Supplementary Information (SI) for Nanoscale.

Key parameter governing lithium ion mobility in monolayer Ionic-liquid tethered on metal oxide nanoparticles as solvent-free hybrid electrolytes.

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1. Reagents and Chemicals

Commercial Zirconium (IV) oxide nanoparticles (particle size of 15 - 25 nm, SSA = 28.44 $m^2.g^{-1}$) and Aluminum oxide nanoparticles (c-Al_2O_3 nanopowder, particle size <50 nm, SSA = 115.1 $m^2.g^{-1}$) were supplied by Alpha Aesar and sigma-aldrich respectively. Tetraethylorthosilicate (TEOS), 28% ammonia solution, 11-bromoundecanoic acid, sodium iodide, *N*-butylimidazole, bis(trifluoromethylsulfonyl)imide lithium salt and acetic acid come from Sigma Aldrich. All the solvents (acetonitrile, acetone) were employed as received without any purification (Fisher Scientific and Acros). Milli-Q water was used for synthesis.

2. Instrumentation

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were respectively recorded at 400 and 100 MHz using a Bruker DRX-400 spectrometer. Chemical shifts are reported in parts per million. For CD_3OD, MeOH was used as standard for ^{13}C (^1H: $\delta = 4.79$ ppm, ^{13}C: $\delta = 49.50$ ppm). *Peak multiplicity is reported as: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m).* Melting points were determined in a Büchi 535 (maximum temperature 275 °C). Concerning Zirconium (IV) oxide nanoparticles, N_2-adsorption isotherms were measured at liquid nitrogen temperature with a Micrometric ASAP 2020 porosimeter. Prior to analysis, the sample surface was outgassed at 120 °C for 3 h under vacuum (ca. 1 mmHg). Brunauer Emmett Edward (BET) surface area was calculated from the adsorption part of the isotherm between $0.03 < P/P_0 < 0.3$ using multi-points method. Hybrid materials were characterized by FTIR spectra in diffuse reflectance mode (DRIFT) using a Nicolet iS10 FTIR spectrometer from Thermo Scientific. The spectra were acquired at room temperature over a range of 4000–400 cm^{-1} with a resolution of 8 cm^{-1}. The electrolyte thermal stability was studied by thermogravimetric analyzes (TGA) performed under ambient air on a Netzsch thermal analyzer STA 449C Jupiter equipped with a Differential analysis microbalance coupled with a mass spectrometer QMS 403Aëolos equipped with SEV detector (Channeltron).

Electrochemical impedance spectroscopy (EIS) measurements were realized with an MTZ-35 frequency response analyzer (BioLogic Company) coupled with an Intermediate Temperature System (ITS) controlling the sample temperature by Peltier effect. The different synthesized materials were cold pressed into pellets of 10 mm diameter under a pressure of 6 tons with around 155 mg of powder per pellet. A thickness of about 0.61 mm is obtained. The pellets were sandwiched in the midst of two PAPYEX® foils (flexible graphite previously dried under vacuum at 150 °C) enhancing the electrical contacts between the pellet surface and the controlled environment sample holder (CESH) gold disks. The combined PAPYEX foil and gold disk ensure an ion blocking electrode. The electrolyte pellet is transferred under argon (within glove box) into an airtight environment asymmetric CESH to be sandwiched between the two ions blocking PAPYEX-gold electrodes. The CESH is then placed in ITS, and AC impedance spectra were recorded in the frequency range from 30 MHz to 0.1 Hz with an excitation signal of 5 mV amplitude and from 20 to 80 °C upon heating and cooling (1 $°C\cdot min^{-1}$) with a temperature stabilization of 15 min before impedance measurement every 20 °C. Modelling and simulation of the EIS data were performed using an equivalent circuit model described in the discussion section.

3. Synthesis of functionalized Ionic liquids

Chloride Imidazolium were synthesized by quaternazing imidazole with a specific anchoring arm. Three types of graftable ILs linker were subsequently obtained and denoted as Im-Spacer-Anchoring function (Sil for silane or Carb for carboxylic acid). All the synthesis procedure and spectroscopic characterization of synthesized final and intermediate compounds are available hereafter.

3.1 Synthesis of [Im-Alkyl-Sil][TFSI⁻] (IAS)

IAS chloride series was obtained by quaternization of imidazole with a chloro-alkyl-triethoxysilane based on the synthesis procedure previously described.[1] Here, chloropropyl- or chloroundecyl-triethoxysilane were used to give respectively Chloride salt of Im-C_3-Sil (IC_3S) and Im-C_{11}-Sil ($IC_{11}S$).

1-Butyl-3-(3-triéthoxysilyl)propyl-imidazol-3-ium bis(trifluorométhylsulfonyl)imide [ImC_3Sil][TFSI]

(3-Chloropropyl)triethoxysilane (5 g, 14.16 mmol) is added to N-butylimidazole (1 eq) under an inert atmosphere. The resulting solution is stirred at 120°C for 36 hours, then the crude product is washed several times with diethyl ether. Obtained product is dissolved in acetonitrile to form a solution to which 1.1 equivalents of LiTFSI are added. After stirring the resulting solution at 50°C for at least 1 hour, the solvent is removed under vacuum. Water and dichloromethane are then added to extract the product. The organic phase is washed 4 to 5 times until no chlorides remain (verified by adding $AgNO_3$). After drying the organic phase on Na_2SO_4 and filtering, the solvent is removed under vacuum to product with a yield of 92%.

