Supporting Information

Deep Eutectic Ion-conductive Hybrids Produced by Combining Hydroxyl-functionalized Silsesquioxane and Mono-/difunctional Hydrogen Bond Acceptors

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EXPERIMENTAL SECTION

Materials

Tetrabutylammonium chloride (TBACl, Tokyo Chemical Industry, 98.0%), choline chloride (ChCl, Tokyo Chemical Industry, 98.0%), and 1-ethyl-3-methylimidazolium bromide (EMIBr, Tokyo Chemical Industry, 98.0%) were used as hydrogen acceptor (HBA) without further purification. *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine (Tokyo Chemical Industry, 98.0%), bis(2-dimethylaminoethyl)ether (Tokyo Chemical Industry, 98.0%), 1-methylimidazole (Tokyo Chemical Industry, 99.0%), bis(2-bromoethyl)ether (Tokyo Chemical Industry, 98.0%), iodomethane (Tokyo Chemical Industry, 99.5%), 1,2-dibromoethane (Tokyo Chemical Industry, 99.0%), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Tokyo Chemical Industry, 98.0%) were used as received. A cross-linkable HBA, $(MITFSI)_2C_4O$, was prepared by the reaction of bis(2-bromoethyl)ether with 1-methylimidazole, and the subsequent anion exchange reaction with LiTFSI, according to the reported procedure.[1] As another imidazolium-type cross-linkable HBA, $(MITFSI)_2C_2$) was prepared from 1,2-dibromoethane using the same procedures. Three quaternary ammonium salt-based cross-linkable HBAs, $[N(CH_3)_3I]_2C_2$, $[N(CH_3)_3TFSI]_2C_2$, and $[N(CH_3)_3TFSI]_2C_4O$, were prepared by the reaction of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine or bis(2-dimethylaminoethyl)ether with iodomethane,[2] followed by the reaction with LiTFSI. Hydroxyl functionalized silsesquioxane (SQ) nanoparticles were prepared by the reaction of (3-aminopropyl)triethoxysilane (Tokyo Chemical Industry, 98.0%)

and glycidol (Kanto Chemical Co., Inc., 95.0%), followed by a hydrolytic condensation, as reported previously.[3,4] Hydrofluoric acid (MORITA CHEMICAL INDUSTRIES, 46.0%-48.0%) diluted to 3.2 wt% in distilled water was used. Acetonitrile (FUJIFILM Wako Chemicals, > 99.0%), *N*,*N'*-dimethylformamide (DMF, FUJIFILM Wako Chemicals, > 99.0%), diethyl ether (FUJIFILM Wako Chemicals, > 99.0%), dichloromethane (FUJIFILM Wako Chemicals, > 99.0%), methanol (FUJIFILM Wako Chemicals, > 99.0%), and other all chemicals were used as received unless otherwise noted.

Preparation of two-component deep eutectic silsesquioxane (DESQ) hybrids

A representative example of the preparation of two-component SQ/TBACl (100/200) using TBACl as a HBA at a molar ratio ([OH group in SQ]/[N^+ in HBA] = 2) is as follows: TBACl (0.148 g, 0.774 mmol) and the hydroxyl functionalized SQ (0.10 g, 0.387 mmol of the repeat group, corresponding to 1.548 mmol of hydroxyl group (theoretical value of the repeating unit $RSiO_{1.5}$, = 258.34 g/mol, where R = $CH_2CH_2CH_2N(CH_2CH(OH)CH_2OH)_2$), were placed in a vial. The solid mixture was stirred at 60 °C for 24 h, in which the mixture was changed into a viscous liquid. The SQ/TBACl (100/200) was obtained as a transparent viscous material at room temperature, which was employed without further purification.

Other two-component DESQ hybrids were prepared using various HBAs (e.g., TBACl and EMIBr) at different feed ratios ([R-$SiO_{1.5}$]/[HBA] = 100/50, 100/100 and 100/200, corresponding to [OH group]/[HBA] = 8/1, 4/1 and 2/1, respectively) in a similar manner under the same conditions.

Preparation of three-component deep eutectic silsesquioxane (DESQ) hybrids

For the preparation of three-component SQ/TBACl/$(MITFSI)_2C_4O$ (100/200/1) using TBACl as a HBA and $(MITFSI)_2C_4O$ as a cross-linkable HBA, TBACl (0.148 g, 0.774 mmol), the hydroxyl functionalized SQ (0.10 g, 0.387 mmol of the repeat group, corresponding to 1.548 mol of hydroxyl group), and $(MITFSI)_2C_4O$ (3.08 mg, 3.87×10^{-3} mmol) were placed in a vial. The transparent solid mixture was stirred at 60 °C for 24 h, in which the mixture was changed into a viscous liquid. The SQ/TBACl/$(MITFSI)_2C_4O$ (100/200/1) was obtained as a transparent viscous material at room temperature, which was employed without further purification.

Other three-component DESQ hybrids were prepared using various monofunctional HBAs (e.g., TBACl and EMIBr) and difunctional HBAs (e.g., $(MITFSI)_2C_4O$ and $(MITFSI)_2C_2$) at different molar ratios ([monofunctional HBA]/[R-$SiO_{1.5}$]/[difunctional HBA] = 50, 100, 200/100/1.0, 5.0, 10) in a similar manner under the same conditions.

Preparation of three-component hybrids with lithium salt (DESQ-Li)

For the preparation of the hybrids with lithium salt, a predetermined amount of LiTFSI (10, 20, 30, and 40 wt%) was added to the three-component DESQ hybrids. A representative example for SQ/TBACl/$(MITFSI)_2C_4O$ (100/200/1) with 10 wt % LiTFSI is as follows: TBACl (0.148 g, 0.774 mmol), the hydroxyl functionalized SQ (0.10 g, 0.387 mmol of the repeat group, corresponding to 1.548 mmol of hydroxyl group), $(MITFSI)_2C_4O$ (3.08 mg, 3.87×10^{-3} mmol), and LiTFSI (27.9 mg, 9.72×10^{-2} mmol) were placed in a vial. The white solid mixture was stirred at 60 ^{o}C for 24 h, in which the mixture was changed into a viscous liquid. The SQ/TBACl/$(MITFSI)_2C_4O$ (100/200/1) with 10 wt % LiTFSI was obtained as a transparent viscous material at room temperature, which was employed without further purification. The compounds and mixing ratios of HBD, HBA, and cross-linkable HBA were the same as for the three-component hybrids. In addition, 20 wt% (62.8 mg, 0.218 mmol), 30 wt% (107 mg, 0.372 mmol), 40 wt% (167 mg, 0.389 mmol) of LiTFSI as Li salt for SQ/TBACl/$(MITFSI)_2C_4O$ (100/200/1).

Instrumentation

Thermogravimetric analysis (TGA) was performed using SEIKO's TGA/6200, with a platinum pan under a nitrogen atmosphere at a temperature increase of 10 °C/min. The temperature range was 40 °C ~ 600 °C or 700 °C. Differential Scanning Calorimetry (DSC) was performed using an EXSTAR DSC6200 under a nitrogen atmosphere in an aluminum pan at a temperature increase of 10 °C/min and a temperature decrease of 20 °C/min. The measurement temperature ranged from -80 °C to 20 °C below the 5% weight loss temperature (T_{d5}) analyzed from TGA.

