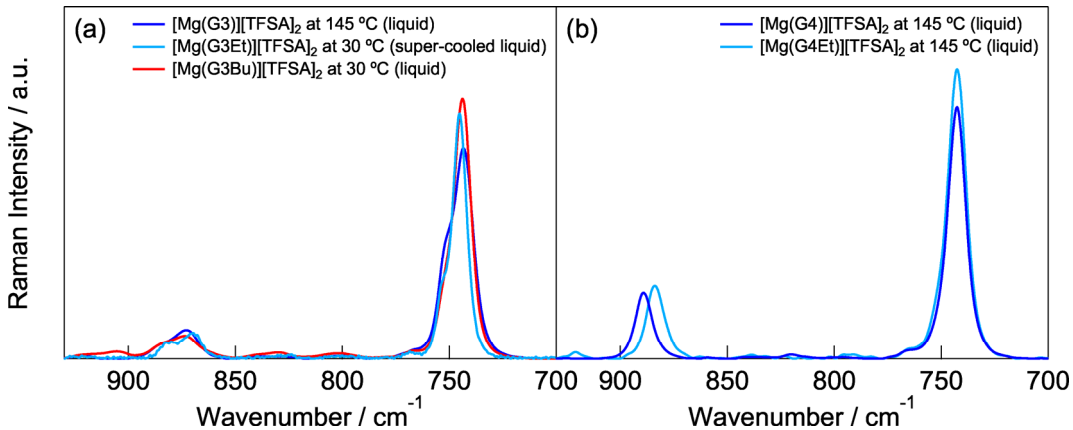

Fig. S5 Raman spectra of (a) $[Mg(G3Et)][TFSA]_2$, $[Mg(G3Bu)][TFSA]_2$ and (b) $[Mg(G4Et)][TFSA]_2$ with corresponding data for the G3 and G4 systems.