^{1}H NMR (CD_3OD, 300MHz): δ (ppm) 8.94 (s, 1 H, N=CH-N), 7.63 (d, $J_{=CH\text{-}HC=}$ = 0.5 Hz, 1 H, =CH-N), 7.62 (d, $J_{=CH\text{-}HC=}$ = 0.5 Hz, 1 H, =CH-N), 4.14−4.30 (m, 4 H, $NCH_2CH_2CH_2Si(OEt)_3$, $CH_3(CH_2)_2CH_2N$), 3.82 (q, $J_{OCH_2\text{-}CH_3}$ = 7.0 Hz, 6 H, $Si(OCH_2CH_3)_3$), 1.79−2.10 (m, 4 H, $NCH_2CH_2CH_2Si(OEt)_3$, $CH_3(CH_2)_2CH_2N$), 1.31−1.48 (m, 2H, $CH_3(CH_2)_2CH_2N$), 1.21 (t, $J_{CH_3\text{-}CH_2O}$ = 7.0 Hz, 9 H, $Si(OCH_2CH_3)_3$), 0.98 (t, $J_{CH_3\text{-}CH_2}$ = 7.3 Hz, 3H, $CH_3(CH_2)_3N$), 0.54−0.67 (m, 2 H, $NCH_2CH_2CH_2Si(OEt)_3$). ^{13}C NMR (CD_3OD, 75 MHz): δ (ppm) 137.2 (N=CH-N), 124.0 (=CH-N), 123.9 (=CH-N), 121.3 (q, $J^1{}_{C,F}$ = 321 Hz, 2 × CF_3), 59.8 ($Si(OCH_2CH_3)_3$), 53.1 ($NCH_2CH_2CH_2Si(OEt)_3$), 50.8 ($CH_3(CH_2)_3N$), 33.2 ($CH_3(CH_2)_3$-N), 25.3 ($NCH_2CH_2CH_2Si(OEt)_3$), 20.6 ($CH_3(CH_2)_3N$), 18.8 ($Si(OCH_2CH_3)_3$), 13.8 ($CH_3CH_2CH_2CH_2N$), 8.1 ($NCH_2CH_2CH_2Si$-$(OEt)_3$). MS (ESI): [M^+] = 329.0 m/z, [M−] = 279.8 m/z.

1-Butyl-3-(11-triéthoxysilyl)undécyl-imidazol-3-ium bis(trifluorométhylsulfonyl)imide [$ImC_{11}Sil$][TFSI]

Wilkinson's catalyst (20 mg, 0.0216 mmol) is dissolved in 25 mL of anhydrous toluene. 11-Chloro-1-undecene (5 mL, 0.0264 mol) and triethoxysilane (1 eq) are added to this solution, which is then stirred at 90°C for 3 hours. After evaporating the solvent under vacuum, the crude product is purified by column chromatography to obtain the compound with a yield of 74%. This latter is added to N-butylimidazole (1 eq) under an inert atmosphere. The resulting solution is stirred at 120°C for 36 hours, then the crude product is washed several times with diethyl ether. Finally, it is dried to obtain compound with a yield of 81%. Anion exchange is carried out by dissovling chloride salt in acetonitrile to form a solution to which 1.1 equivalents of

LiTFSI are added. After stirring the resulting solution at 50°C for at least 1 hour, the solvent is removed under vacuum. Water and dichloromethane are then added to extract the product. The organic phase is washed 4 to 5 times until no chlorides remain (verified by adding $AgNO_3$). After drying the organic phase on Na_2SO_4 and filtering, the solvent is removed under vacuum to obtain compound (5) with a yield of 95%.

IR (ATR): ν (cm^{-1}) 3149, 3113, 3093, 2971, 2927, 2852, 2359, 2325, 1351, 1189, 1135, 1056, 789, 740. T°g: −66.0 °C. T°c: not determined. T°f: not determined. ^1H NMR (CD_3OD, 300 MHz): δ (ppm) 8.95 (s, 1 H, N=CH-N), 7.63 (d, $J_{=CH\text{-}HC=}$ = 0.5 Hz, 1 H, =CH-N), 7.62 (d, $J_{=CH\text{-}HC=}$ = 0.5 Hz, 1 H, =CH-N), 4.22 (t, $J_{NCH_2\text{-}CH_2}$ = 7.3 Hz, 2 H, $NCH_2(CH_2)_8CH_2CH_2Si(OEt)_3$), 4.21 (t, $J_{CH_2\text{-}CH_2N}$ = 7.3 Hz, 2 H, $CH_3(CH_2)_2CH_2N$), 3.81 (q, $J_{OCH_2\text{-}CH_3}$ = 7.0 Hz, 6 H, $Si(OCH_2CH_3)_3$), 1.81−1.96 (m, 2H, 2H, $NCH_2(CH_2)_8CH_2CH_2Si(OEt)_3$, $CH_3(CH_2)_2CH_2N$), 1.25−1.50 (m, 16H, 2H, $NCH_2(CH_2)_8CH_2CH_2Si(OEt)_3$, $CH_3(CH_2)_2CH_2$), 1.21 (t, $J_{CH_3\text{-}CH_2O}$ = 7.0 Hz, 9 H, $Si(OCH_2CH_3)_3$), 0.98 (t, $J_{CH_3\text{-}CH_2}$ = 7.3 Hz, 3H, $CH_3(CH_2)_3N$), 0.57−0.67 (m, 2 H, $NCH_2(CH_2)_8CH_2CH_2Si\text{-}(OEt)_3$). ^{13}C NMR (CD_3OD, 75 MHz): δ (ppm) 137.1 (N=CH-N), 123.9 (=CH-N), 121.3 (q, $J^1_{C,F}$ = 321 Hz, 2 × CF_3), 59.5 ($Si(OCH_2CH_3)_3$), 51.0 ($NCH_2(CH_2)_9CH_2Si(OEt)_3$), 50.8 ($CH_3\text{-}(CH_2)_2CH_2N$), 34.2 ($NCH_2(CH_2)_9CH_2Si(OEt)_3$), 33.2 ($CH_3(CH_2)_2\text{-}CH_2N$), 31.2, 30.7, 30.6, 30.5, 30.2, 27.4, 24.0 (8 × $NCH_2(CH_2)_9\text{-}\ CH_2Si(OEt)_3$), 20.6 ($CH_3(CH_2)_2CH_2N$), 18.8 ($Si(OCH_2CH_3)_3$), 13.8 ($CH_3CH_2CH_2CH_2N$), 11.3 ($NCH_2(CH_2)_9CH_2Si(OEt)_3$). MS (ESI): [$M^+$] = 441.3 m/z, [M−] = 279.7 m/z.