Ionic conductivity was measured in the range of 90 °C ~ 20 °C in a thermostatic chamber by the AC impedance method using a HIOKI chemical impedance meter (5 to 10^5 Hz, Hioki 3532-80). Initially, the sample solution was prepared by dissolving 60 mg of sample in 0.10 mL of dehydrated methanol. The solution was drop-cast onto the substrate and dried at 65 ^{o}C for 10 min. The process was repeated three times, followed by drying at 65 ^{o}C overnight and then at 90 ^{o}C for 150 min on a hot plate in air. After annealing at 90 ^{o}C for 30 min under vacuum, their ion conductivities were evaluated under ambient humidity conditions (relative humidity = 30–50%). Ionic conductivity was calculated via the equation $\sigma = d/(L_s w_s R)$, where d corresponds to the distance between the two electrodes, L_s and w_s correspond to the thickness and width of the membrane, and R corresponds to the resistance value.[5,6] Viscoelasticity and complex viscosity were measured using MCR 702 Multidrive (Anton Paar). Samples were placed in a circular shape of 2 cm diameter on a plate and held down from above with a stainless-steel module. Measurements were made in a nitrogen atmosphere with 0.05% strain at temperatures ranging from 25 °C to 100 °C when EMIBr-based hybrid was used and from 50 °C to 100 °C when TBACl-based hybrid was used to separate the layers, respectively. Cyclic voltammetry

(CV) experiments were performed on a BAS electrochemical analyzer (model660C, BAS, Tokyo, Japan) in anhydrous *N*,*N'*-dimethylformamide solutions with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. A three-electrode cell with platinum electrodes as both the counter and working electrodes was used. Ag/Ag^+ (Ag in 0.01 M $AgNO_3$ solution) was used as the reference electrode. Ferrocene/Ferrocenium (Fc/Fc^+) was used as the internal standard. Based on the assumption that electronic potentials are +0.799 V (Ag+/Ag) and -3.045 V (Li+/Li),[6] the measurement range (-2.4–1.2 V vs Ag+/Ag) can be converted into 1.444–5.044 V (vs Li+/Li).

^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) were performed using a JEOL JNM-ECX400. Deuterated water (D_2O) and deuterated dimethyl sulfoxide (DMSO-d_6) were used as solvents, and tetramethylsilane (TMS) was used as the reference material. Infrared (IR) absorption spectra were measured by KBr method using FT-IR 210 (400 cm^{-1} ~ 4000 cm^{-1}, integrated 8 times) manufactured by JASCO Co.

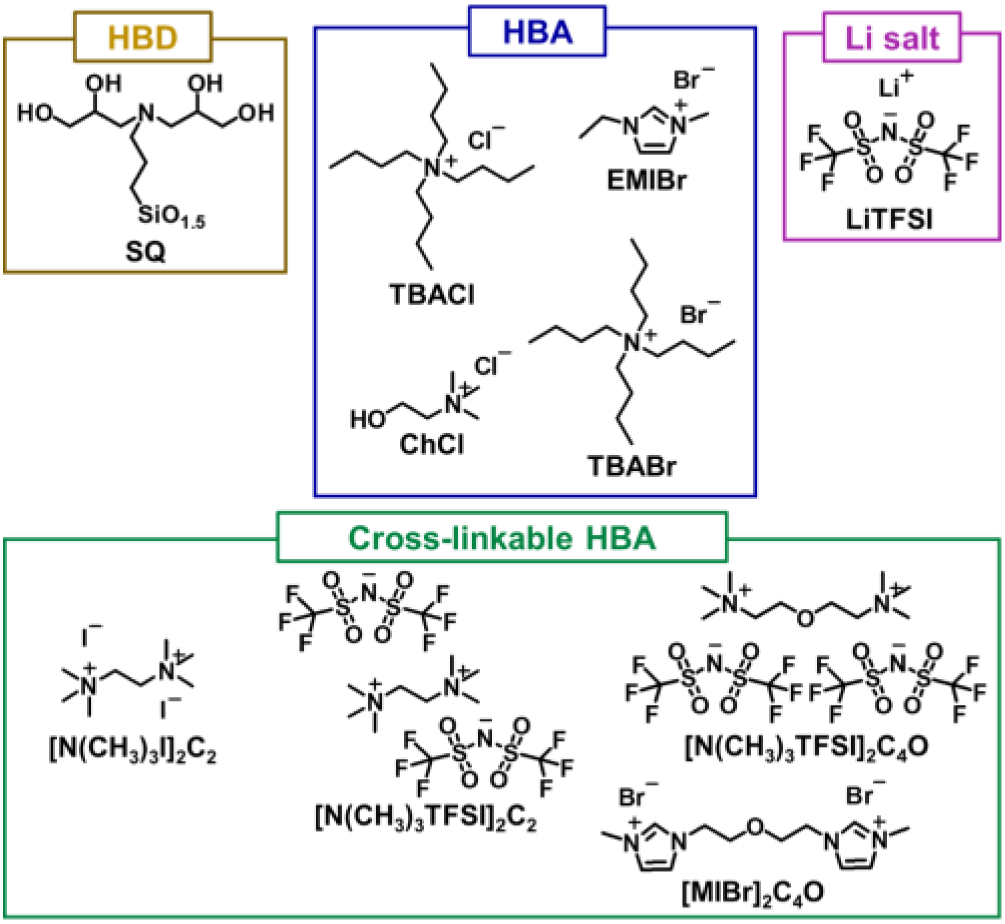

Figure S1. Chemical structures of HBD, HBA, and cross-linkable HBAs used in this study.

Table S1. Thermal properties of constituents used in the study

	Chemical	T_m [a] (°C)	T_g [a] (°C)	T_{d5} [b] (°C)
HBD	Hydroxyl functionalized-SQ	-	54	229
Cross-linkable HBA	$(MITFSI)_2C_4O$	-	-62	344
	$(MITFSI)_2C_2$	138	-	418
	$[N(CH_3)_3I]_2C_2$	149	-	240
	$[N(CH_3)_3TFSI]_2C_2$	207	-	401
	$[N(CH_3)_3TFSI]_2C_4O$	150	-	398
HBA	Tetrabutylammonium chloride (TBACl)	70 [c]	-	187
	1-Ethyl-3-methylimidazolium bromide (EMIBr)	74 [c]	-	235
	Choline chloride (ChCl)	302 [c]	-	280
	Tetrabutylammonium bromide (TBABr)	103 [c]	-	-
Li salt	Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)	235 [c]	-	368

a) Melting point (T_m) and glass transition temperature (T_g) evaluated by DSC measurement.

b) Temperature for 5 wt.% weight loss under nitrogen.

c) SDS data (Tokyo chemical industry CO., LTD.)

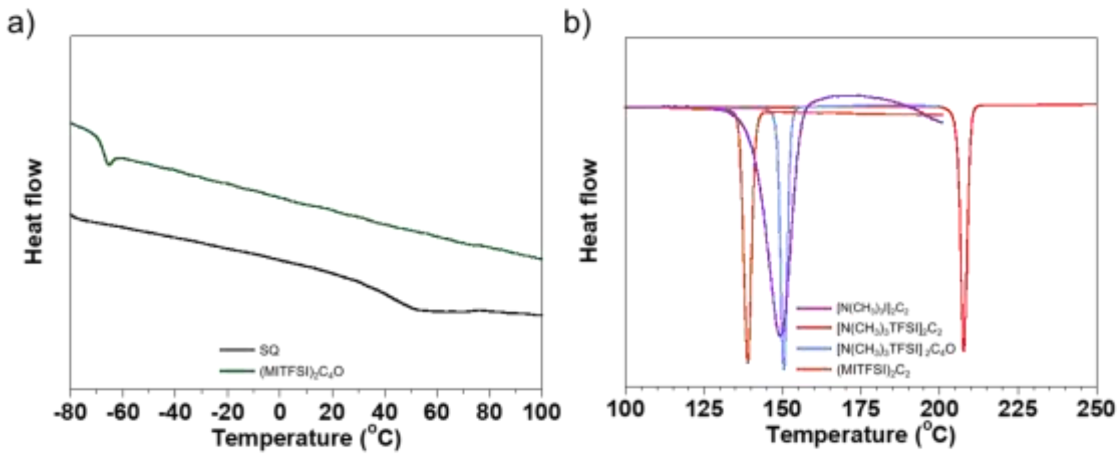

Figure S2. DSC traces of the constituents used in this study.