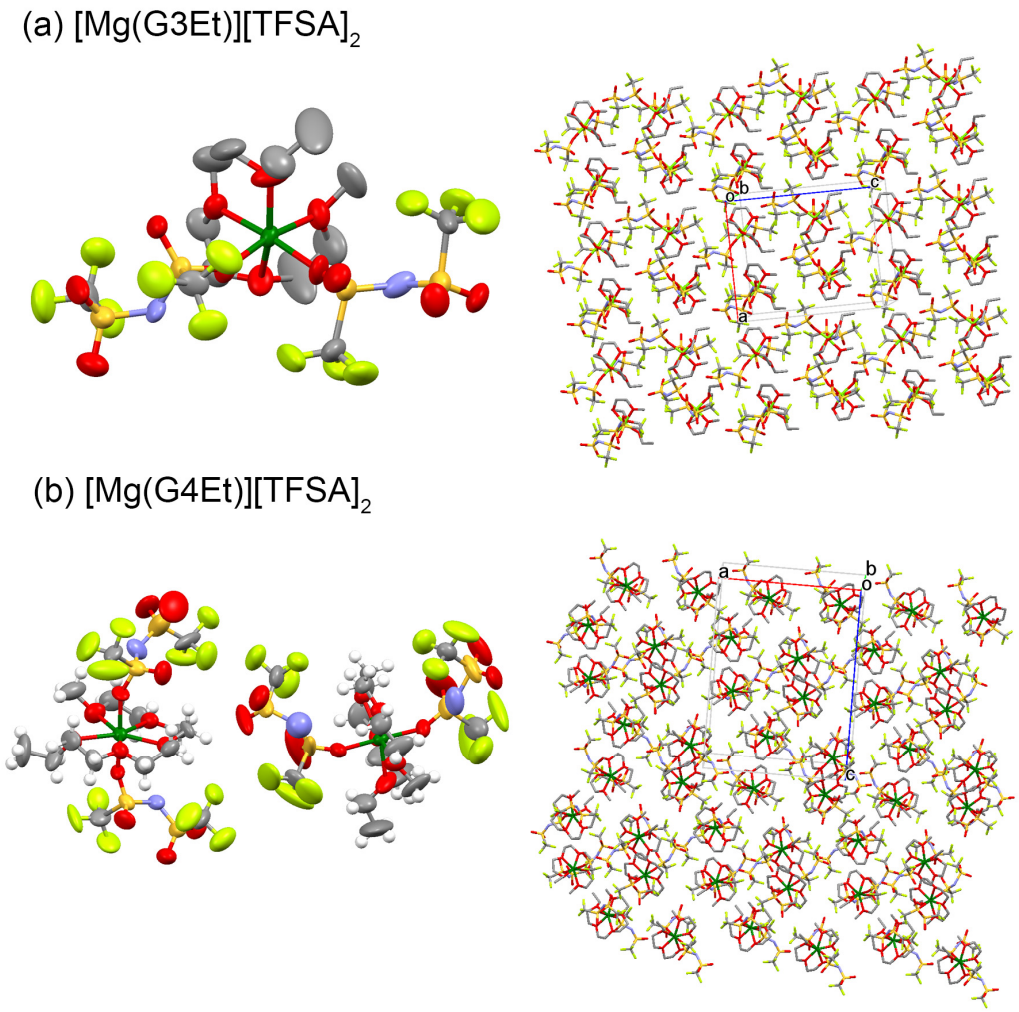

Fig. S6 Thermal ellipsoid models (left) and packing diagrams (right) of (a) [Mg(G3Et)][TFSA]$_2$ and (b) [Mg(G4Et)][TFSA]$_2$ crystals.

Table S3 Densities (ρ), concentration of $Mg[TFSA]_2$ (c), viscosities (η) and ionic conductivities (σ) at various temperatures (T) for the equimolar mixture of $Mg[TFSA]_2$ and G3Bu.

T / °C	ρ / g cm^{-3}	c / mol dm^{-3}	η / mPa s	σ / S cm^{-1}
30	1.573	1.954	2.702×10^4	5.35×10^{-6}
35	1.568	1.948	1.620×10^4	-[a]
40	1.563	1.942	1.002×10^4	1.20×10^{-5}
45	1.558	1.936	6.405×10^3	-[a]
50	1.552	1.928	4.218×10^3	2.41×10^{-5}
60	1.542	1.916	1.978×10^3	4.46×10^{-5}
70	1.532	1.903	1.016×10^3	7.67×10^{-5}
80	1.520	1.888	5.638×10^2	1.23×10^{-4}
90	-[a]	-[a]	3.360×10^2	1.89×10^{-4}
100	-[a]	-[a]	2.115×10^2	2.73×10^{-4}
110	-[a]	-[a]	1.392×10^2	3.85×10^{-4}
120	-[a]	-[a]	9.430×10^1	5.28×10^{-4}
130	-[a]	-[a]	6.820×10^1	7.01×10^{-4}
140	-[a]	-[a]	4.989×10^1	9.11×10^{-4}
150	-[a]	-[a]	3.772×10^1	1.15×10^{-3}

[a] N.A.

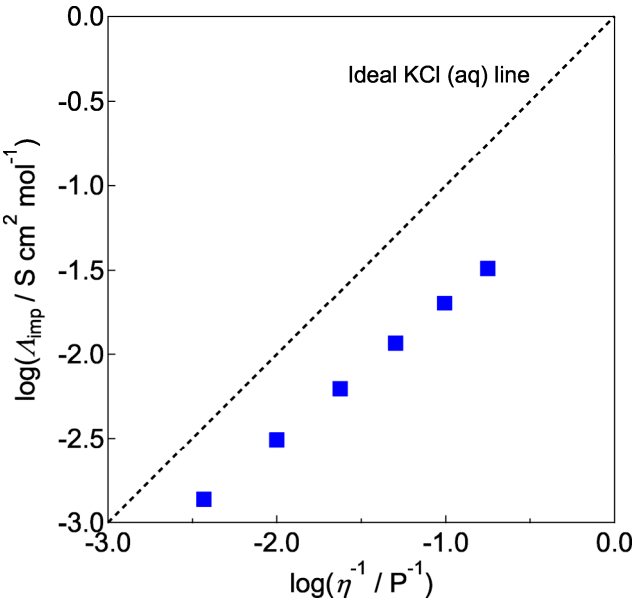

Fig. S7 Walden plot for [Mg(G3Bu)][TFSA]$_2$. The molar conductivities (Λ_{imp}) were corrected as 1/2 of the original values.

Reference

S1 S. Tsuzuki, T. Mandai, S. Suzuki, W. Shinoda, T. Nakamura, T. Morishita, K. Ueno, S.Seki, Y. Umebayashi, K. Dokko and M. Watanabe, *Phys. Chem. Chem. Phys.*, 2017, **19**, 18262–18272.