3.2. Synthesis of [Im-PEG-Sil][TFSI$^-$] (IPS)

IPS series were obtained by quaternization of imidazole with a PEG-based silane obtained by hydrosilylation reaction using Karstedt's catalyst. Here, triethylene glycol, tetraethylene glycol or hexaethylene silane were used to give respectively Chloride salt of Im-PEG_3-Sil (IP_3S), Im-PEG_4-Sil (IP_4S) and Im-PEG_6-Sil (IP_6S).

Synthesis of [ImPEG$_3$Sil][TFSI]

A solution of triethylene glycol (20 mL, 0.149 mol) and tBuOK (8.22 g, 0.068 mol) are mixed in anhydrous THF (100 mL). Allyl bromide (6.9 mL, 0.081 mol) is added after stirring at room temperature for 30 minutes, and the reaction mixture is left to stir overnight. After filtration and removal of the solvent under vacuum, the crude reaction mixture is purified by column chromatography using silica gel and a mixture of DCM/MeOH (100/0 to 90/10 v/v) as eluent. The pure compound is obtained in liquid form (7.7 g, 50% yield).

^{1}H NMR (CD$_3$OD, 25 °C, 400 MHz) : δ_H 5.94 (m, 1H, CH=), 5.30 (d, 1H, J = 17.3 Hz, H$_a$ CH$_2$=), 5.18 (d, 1H, J = 10.4 Hz, H$_b$ CH$_2$=), 4.04 (dd, 2H, J = 1.4 Hz, J = 5.6 Hz, CH_2OH), 3.69-3.57 (m, 12H, 6 x OCH$_2$) ; ^{13}C NMR (CD$_3$OD, 25 °C, 100 MHz) : δ_C 134.6 (CH=), 115.8 (CH$_2$=), 72.2, 71.7, 70.2, 70.1, 69.1 (6 x OCH$_2$), 60.8 (CH$_2$OH).

HRMS (ESI$^+$) calculated pour $C_9H_{18}O_4Na$ [M+Na]$^+$ 213.1103, measured 213.1109.

Pyridine (1.6 mL, 19.74 mmol) and thionyl chloride (1.4 mL, 19.74 mmol) are added dropwise (under an inert atmosphere) to a solution composed of 2.5 g (13.16 mmol) of previous derivative in 25 mL of chloroform. The mixture is stirred under reflux for 4 hours, then the organic phase is washed four times with water (4 x 100 mL). After drying the organic phase on MgSO$_4$, filtering and removing the solvent under vacuum, the chloride derivative is obtained in liquid form. It is used in the next step without further purification.

NMR ^{1}H (CD$_3$OD, 25 °C, 400 MHz) : δ_H 5.94 (m, 1H, CH=), 5.30 (d, 1H, J = 17.2 Hz, H$_a$ CH$_2$=), 5.18 (d, 1H, J = 10.2 Hz, H$_b$ CH$_2$=), 4.04 (dd, 2H, J = 1.0 Hz, J = 5.6 Hz, CH_2OH), 3.76 (dd, 2H, J = 4.8 Hz, J = 6.0 Hz, OCH$_2$), 3.68-3.60 (m, 10H, 5 x OCH$_2$) ; NMR ^{13}C (CD$_3$OD, 25 °C, 100 MHz) : δ_C 134.7 (CH=), 115.8 (CH$_2$=), 71.7, 71.1, 70.2, 70.1, 69.1 (5 x OCH$_2$), 42.4 (CH$_2$Cl).

HRMS (ESI$^+$) calculated for $C_9H_{17}ClO_3Na$ [M+Na]$^+$ 231.0764, measured 231.0764

A solution containing 2.5 g (12 mmol) of the chloride derivative and 0.2 mL (0.54 mmol) of Karstedt's catalyst in triethoxysilane (22 mL, 120 mmol) is stirred under argon at 80°C for 20 hours. After removal of the solvent under reduced pressure, the crude organosilane, obtained in a yield of 92%, is used in the next step without further purification.

NMR ^{1}H (CD_3OD, 25 °C, 400 MHz) : δ_H 9.08 (s, 1H, CH=), 7.72 (s, 1H, CH=), 7.69 (s, 1H, CH=), 4.44 (t, 2H, J = 4.7 Hz, NCH_2), 4.28 (t, 2H, J = 7.3 Hz, $NCH_{2(But)}$), 3.88 (t, 2H, J = 4.8 Hz, OCH_2), 3.84 (q, 6H, J = 7.0 Hz, 3 x $OCH_{2\ (OEt)}$), 3.64 (m, 8H, 4 x OCH_2), 3.47 (t, 2H, J = 6.7 Hz, OCH_2), 1.91 (qt, 2H, J = 7.3 Hz, $CH_{2\ (But)}$), 1.67 (qt, 2H, J = 6.9 Hz, CH_2CH_2Si), 1.40 (sx, 2H, J = 7.4 Hz, $CH_{2\ (But)}$), 1.23 (t, 9H, J = 7.0 Hz, 3 x $CH_{3\ (OEt)}$), 1.02 (t, 3H, J = 7.0 Hz, $CH_{3\ (But)}$), 0.64 (t, 2H, J = 8.6 Hz, $SiCH_2$) ; NMR ^{13}C (CD_3OD, 25 °C, 100 MHz) : δ_C 136.4 (CH=), 122.9 (CH=), 122.0 (CH=), 73.0, 70.0, 69.9, 69.7, 68.3 (6 x OCH_2), 58.0 (3 x OCH_2CH_3), 49.5, 49.2 (2 x NCH_2), 31.7 ($CH_{2\ (But)}$), 22.7 ($CH_{2\ (Si)}$), 19.1 ($CH_{2\ (But)}$), 17.3 (3 x OCH_2CH_3), 12.4 ($CH_{3\ (But)}$), 6.0 ($SiCH_2$).