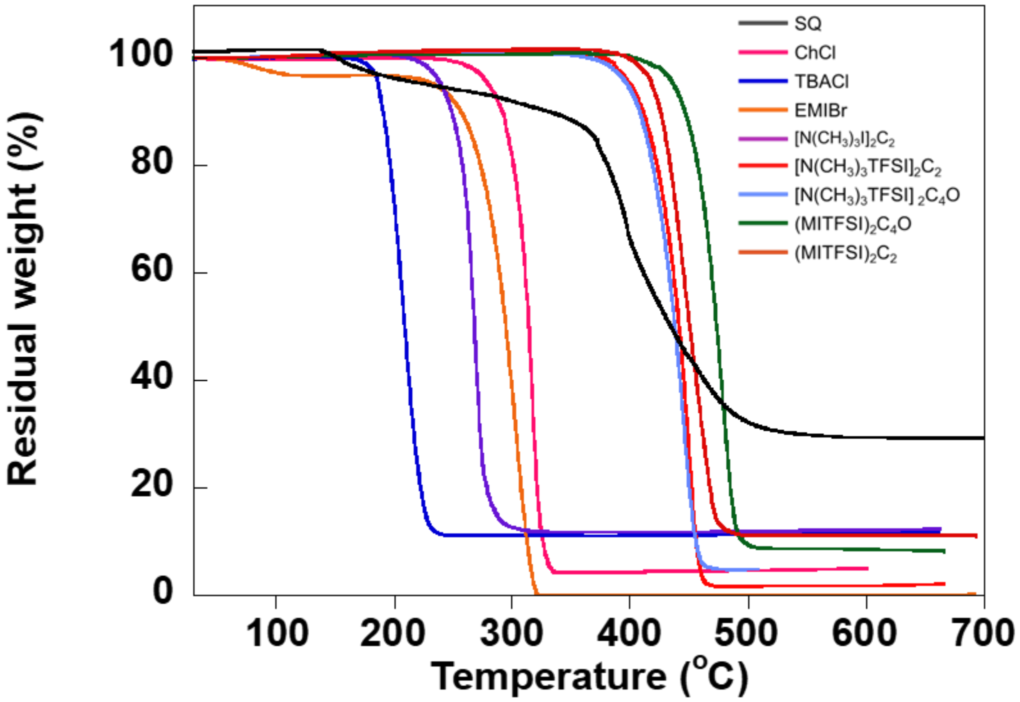

Figure S3. TGA results of the constituents used in this study

Table S2. Preparation of two-component deep eutectic silsesquioxane (DESQ) hybrids by the reaction of hydroxy-functionalized SQ with HBA

Run	HBA	[R-SiO$_{1.5}$]/[HBA]	Temp. (°C)	Time (h)	appearance at r.t.[a]
1	ChCl	100/50	80	48	c
2		100/100			c
3	TBACl	100/50	60	24	a
4		100/100			a
5		100/200			a
6	EMIBr	100/50	60	24	a
7		100/100			a
8		100/200			a
9	$[N(CH_3)_3I]_2C_2$	100/1	60	24	c
10		100/5			c
11		100/10			c
12	$[N(CH_3)_3TFSI]_2C_2$	100/1	60	24	b
13		100/5			b
14		100/10			b
15	$[N(CH_3)_3TFSI]_2C_4O$	100/1	60	24	b
16		100/5			b
17		100/10			b
18	$(MITFSI)_2C_4O$	100/1	60	24	b
19		100/5			b
20		100/10			b
21	$(MITFSI)_2C_2$	100/1	60	24	b
22		100/5			b
23		100/10			b
24	TBABr	100/50	60	24	b
25		100/100			b
26		100/200			b

[a] a: viscous material, b: solid + solid, c: viscous material + solid.

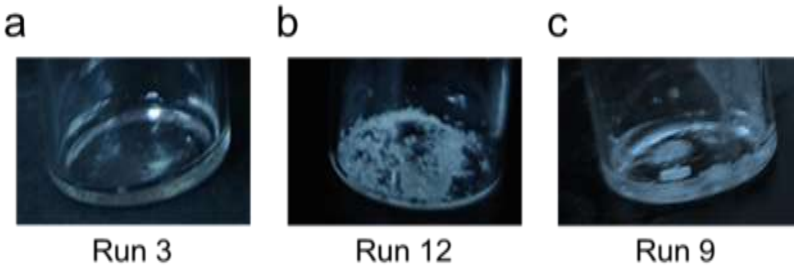

Figure S4. Appearance of two-component DESQ hybrids, a: viscous material, b: solid + solid, c: viscous material + solid.

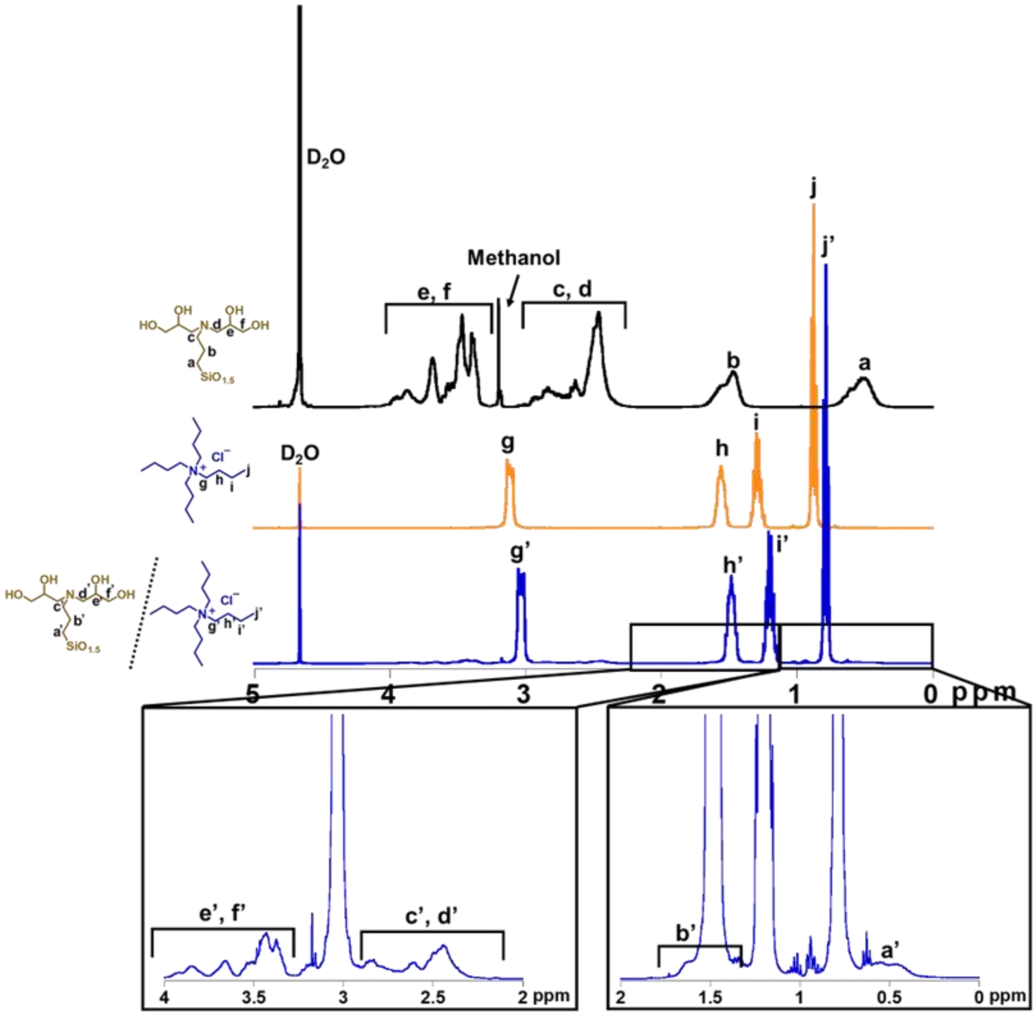

Figure S5. ^{1}H NMR spectra (D_2O) of SQ/TBACl (100/200) (blue), SQ (black), and TBACl (orange).

^{1}H NMR of SQ/TBACl (100/200) in D_2O: $\delta = 0.45\text{-}0.73$ ($-SiCH_2-$), 0.78-0.90 (CH_3- in TBACl), 1.15-1.34 (CH_3CH_2- in TBACl), 1.44-1.73 ($-SiCH_2CH_2-$), 1.52-1.62 ($-CH_2CH_2CH_2-$ in TBACl), 2.39-2.91 ($-CH_2CH_2N-$, $-NCH_2CHOH$), 2.96-3.15 ($-NCH_2CH_2-$ in TBACl), 3.23-3.92 ($-CH_2CHOHCH_2$, $CHOHCH_2OH$).