To a mixture composed of 500 mg (1.00 mmol) of chloride derivative in 20 mL of acetonitrile, LiTFSI (0.35 g, 1.21 mmol) is added. After 2.5 hours of stirring at room temperature, the solvent is removed under reduced pressure. The reaction mixture is filtered after adding dichloromethane. The pure compound (80% yield) is obtained in liquid form after removing the solvent under reduced pressure.

NMR ^{1}H (CD_3OD, 25 °C, 400 MHz) : δ_H 8.97 (s, 1H, CH=), 7.67 (s, 1H, CH=), 7.64 (s, 1H, CH=), 4.41 (t, 2H, J = 4.8 Hz, NCH_2), 4.25 (t, 2H, J = 7.3 Hz, $NCH_{2(But)}$), 3.85 (m, 8H, 3 x OCH_2CH_3, OCH_2), 3.64 (m, 8H, 4 x OCH_2), 3.47 (t, 2H, J = 6.8 Hz, OCH_2), 1.90 (qt, 2H, J = 7.4 Hz, $CH_{2\ (But)}$), 1.67 (qt, 2H, J = 7.0 Hz, CH_2CH_2Si), 1.40 (sx, 2H, J = 7.4 Hz, $CH_{2\ (But)}$), 1.23 (t, 9H, J = 7.0 Hz, 3 x $CH_{3\ (OEt)}$), 1.01 (t, 3H, J = 7.4 Hz, $CH_{3\ (But)}$), 0.64 (t, 2H, J = 8.8 Hz, $SiCH_2$) ; NMR ^{13}C (CD_3OD, 25 °C, 100 MHz) : δ_C 136.3 (CH=), 122.9 (CH=), 121.9 (CH=), 124.6, 121.4, 118.2, 115.0 (q, J = 319 Hz, 2 x CF_3), 73.0, 70.0, 69.9, 69.6, 68.3 (6 x OCH_2), 58.1 (3 x OCH_2CH_3), 49.4, 49.2 (2 x NCH_2), 31.7 ($CH_{2\ (But)}$), 22.6 ($CH_{2\ (Si)}$), 19.0 ($CH_{2\ (But)}$), 17.3 (3 x OCH_2CH_3), 12.3 ($CH_{3\ (But)}$), 5.9 ($SiCH_2$).

Synthesis of [Im(PEG)$_4$Sil][TFSI]

A solution of tetraethylene glycol (20 mL, 0.11 mol) and tBuOK (6.72 g, 0.05 mol) are mixed in anhydrous THF (100 mL). Allyl bromide (5.18 mL, 0.06 mol) is added after stirring at room temperature for 30 minutes, and the reaction mixture is left to stir overnight. After filtration and removal of the solvent under vacuum, the crude reaction mixture is purified by column chromatography using silica gel and a mixture of DCM/MeOH (100/0 to 90/10 v/v) as eluent. The pure compound is obtained in liquid form (10.3 g, 38% yield).

Pyridine (0.86 mL, 10.7 mmol) and thionyl chloride (1.6 mL, 16.05 mmol) are added dropwise (under an inert atmosphere) to a solution composed of 2.5 g (10.7 mmol) of functionalized tetraethylene glcol derivative in 25 mL of chloroform. The mixture is stirred under reflux for 4 hours, then the organic phase is washed four times with water (4 x 100 mL). After drying the organic phase on $MgSO_4$, filtering and removing the solvent under vacuum, the chloride derivative is obtained in liquid form with 96% yield. It is used in the next step without further purification.

NMR ^{1}H ($CDCl_3$, 25 °C, 400 MHz) : δ_H 5.93 (m, 1H, CH=), 5.29 (dq, 1H, J = 1.65 Hz, J = 17.2 Hz, Ha CH_2=), 5.19 (m, 1H, Hb CH_2=), 4.05 (t, 1H, J = 1.40 Hz, Ha CH_2CH=), 4.03 (t, 1H, J = 1.40 Hz, Hb CH_2CH=), 3.78 (t, 2H, J = 6.08 Hz, CH_2Cl), 3.76-3.60 (m, 14H, 7 x OCH_2) ; NMR ^{13}C ($CDCl_3$, 25 °C, 100 MHz) : δ_C 134.7 (CH=), 117.1 (CH_2=), 72.2, 71.3, 70.7, 70.6, 69.4 (8 x OCH_2), 42.7 (CH_2Cl).

HRMS (ESI+) calculated for $C_{11}H_{21}ClO_4Na$ $[M+Na]^+$ 252.1026, measured 252.1023.

A solution containing 2.5 g (9.9 mmol) of the chloride derivative and 0.2 mL (0.44 mmol) of Karstedt's catalyst in triethoxysilane (18 mL, 99 mmol) is stirred under argon at 80°C for 20 hours. After removal of the solvent under reduced pressure, the crude organosilane obtained is used in the next step without further purification. *N*-butylimidazole (1.9 mL, 14.45 mmol) and organosilane are placed in microwave reactor (150°C, 2000 W, open vessel). After stirring for 2h and elimination of the solvent under reduced pressure, the crude mixture is purified by silica gel using DCM/MeOH (100/0 to 50/50 v/v) as eluent. The pure compound is obtained in liquid form (0.87 g, 16% yield).

NMR ^{1}H (CD$_3$OD, 25 °C, 400 MHz) : δ_H 8.93 (s, 1H, CH=), 7.59 (s, 1H, CH=), 7.57 (s, 1H, CH=), 4.30 (t, 2H, *J* = 4.7 Hz, NCH$_2$), 4.15 (t, 2H, *J* = 7.3 Hz, NCH$_{2\ (But)}$), 3.77-3.70 (m, 8H, OCH$_2$, 3 x OCH$_2$CH$_3$), 3.56-3.47 (m, 12H, 6 x OCH$_2$), 3.33 (t, 2H, *J* = 6.7 Hz, OCH$_2$), 1.79 (qt, 2H, *J* = 7.3 Hz, CH$_{2\ (But)}$), 1.53 (m, 2H, SiCH$_2$C*H*$_2$), 1.29 (sx, 2H, *J* = 7.3 Hz, CH$_{2\ (But)}$), 1.11 (t, 9H, *J* = 7.0 Hz, 3 x OCH$_2$C*H*$_3$), 0.90 (t, 3H, *J* = 7.3 Hz, CH$_{3\ (But)}$), 0.52 (t, 2H, *J* = 8.4 Hz, SiCH$_2$) ; NMR ^{13}C (CD$_3$OD, 25 °C, 100 MHz) : δ_C 136.5 (CH=), 122.9 (CH=), 121.9 (CH=), 73.0, 70.2, 70.1, 70.0, 69.9, 69.8, 69.7, 68.3 (8 x OCH$_2$), 58.0 (3 x O*C*H$_2$CH$_3$), 49.4, 49.2 (2 x NCH$_2$), 31.7 (CH$_{2\ (But)}$), 22.7 (CH$_{2\ (Si)}$), 19.0 (CH$_{2\ (But)}$), 17.3 (3 x OCH$_2$*C*H$_3$), 12.3 (CH$_{3\ (But)}$), 6.0 (SiCH$_2$).

To a mixture composed of 500 mg (0.99 mmol) of chloride derivative in 20 mL of acetonitrile, LiTFSI (0.35 g, 1.21 mmol) is added. After 2.5 hours of stirring at room temperature, the solvent is removed under reduced pressure. The reaction mixture is filtered after adding dichloromethane. The pure compound (0.77 g, 96% yield) is obtained in liquid form after removing the solvent under reduced pressure.

NMR ^{1}H (CD$_3$OD, 25 °C, 400 MHz) : δ_H 8.88 (s, 1H, CH=), 7.56 (s, 1H, CH=), 7.54 (s, 1H, CH=), 4.29 (t, 2H, *J* = 4.7 Hz, NCH$_2$), 4.14 (t, 2H, *J* = 7.3 Hz, NCH$_{2\ (But)}$), 3.77-3.70 (m, 8H, OCH$_2$, 3 x OC*H*$_2$CH$_3$), 3.56-3.47 (m, 12H, 6 x OCH$_2$), 3.33 (t, 2H, *J* = 6,7 Hz, OCH$_2$), 1.79 (qt, 2H, *J* = 7.3 Hz, $CH_{2\ (But)}$), 1.53 (m, 2H, $SiCH_2CH_2$), 1.29 (sx, 2H, *J* = 7.3 Hz, $CH_{2\ (But)}$), 1.11 (t, 9H, *J* = 7.0 Hz, 3 x OCH_2CH_3), 0.90 (t, 3H, *J* = 7.3 Hz, $CH_{3\ (But)}$), 0.52 (t, 2H, *J* = 8.4 Hz, $SiCH_2$) ; NMR ^{13}C (CD_3OD, 25 °C, 100 MHz) : δ_C 136.4 (CH=), 122.9 (CH=), 121.9 (CH=), 124.6, 121.4, 118.2, 115.0 (q, *J* = 319 Hz, 2 x CF_3), 73.0, 70.2, 70.1, 70.0, 69.9, 69.8, 69.7, 68.3 (8 x OCH_2), 58.1 (3 x OCH_2CH_3), 49.4, 49.2 (2 x NCH_2), 31.7 ($CH_{2\ (But)}$), 22.6 ($CH_{2\ (Si)}$), 19.0 ($CH_{2\ (But)}$), 17.2 (3 x OCH_2CH_3), 12.3 ($CH_{3\ (But)}$), 5.9 ($SiCH_2$).

HRMS (ESI+) calculated for $C_{24}H_{49}N_2O_7Si$ $[M]^+$ 505.3309, measured 505.3322.

Synthesis of [ImPEG$_6$Sil][TFSI]

A solution of hexaethylene glycol (10.8 g, 38.18 mmol) and tBuOK (7.0 g, 49.64 mmol) are mixed in anhydrous THF (50 mL). Allyl bromide (2.0 mL, 34.36 mmol) is added after stirring at room temperature for 30 minutes, and the reaction mixture is left to stir overnight. After filtration and removal of the solvent under vacuum, the crude reaction mixture is purified by column chromatography using silica gel and a mixture of DCM/MeOH (100/0 to 90/10 v/v) as eluent. The pure compound is obtained in liquid form (5.8 g, 50% yield).

Pyridine (0.75 mL, 9.31 mmol) and thionyl chloride (1.0 mL, 13.96 mmol) are added dropwise (under an inert atmosphere) to a solution composed of 3.0 g (9.31 mmol) of functionalized hexaethylene glcol derivative in 25 mL of chloroform. The mixture is stirred under reflux for 4 hours, then the organic phase is washed four times with water (4 x 100 mL). After drying the organic phase on $MgSO_4$, filtering and removing the solvent under vacuum, the chloride derivative is obtained in liquid form with 96% yield. It is used in the next step without further purification.

NMR ^1H (CD_3OD, 25 °C, 400 MHz) : δ_H 5,93 (m, 1H, CH=), 5.30 (d, 1H, *J* = 17.3 Hz, Ha CH_2=), 5.18 (d, 1H, *J* = 10.4 Hz, Hb CH_2=), 4.03 (dd, 2H, *J* = 1.5 Hz, *J* = 5.6 Hz, CH_2), 3.76

(t, 2H, *J* = 4.7 Hz, CH_2), 3.69-3.60 (m, 22H, 11 x CH_2) ; NMR ^{13}C (CD_3OD, 25 °C, 100 MHz) : δ_C 134.7 (CH=), 115.8 (CH_2=), 71.6, 71.1, 70.3, 70.2, 70.1, 70.0, 69.2 (12 x CH_2), 42.4 (CH_2Cl). HRMS (ESI+) calculated for $C_{15}H_{29}ClO_6Na$ $[M+Na]^+$ 363.1550, measured 363.1540.