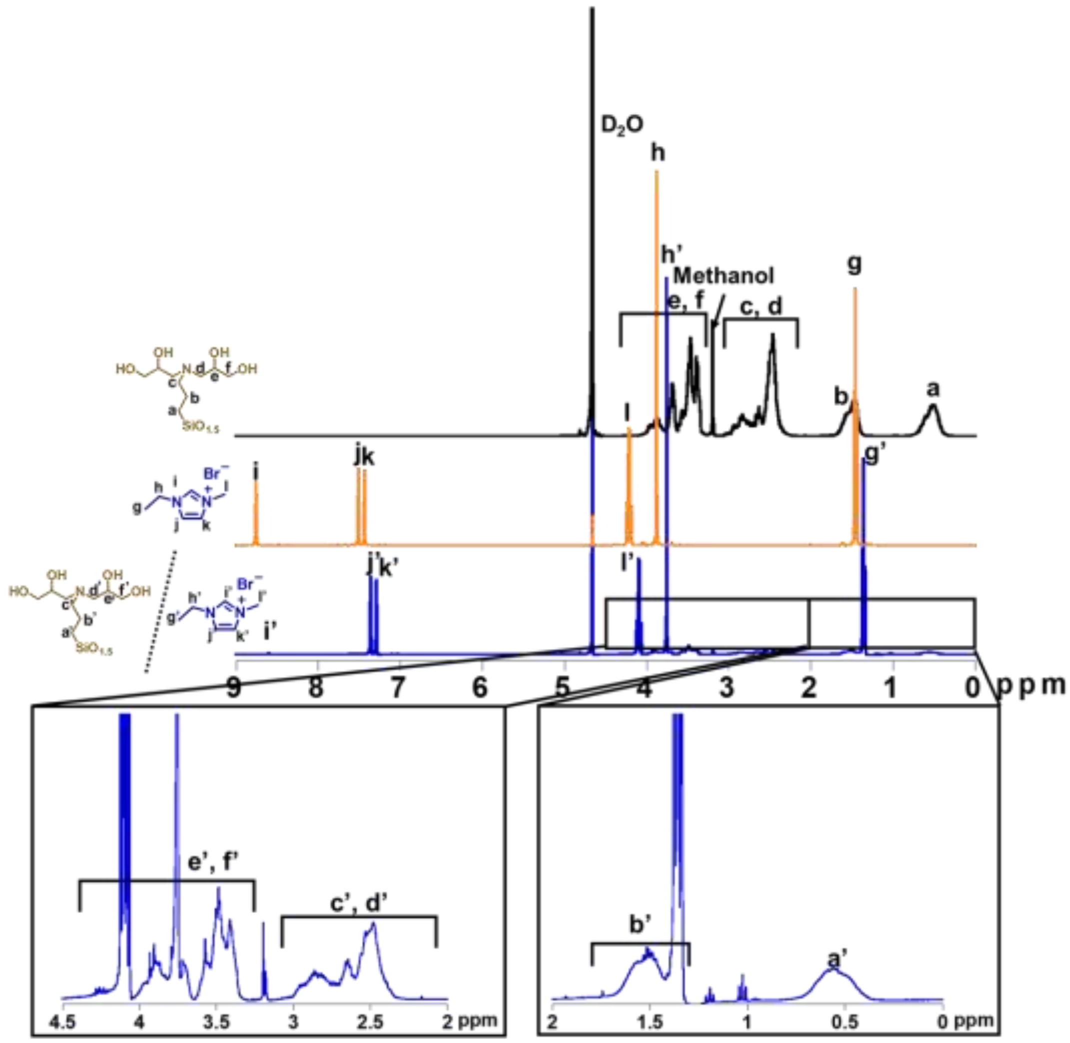

Figure S6. ^{1}H NMR spectra (D_2O) of SQ/EMIBr (100/200) (blue), SQ (black) and EMIBr (orange).

^{1}H NMR of SQ/EMIBr (100/200) in D_2O: δ = 0.54-0.59 (-$SiCH_2$-), 1.34-1.38 (CH_3CH_2- in EMIBr), 1.41-1.56 (-$SiCH_2CH_2$-), 2.48-2.93 (-CH_2CH_2N-, -NCH_2CHOH), 3.41-3.93 (-$CH_2CHOHCH_2$, $CHOHCH_2OH$), 3.76 (CH_3CH_2N- in EMIBr), 4.08-4.10 (CH_3N- in EMIBr), 7.29,7.36 (=NCHCHN- in EMIBr), 8.60 (-NCHN- in EMIBr).

Table S3. Thermal properties and ionic conductivity of two-component DESQ hybrids

Run	HBA	[R-SiO$_{1.5}$]/[HBA]	T$_g$ (^{o}C)[a]	T$_{d5}$ (^{o}C)[b]	Residual weight (%)[c]	ionic conductivity at 25 ^{o}C (S/cm)
1	ChCl	100/50	-	-	-	-
2		100/100	-	-	-	-
3	TBACl	100/50	-12.4	214	19.8	-
4		100/100	-12.5	198	14.7	-
5		100/200	-30.2	196	14.1	5.79×10^{-6}
6	EMIBr	100/50	-14.0	257	15.9	-
7		100/100	-17.6	257	22.6	-
8		100/200	17.2	258	20.7	4.91×10^{-4}

[a] Determined by DSC. [b] Temperature for 5 wt.% weight loss under nitrogen. [c] Residual weight of sample heated at 10 °C/min until 700 °C in TGA under nitrogen.

Table S4. Preparation of three-component DESQ hybrids by the reaction of hydroxy-functionalized SQ with HBA in the presence of cross-linkable HBA

Run	HBA	Cross-linkable HBA	$[R\text{-}SiO_{1.5}]$/[HBA] /[Cross-linkable HBA]	Temp. (°C)	Time (h)	appearance at r.t.[a]
1	ChCl	$[N(CH_3)_3I]_2C_2$	100/50/1	80	48	c
2			100/50/5			c
3			100/50/10			c
4	ChCl	$[N(CH_3)_3TFSI]_2C_2$	100/50/1	80	48	c
5			100/50/5			c
6			100/50/10			c
7	ChCl	$[N(CH_3)_3TFSI]_2C_4O$	100/50/1	80	48	b
8			100/50/5			b
9			100/50/10			b
10	ChCl	$(MITFSI)_2C_4O$	100/50/1	80	48	a
11			100/50/5			c
12			100/50/10			c
13	TBACl	$[N(CH_3)_3I]_2C_2$	100/200/1	60	24	c
14			100/200/5			c
15			100/200/10			c
16	TBACl	$[N(CH_3)_3TFSI]_2C_2$	100/200/1	60	24	c
17			100/200/5			c
18			100/200/10			c
19	TBACl	$[N(CH_3)_3TFSI]_2C_4O$	100/200/1	60	24	c
20			100/200/5			c
21			100/200/10			c
22	TBACl	$(MIBr)_2C_4O$	100/200/1	60	24	b
23			100/200/5			b
24			100/200/10			b
25	TBACl	$(MITFSI)_2C_4O$	100/200/1	60	24	a
26			100/200/5			a
27			100/200/10			a
28	TBACl	$(MITFSI)_2C_4O$	100/100/1	60	24	a
29			100/100/5			a
30			100/100/10			a
31	TBACl	$(MITFSI)_2C_4O$	100/50/1	60	24	a
32			100/50/5			a
33			100/50/10			a
34	TBACl	$(MITFSI)_2C_2$	100/200/1	60	24	c
35			100/200/5			c
36			100/200/10			c
37	TBACl	$(MITFSI)_2C_2$	100/100/1	60	24	c
38			100/100/5			c
39			100/100/10			c
40	TBACl	$(MITFSI)_2C_2$	100/50/1	60	24	c
41			100/50/5			c
42			100/50/10			c

Run	HBA	Cross-linkable HBA	$[R\text{-}SiO_{1.5}]$/[HBA] /[Cross-linkable HBA]	Temp. (°C)	Time (h)	appearance at r.t.[a]
43	EMIBr	$(MITFSI)_2C_4O$	100/200/1	60	24	a
44			100/200/5			a
45			100/200/10			a
46	EMIBr	$(MITFSI)_2C_4O$	100/100/1	60	24	a
47			100/100/5			a
48			100/100/10			a
49	EMIBr	$(MITFSI)_2C_4O$	100/50/1	60	24	a
50			100/50/5			a
51			100/50/10			a
52	EMIBr	$(MITFSI)_2C_2$	100/200/1	60	24	a
53			100/200/5			a
54			100/200/10			a
55	EMIBr	$(MITFSI)_2C_2$	100/100/1	60	24	a
56			100/100/5			a
57			100/100/10			a
58	EMIBr	$(MITFSI)_2C_2$	100/50/1	60	24	a
59			100/50/5			a
60			100/50/10			a
61	TBABr	$(MITFSI)_2C_4O$	100/200/1	60	24	c
62			100/200/5			c
63			100/200/10			c
64	TBABr	$(MITFSI)_2C_4O$	100/100/1	60	24	c
65			100/100/5			c
66			100/100/10			c
67	TBABr	$(MITFSI)_2C_4O$	100/50/1	60	24	c
68			100/50/5			c
69			100/50/10			c
70	TBABr	$(MITFSI)_2C_2$	100/200/1	60	24	c
71			100/200/5			c
72			100/200/10			c
73	TBABr	$(MITFSI)_2C_2$	100/100/1	60	24	c
74			100/100/5			c
75			100/100/10			c
76	TBABr	$(MITFSI)_2C_2$	100/50/1	60	24	c
77			100/50/5			c
78			100/50/10			c

[a] a: viscous material, b: solid + solid, c: viscous material + solid.

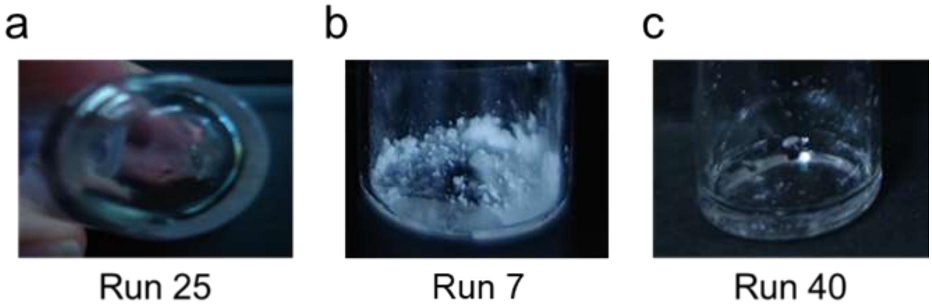

Figure S7. Appearance of two-component DESQ hybrids, a: viscous material, b: solid + solid, c: viscous material + solid.

Table S5. Thermal properties and ionic conductivity of three-component DESQ hybrids

Run	HBA	Cross-linkable HBA	$[R\text{-}SiO_{1.5}]$/[HBA]/[Cross-linkable HBA]	T_g (°C)[a]	T_{d5} (°C)[b]	Residual weight (%)[c]	ionic conductivity at 25 °C (S/cm)
1	ChCl	$(MITFSI)_2C_4O$	100/50/1	-24.9	244	30.0[d]	2.20×10^{-7}
2			100/50/5	-	-	-	-
3			100/50/10				
4	TBACl	$(MITFSI)_2C_4O$	100/200/1	0.0	233	30.6	7.64×10^{-8}
5			100/200/5	-38.4	188	7.32	4.48×10^{-5}
6			100/200/10	-41.0	189	9.97	1.13×10^{-4}
7	TBACl	$(MITFSI)_2C_4O$	100/100/1	-37.6	191	12.3	-
8			100/100/5	-35.4	198	18.4	-
9			100/100/10	-17.4	191	0.964	-
10	EMIBr	$(MITFSI)_2C_4O$	100/200/1	38.1	252	16.3	4.17×10^{-4}
11			100/200/5	-	-	-	-
12			100/200/10				
13	EMIBr	$(MITFSI)_2C_4O$	100/100/1	15.2	252	16.7	-
14			100/100/5	3.6	256	15.5	
15			100/100/10	-1.8	243	14.1	
16	EMIBr	$(MITFSI)_2C_2$	100/200/1	32.6	255	17.7	2.97×10^{-4}
17			100/200/5	3.1	248	15.3	-
18			100/200/10	2.4	254	14.7	

[a] Determined by DSC. [b] Temperature for 5 wt.% weight loss under nitrogen. [c,d] Residual weight of the sample heated at 10 °C/min until 700 °C[c] or 600 °C[d] in TGA under nitrogen.

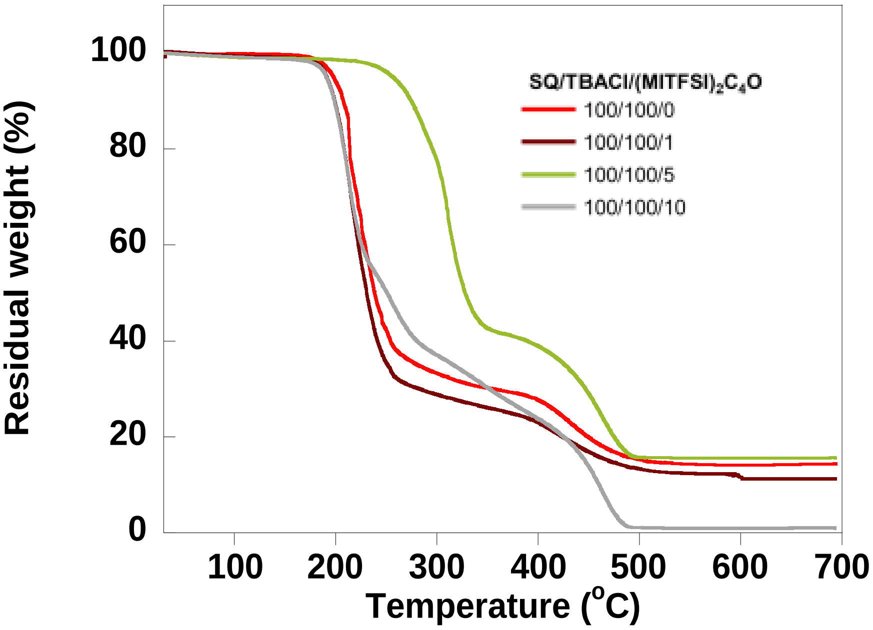

Figure S8. TGA results of three-component SQ/TBACl/(MITFSI)$_2$C$_4$O hybrids having different cross-linkable HBA contents.

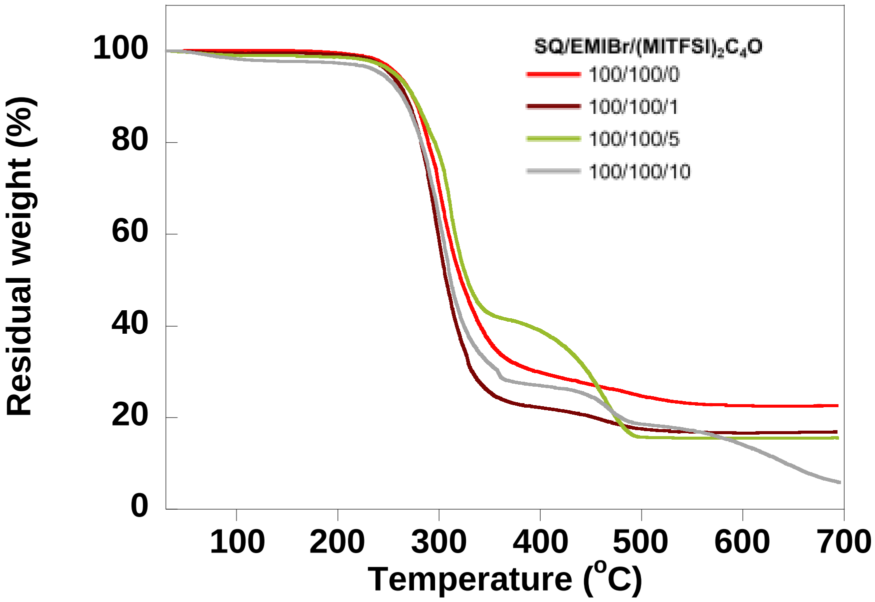

Figure S9. TGA results of three-component SQ/EMIBr/(MITFSI)$_2$C$_4$O hybrids having different cross-linkable HBA contents.