A solution containing 2.9 g (8.5 mmol) of the chloride derivative and 0.2 mL (0.44 mmol) of Karstedt's catalyst in triethoxysilane (15 mL, 85 mmol) is stirred under argon at 80°C for 20 hours. After removal of the solvent under reduced pressure, the crude organosilane obtained is used in the next step without further purification. *N*-butylimidazole (1.9 mL, 14.45 mmol) and organosilane are placed in microwave reactor (150°C, 2000 W, open vessel). After stirring for 2h and elimination of the solvent under reduced pressure, the crude mixture is purified by silica gel using DCM/MeOH (100/0 to 50/50 v/v) as eluent. The pure compound is obtained in liquid form (1.89 g, 37% yield).

NMR ^1H (CD_3OD, 25 °C, 400 MHz) : δ_H 9.06 (s, 1H, CH=), 7.71 (s, 1H, CH=), 7.69 (s, 1H, CH=), 4.43 (t, 2H, *J* = 4.8 Hz, NCH_2), 4.27 (t, 2H, *J* = 7.3 Hz, $NCH_{2\ (But)}$), 3.89-3.81 (m, 6H, 3 x $OC\mathit{H}_2CH_3$), 3.68-3.58 (m, 22H, 11 x OCH_2), 3.46 (t, 2H, *J* = 6.7 Hz, OCH_2), 1.91 (qt, 2H, *J* = 7.2 Hz, $CH_{2\ (But)}$), 1.66 (qt, 2H, *J* = 6.9 Hz, $CH_{2\ (Si)}$), 1.40 (sx, 2H, *J* = 7.4 Hz, $CH_{2\ (But)}$), 1.25 (t, 9H, *J* = 7.0 Hz, 3 x $OCH_2C\mathit{H}_3$), 1.02 (t, 3H, *J* = 7.3 Hz, $CH_{3\ (But)}$), 0.65 (m, 2H, $SiCH_2$) ; NMR ^{13}C (CD_3OD, 25 °C, 100 MHz) : δ_C 136.6 (CH=), 122.9 (CH=), 121.9 (CH=), 73.0, 70.2, 70.1, 70.0, 69.9, 69.8, 69.7, 68.3 (12 x OCH_2), 58.0 (3 x $O\mathit{C}H_2CH_3$), 49.5, 49.2 (2 x NCH_2), 31.7 ($CH_{2\ (But)}$), 22.7 ($CH_{2\ (Si)}$), 19.1 ($CH_{2\ (But)}$), 17.3 (3 x $OCH_2\mathit{C}H_3$), 12.4 ($CH_{3\ (But)}$), 6.0 ($SiCH_2$).

To a mixture composed of 1.89 g (3.18 mmol) of chloride derivative in 90 mL of acetonitrile, LiTFSI (0.35 g, 1.21 mmol) is added. After 2.5 hours of stirring at room temperature, the solvent is removed under reduced pressure. The reaction mixture is filtered after adding dichloromethane. The pure compound (96% yield) is obtained in liquid form after removing the solvent under reduced pressure.

NMR ^{1}H (CD_3OD, 25 °C, 400 MHz) : δ_H 9.01 (s, 1H, CH=), 7.68 (s, 1H, CH=), 7.66 (s, 1H, CH=), 4.41 (t, 2H, J = 4.7 Hz, NCH_2), 4.26 (t, 2H, J = 7.3 Hz, $NCH_{2\ (But)}$), 3.89-3.81 (m, 6H, 3 x OCH_2CH_3), 3.67-3.58 (m, 22H, 11 x OCH_2), 3.33 (t, 2H, J = 6.7 Hz, OCH_2), 1.90 (qt, 2H, J = 7.6 Hz, $CH_{2\ (But)}$), 1.67 (qt, 2H, J = 6.7 Hz, $CH_{2\ (Si)}$), 1.40 (sx, 2H, J = 7.6 Hz, $CH_{2\ (But)}$), 1.23 (t, 9H, J = 7.0 Hz, 3 x OCH_2CH_3), 1.01 (t, 3H, J = 7.6 Hz, $CH_{3\ (But)}$), 0.65 (m, 2H, $SiCH_2$) ; NMR^{13}C (CD_3OD, 25 °C, 100 MHz) : δ_C 136.6 (CH=), 122.9 (CH=), 121.9 (CH=), 119.8 (q, 2C, J = 319 Hz, 2 x CF_3), 73.0, 70.2, 70.1, 70.0, 69.9, 69.8, 69.7, 68.3 (12 x OCH_2), 58.0 (3 x OCH_2CH_3), 49.5, 49.2 (2 x NCH_2), 31.7 ($CH_{2\ (But)}$), 22.7 ($CH_{2\ (Si)}$), 19.0 ($CH_{2\ (But)}$), 17.2 (3 x OCH_2CH_3), 12.4 ($CH_{3\ (But)}$), 5.9 ($SiCH_2$).

HRMS (ESI+) calculated for $C_{28}H_{57}N_2O_9Si$ $[M]^+$ 593,3833, measured 593,3846.

3.3 Synthesis of [Im-Alkyl-carb][Cl$^-$] (IAC)

IAC chloride was obtained by quaternization of imidazole with iodo-decyl-carboxylic acid using the procedure previously described to give Chloride salt of Im-C_{10}-Carb ($IC_{10}C$).[2]

Synthesis of [C_4C_{11}Carb][I$^-$]

11-bromoundecanoic acid (12.5 g, 47.2 mmol) and NaI (16.98 g, 113.3 mmol) are dissolved in acetone (100 mL). After stirring at room temperature for 3h, water (20 mL) is added followed by EtOAc (4 x 25 mL). After gathering, the organic phase is washed with a saturated solution of sodium thiosulfate (20 mL), dried over $MgSO_4$, filtered and the solvent removed under vacuum. The compound is obtained as a solid in 87 % yield.[3]

7.00 g (22.43 mmol) of 11-iodoundecanoic acid and 2.94 mL (22.43 mmol) of *N*-butylimidazole were refluxed in acetonitrile (50 mL) for 4 days. After elimination of the solvent under reduced pressure, the crude reaction mixture was triturated in EtOAc and filtered to afford the pure compound as a slight yellowish solid compound (8.33 g, 85% yield).