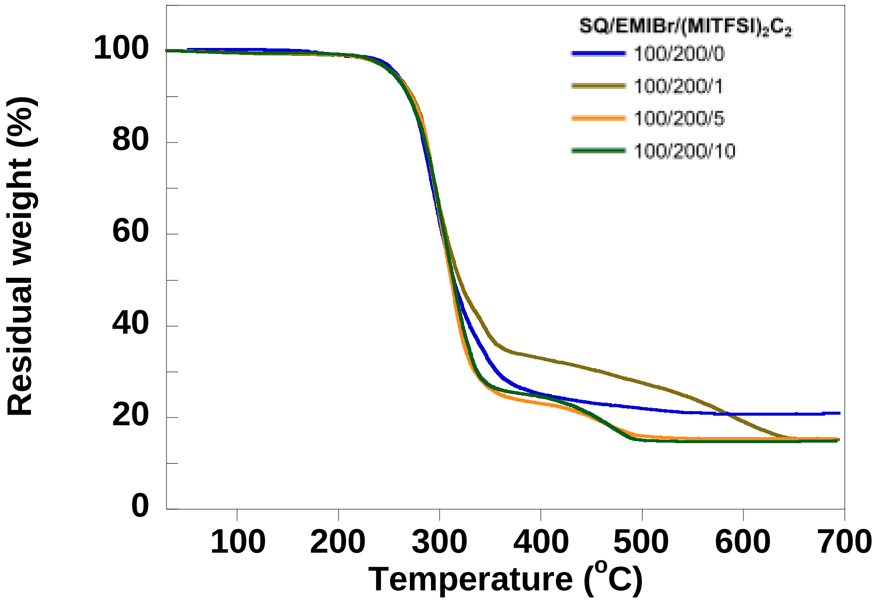

Figure S10. TGA results of three-component SQ/EMIBr/$(MITFSI)_2C_2$ hybrids having different cross-linkable HBA contents.

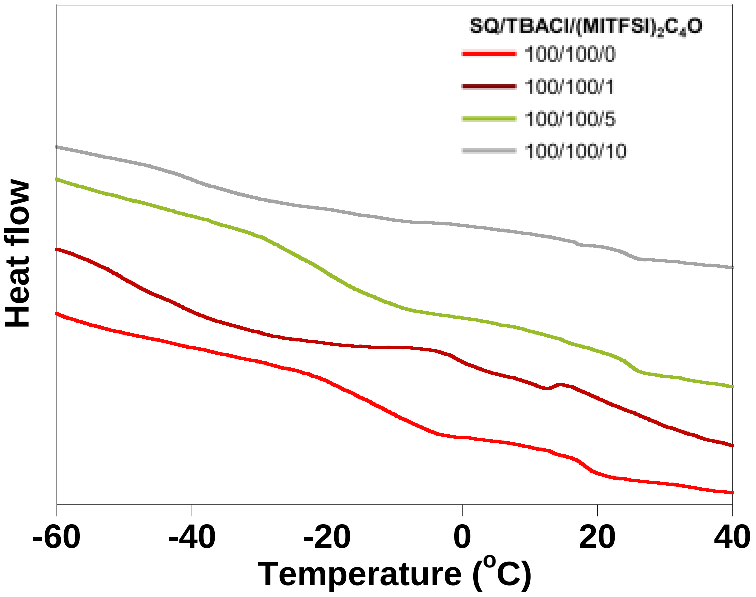

Figure S11. DSC traces of three-component SQ/TBACl/$(MITFSI)_2C_4O$ hybrids having different cross-linkable HBA contents.

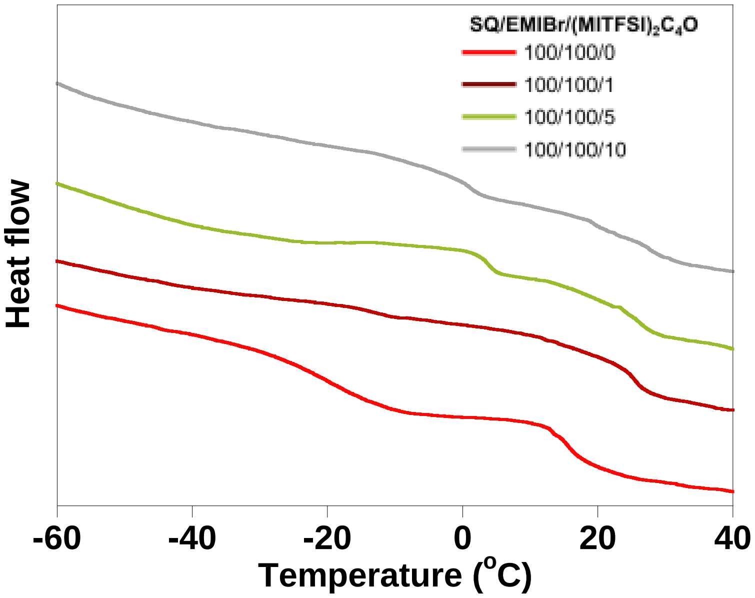

Figure S12. DSC traces of three-component SQ/EMIBr/$(MITFSI)_2C_4O$ hybrids having different cross-linkable HBA contents.

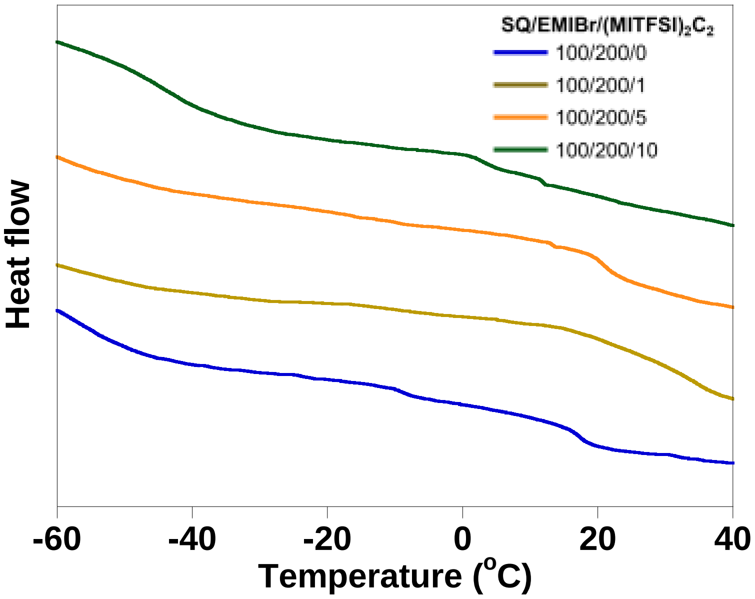

Figure S13. DSC traces of three-component SQ/EMIBr/$(MITFSI)_2C_2$ hybrids having different cross-linkable HBA contents.

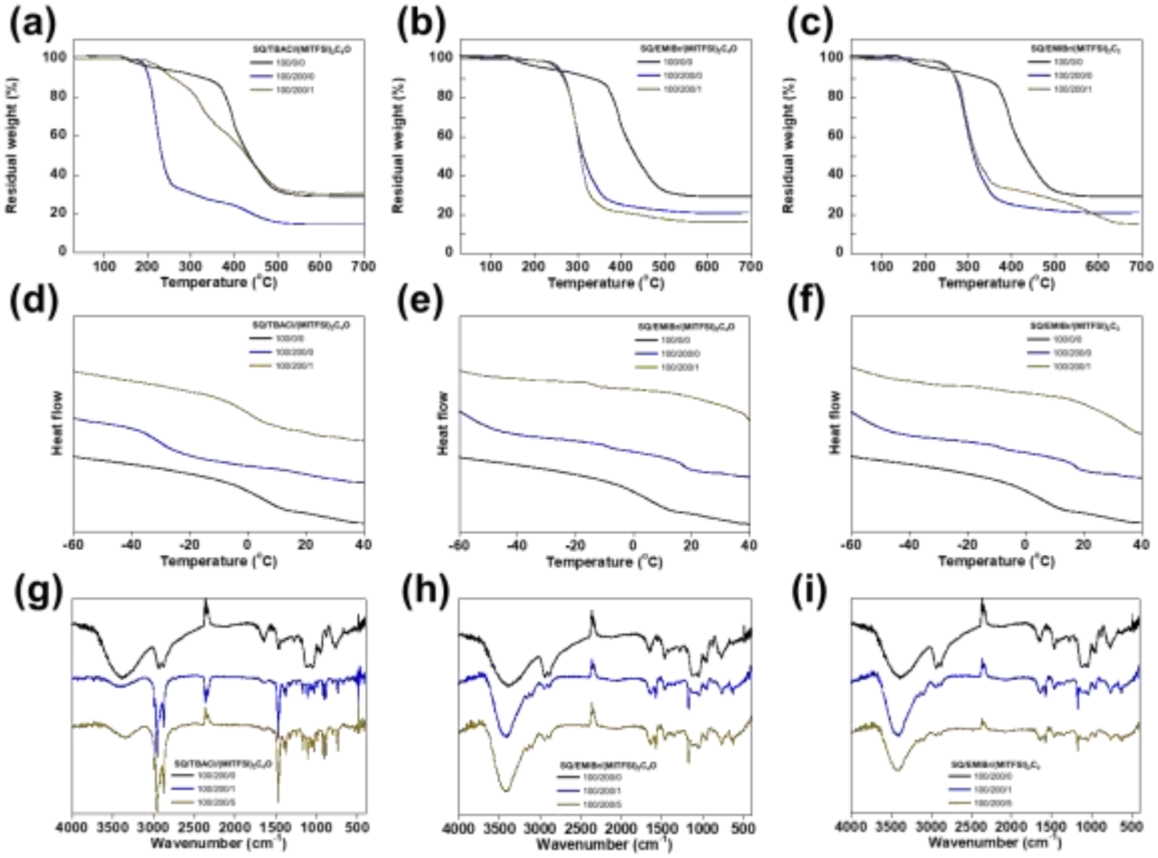

Figure S14. (a-c) TGA curves, (d-f) DSC curves, and (g-i) FT-IR spectra of three-component (100/200/1) and two-component (100/200) hybrids. (a,d,g) SQ/TBACl/$(MITFSI)_2C_4O$, (b,e,h) SQ/EMIBr/$(MITFSI)_2C_4O$, and (c,f,i) SQ/EMIBr/$(MITFSI)_2C_2$.

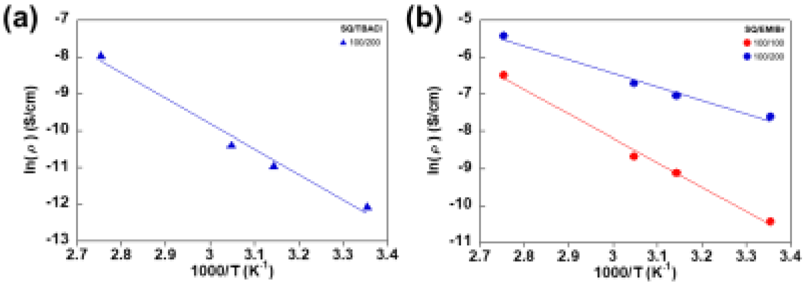

Figure S15. Arrhenius plots of (a) SQ/TBACl and (b) SQ/EMIBr hybrids.

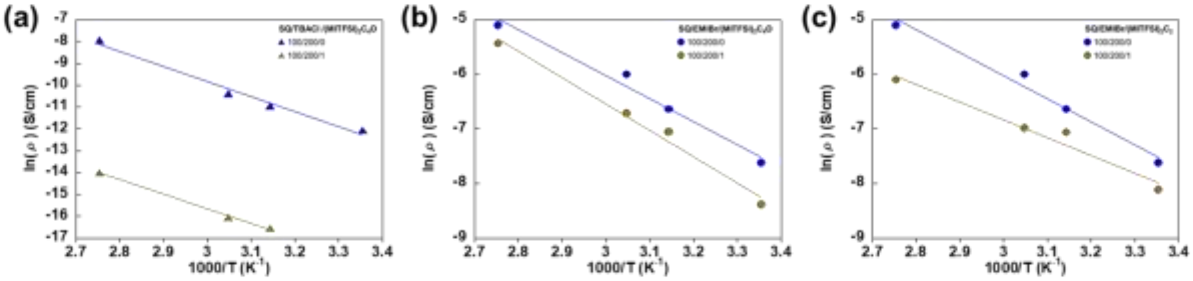

Figure S16. Arrhenius plots of three-component hybrids (100/200/1). (a) SQ/TBACl/(MITFSI)$_2$C$_4$O, (b) SQ/EMIBr/(MITFSI)$_2$C$_4$O, and (c) SQ/EMIBr/(MITFSI)$_2$C$_2$.

Table S6. Activation energies of two- and three-component DESQ and DESQ-Li Hybrids.

DESQ	Mixing ratio	Activation energy (E_a) [kJ/mol][a]
[SQ]/[TBACl]	100/200	57.25
[SQ]/[EMIBr]	100/200	34.98
	100/100	54.54
[SQ]/[TBACl]/[$(MITFSI)_2C_4O$]	100/200/1	55.50
[SQ]/[EMIBr]/[$(MITFSI)_2C_4O$]		40.08
[SQ]/[EMIBr]/[$(MITFSI)_2C_2$]		27.01
[SQ]/[TBACl]/[$(MITFSI)_2C_4O$]+LiTFSI	100/200/1+10wt%	31.80
[SQ]/[EMIBr]/[$(MITFSI)_2C_4O$]+LiTFSI		35.48
[SQ]/[EMIBr]/[$(MITFSI)_2C_2$]+LiTFSI		24.56

[a] Calculated from an Arrhenius plot of ionic conductivity.

Table S7. Preparation of three-component DESQ hybrids by the reaction of hydroxy-functionalized SQ with HBA in the presence of cross-linkable HB and LiTFSI

Run	HBA	Cross-linkable HBA	[R-SiO$_{1.5}$]/[HBA]/[Cross-linkable HBA]	[LiTFSI] (wt%)	Temp. (°C)	Time (h)	appearance at r.t.[a]
1	TBACl	(MITFSI)$_2$C$_4$O	100/200/1	10	60	24	a
2				20			c
3				30			c
4				40			c
5	EMIBr	(MITFSI)$_2$C$_4$O	100/200/1	10	60	24	a
6				20			c
7				30			c
8				40			c
9	EMIBr	(MITFSI)$_2$C$_2$	100/200/1	10	60	24	a
10				20			c
11				30			c
12				40			c

[a] a: viscous material, b: solid + solid, c: viscous material + solid.

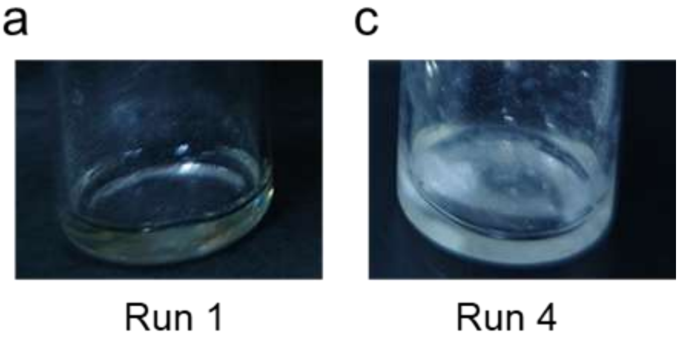

Figure S17. Appearance of three-component DESQ hybrids with LiTFSI, a: viscous material, b: solid + solid, c: viscous material + solid.