NMR ^{1}H (CD_3OD, 25 °C, 400 MHz): δ_H 9.13 (s, 1H, NCHN), 7.70 (s, 2H, 2× CH), 4.27 (m, 4H, 2 × NCH_2), 2.29 (t, 2H, J = 7.36 Hz, CH_2COOH), 1.92 (m, 4H, 2 × CH_2), 1.61 (m, 2H, CH_2), 1.37 (m, 14H, 7 × CH_2), 1.01 (t, 3H, J = 7.36 Hz, CH_3); NMR ^{13}C (CD_3OD, 25 °C, 100 MHz): δ_C 176.2 (COOH), 135.7 (NCHN), 122.4 (2 × CH), 49.5 (NCH_2), 49.3 (NCH_2), 33.5, 31.7, 29.7, 29.0, 28.9, 28.8, 28.7, 28.6, 25.8, 24.7 (10 × CH_2), 19.1 (CH_2CH_3), 12.4 (CH_3).

Synthesis of [C_4C_{11}Carb][TFSI]

To 4.00 g (9.17 mmol) of chloride derivative in osmosed water (20 mL) was added LiTFSI (2.89 g, 10.09 mmol). After stirring at 50 °C for 4 h and cooling to room temperature, CH_2Cl_2 was added, and the organic phase was extracted and washed twice with water. After drying the organic phase with Na_2SO_4 and filtration, a pure compound was obtained as a yellow oil (5.40 g, >99% yield).

NMR ^{1}H (CD_3OD, 25 °C, 400 MHz): δ_H 8.97 (s, 1H, NCHN), 7.65 (s, 2H, 2 × CH), 4.23 (m, 4H, 2 × NCH_2), 2.29 (t, 2H, J = 7.37 Hz, CH_2COOH), 1.90 (m, 4H, 2 × CH_2), 1.61 (m, 2H, CH_2), 1.38 (m, 14H, 7 × CH_2), 1.00 (t, 3H, J = 7.37 Hz, CH_3); NMR ^{13}C (CD_3OD, 25 °C, 100 MHz): δ_C 176.3 (COOH), 135.6 (NCHN), 122.4 (2 × CH), 119.8 (q, 2C, J = 318 Hz, 2 × CF_3), 49.5 (NCH_2), 49.2 (NCH_2), 33.5, 31.7, 29.6, 29.0, 28.9, 28.8, 28.5, 25.8, 24.7 (10 × CH_2), 19.0 (CH_2CH_3), 12.3 (CH_3).

3.4 General procedure for metathesis exchange of chloride by TFSI anion

A synthesized chloride imidazolium salts were submitted to a metathesis exchange in order to replace chloride by TFSI anion. To a mixture of chloride imidazolium in acetonitrile, was added 1.2eq of LiTFSI. After stirring at room temperature for 2.5h, the solvent was removed under reduced pressure. The reaction mixture was filtered after addition of dichloromethane. Pure TFSI-based ILs were obtained as a liquid after removal of the solvent under reduced pressure.

4. Synthesis of hybrid materials and associated composite electrolytes

4.1 Synthesis of spherical silica nanoparticles

A solution of absolute ethanol (500 mL) was mixed with ammonia solution (30 wt%, 38 mL, 0.29 mol) and stirred for 1 h at 80 °C.[4,5] A solution of TEOS (15 mL, 67.25 mmol) was added dropwise and stirred for 12 h. The silica nanoparticles were recovered by centrifugation (8000 rpm) and washed several times with absolute ethanol and distilled water. The inorganic nanoparticles are calcined at 500 °C for 6 h (heating rate 5 °C/min) to remove residual solvents and organic species on the silica surface. After cooling to room temperature, the silica nanoparticles are hydrated in a concentrated HCl solution (37%) at 100 °C for 12 h. The silica is then washed with water by centrifugation to pH 6-7 and finally dried under vacuum at 100 °C before use. Specific surface area of 136 m^2/g was determined using N_2-Adsorption/desorption isotherms.

4.2 Grafting procedure for coordinative anchoring (using carboxylic acid)

Hybrid materials were prepared under air condition at room temperature. 1-butyl-3-(carboxyundecyl)imidazolium bis(trifluoromethylsulfonyl)imide (1.16 mmol) was dissolved in 40 mL of acetone. To this solution was added 1 g of metal oxide (ZrO_2 or Al_2O_3 nanoparticles) and the suspension was stirred for 40 h. Hybrid materials were recovered through centrifugation (20 min at 10000 rpm, room temperature), washed several times with acetone and finally dried under vacuum overnight at 70 °C.

4.3. Grafting procedure for covalent anchoring (using silane)

Synthesized Silane (0.10-0.70 mmol) was added to a suspension of 1.0 g of SiO_2 or ZrO_2 nanoparticles and 0.38 mmol of triethylamine in 60 mL dry toluene. The solution was stirred at 90 °C for 72 h under argon. The modified SiO_2 or ZrO_2 nanoparticles were recovered by centrifugation (10 min at 10000 rpm, 10 °C), and washed with pure toluene (3 x 35 mL), and then with ethanol (3 x 35 mL).

4.4 Preparation of composite electrolyte

Depending on the LiTFSI weight percentage desired in the final electrolyte, a precise amount of LiTFSI was added to the synthesized hybrid material (1 g) in 20 mL ethanol and a uniform phase was obtained after sonification step. Solvent was then removed through stirring and evaporation during one night at 70 °C. The obtained powder was dried overnight in a vacuum oven at 110 °C before being stored in an argon-filled glove box to avoid any water presence.