Table S8. Thermal properties and ionic conductivity of three-component DESQ hybrids with LiTFSI

Run	HBA	Cross-linkable HBA	[R-SiO$_{1.5}$]/[HBA] /[Cross-linkable HBA]	[LiTFSI] (wt%)	T$_g$ (°C)[a]	T$_{d5}$ (°C)[b]	Residual weight (%)[c]	ionic conductivity at 25 °C (S/cm)
1	TBACl	$(MITFSI)_2C_4O$	100/200/1	10	-22.8	195	14.3	3.77×10^{-5}
2				20	-	-	-	-
3				30				
4				40				
5	EMIBr	$(MITFSI)_2C_4O$	100/200/1	10	2.5	257	25.3	2.23×10^{-3}
6				20	-	-	-	-
7				30				
8				40				
9	EMIBr	$(MITFSI)_2C_2$	100/200/1	10	11.1	257	24.3	3.50×10^{-4}
10				20	-	-	-	-
11				30				
12				40				

[a] Determined by DSC. [b] Temperature for 5 wt.% weight loss under nitrogen. [c] Residual weight of the sample heated at 10 °C/min until 700 °C in TGA under nitrogen.

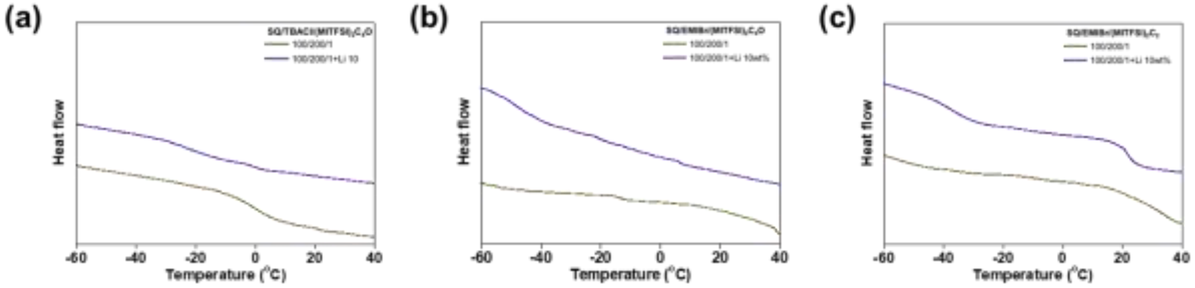

Figure S18. DSC traces of DESQ (100/200/1) hybrids with and without LiTFSI 10wt%. (a) SQ/TBACl/$(MITFSI)_2C_4O$, (b) SQ/EMIBr/$(MITFSI)_2C_4O$, (c) SQ/EMIBr/$(MITFSI)_2C_2$.

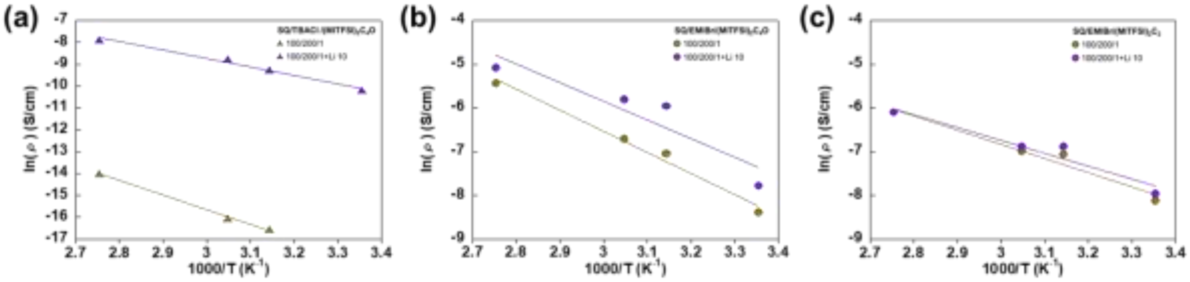

Figure S19. Arrhenius plots of three component-Li hybrids (100/200/1+LiTFSI 10wt%). (a) SQ/TBACl/(MITFSI)$_2$C$_4$O-Li, (b) SQ/EMIBr/(MITFSI)$_2$C$_4$O-Li, and (c) SQ/EMIBr/(MITFSI)$_2$C$_2$ -Li hybrids.

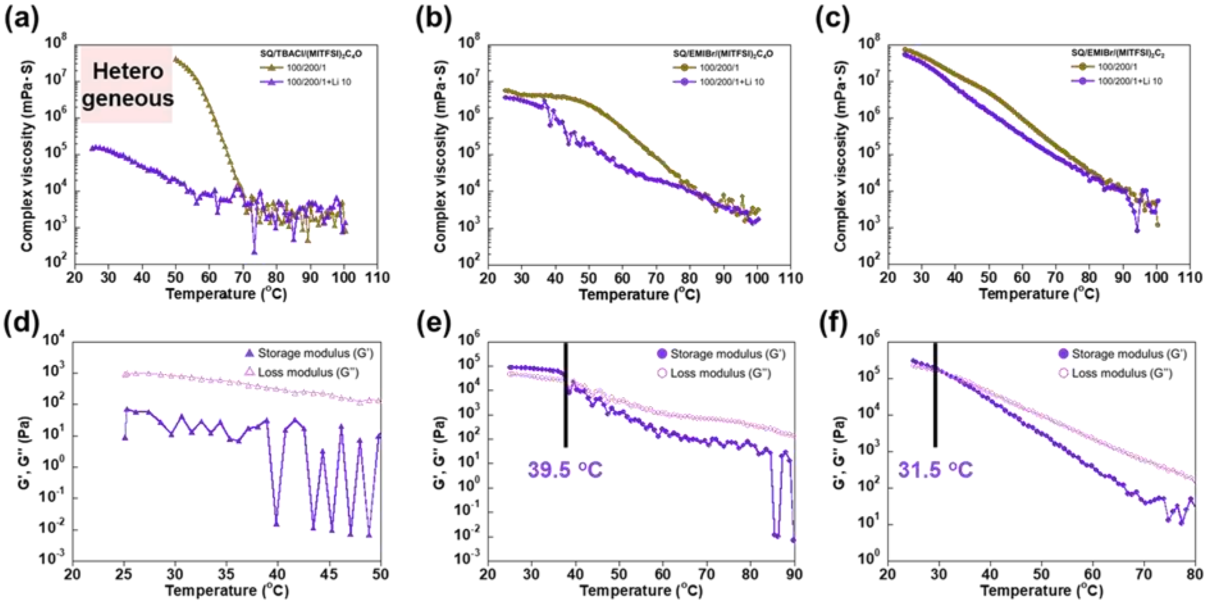

Figure S20. (a-c) Complex viscosities, (d-f) storage (G') and loss (G'') modulus against temperature of three-component-Li hybrids (100/200/1+LiTFSI 10wt%). (a,d) SQ/TBACl/$(MITFSI)_2C_4O$-Li, (b,e) SQ/EMIBr/$(MITFSI)_2C_4O$-Li, and (c,f) SQ/EMIBr/$(MITFSI)_2C_2$ -Li hybrids.

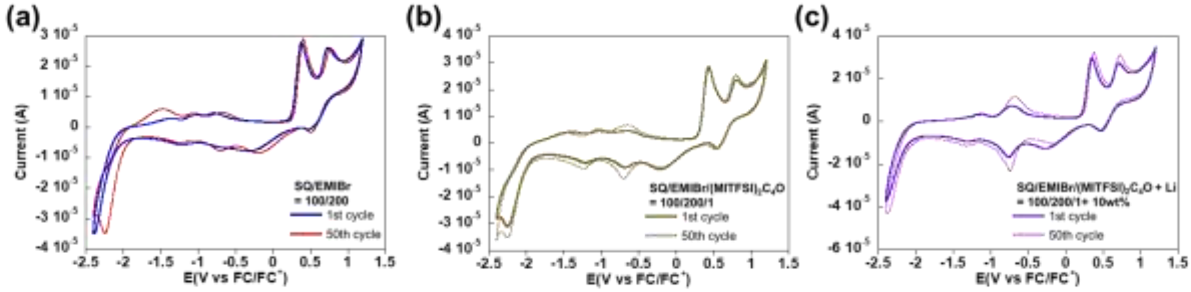

Figure S21. Cyclic voltammetry (CV) measurements of (a) two- and (b) three-component DESQ, and (c) DESQ-Li hybrids ([R-$SiO_{1.5}$]/[EMIBr]/[$(MITFSI)_2C_4O$] = 100200/0, 100/200/1, 100/200/1+ Li 10wt%).

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