5. Characterization of hybrid materials

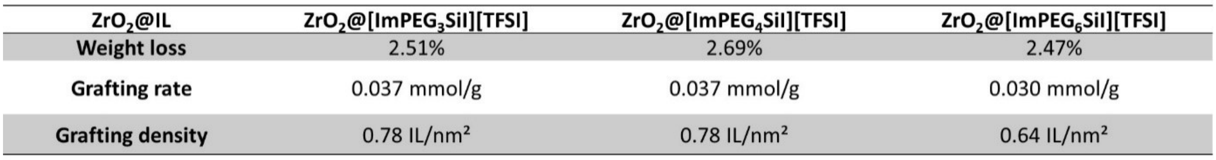
Table S1. Grafing rate and density determined using thermal analysis for SiO_2@[ImC$_{11}$Sil][TFSI] and SiO_2@[ImC$_3$Sil][TFSI].

SiO_2@IL	SiO_2@[ImC$_3$Sil] [TFSI]	SiO_2@[ImC$_{11}$Sil] [TFSI]
1st max. DTG	93°C	108°C
2nd max. DTG	451°C	455°C
Weight loss	17.4%	24.5%
Grafting rate	0.315 mmol/g	0.369 mmol/g
Grafting density	1.4 IL/nm^2	1.6 IL/nm^2

Table S2. Grafting rate and density for ZrO_2@[ImC$_n$Sil][TFSI] with different initial IL content estimated using TGA analysis.

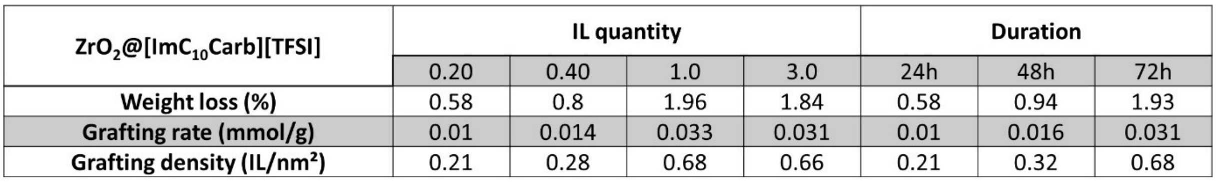
ZrO_2@IL	ZrO_2@[ImC$_3$Sil] [TFSI]			ZrO_2@[ImC$_{11}$Sil] [TFSI]	
IL (mmol)	0.10	0.40	0.70	0.10	0.20
Weight loss (%)	1.76	7.92	9.40	1.96	4.97
Grafting rate (mmol/g)	0.032	0.143	0.170	0.030	0.075
Grafting density (IL/nm^2)	0.68	3.0	3.6	0.64	1.6

Table S3. Grafting rate and density for ZrO_2@[Im(PEG)*n*Sil][TFSI] with *n* = 3, 4, 6 estimated using TGA analysis.



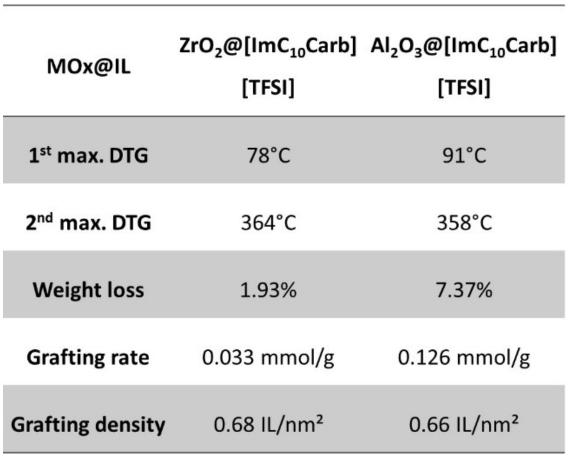
ZrO_2@IL	ZrO_2@[ImPEG$_3$Sil][TFSI]	ZrO_2@[ImPEG$_4$Sil][TFSI]	ZrO_2@[ImPEG$_6$Sil][TFSI]
Weight loss	2.51%	2.69%	2.47%
Grafting rate	0.037 mmol/g	0.037 mmol/g	0.030 mmol/g
Grafting density	0.78 IL/nm²	0.78 IL/nm²	0.64 IL/nm²

Table S4. Evolution of the grafting rate and density for ZrO_2@[ImC$_{10}$Carb][TFSI] as a function of initial IL quantity and synthesis duration time estimated using TGA analysis.



ZrO_2@[ImC$_{10}$Carb][TFSI]	IL quantity				Duration		
	0.20	0.40	1.0	3.0	24h	48h	72h
Weight loss (%)	0.58	0.8	1.96	1.84	0.58	0.94	1.93
Grafting rate (mmol/g)	0.01	0.014	0.033	0.031	0.01	0.016	0.031
Grafting density (IL/nm²)	0.21	0.28	0.68	0.66	0.21	0.32	0.68

Table S5. Grafting rate and density for ZrO_2@[ImC$_{10}$Carb][TFSI] and Al_2O_3@[ImC$_{10}$Carb][TFSI] estimated using TGA analysis.



MOx@IL	ZrO_2@[ImC$_{10}$Carb] [TFSI]	Al_2O_3@[ImC$_{10}$Carb] [TFSI]
1st max. DTG	78°C	91°C
2nd max. DTG	364°C	358°C
Weight loss	1.93%	7.37%
Grafting rate	0.033 mmol/g	0.126 mmol/g
Grafting density	0.68 IL/nm²	0.66 IL/nm²

Table S6. Correlating grafting rate and density with conductivity.

Material	**Grafting rate (mmol/g)**	**Specific surface area (m²/g)**	**Grafting density (molecule/nm²)**	**Conductivity @ 20°C (S/cm)**
SiO_2@[ImC$_{11}$Sil][TFSI]	0.110	136	0.54	$1.19.10^{-5}$

	mmol/g			
ZrO_2@[ImC$_{11}$Sil][TFSI]	0.075	28	1.54	$1.37.10^{-6}$
ZrO_2@[ImC$_{11}$Carb][TFSI]	0.033	28	0.68	$1.3.10^{-6}$
Al_2O_3@[ImC$_{11}$Carb][TFSI]	0.126	115	0.66	$6.6.10^{-7}$

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