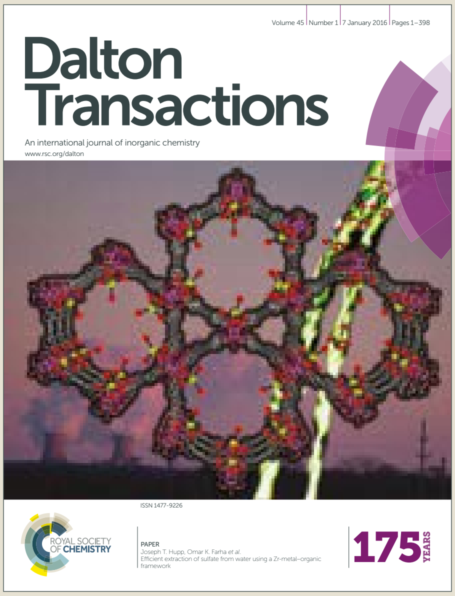
Dalton Transactions

This article can be cited before page numbers have been issued, to do this please use: A. Venker, T. Vollgraff and J. Sundermeyer, *Dalton Trans.*, 2017, DOI: 10.1039/C7DT04139J.



View Article Online
DOI: 10.1039/C7DT04139J

Journal Name

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ferrocenyl-Sulfonium Ionic Liquids - Synthesis, Characterization and Electrochemistry

Alexander Venker,[a] Tobias Vollgraff, [a] Jörg Sundermeyer*[a]

New ferrocenylsulfonium cation based ionic liquids were prepared by direct alkylation of corresponding ferrocenyl-based thioethers with N-alkylbis(trifluoromethanesulfonyl)imides (R'TFSI). This convenient direct access to organometallic sulfonium bis(trifluoromethanesulfonyl)imide (TFSI) salts without need for ion exchange was chosen in order to get highly pure and reversibly redox active room temperature ILs in many cases. In other cases anion cation interaction in the solid state was studied by XRD analyses. Moreover a diferrocenylmethylsulfonium tetrafluoroborate with two redoxactive centers was synthesized. The redoxchemistry of these sulfonium salts was investigated via cyclic voltammetry. Furthermore, UV-Vis spectra and thermoanalytical data are discussed. The electron-withdrawing sulfonium group is directly bonded to the ferrocenyl unit, therefore this cationic group influences the potential of these ionic liquids in a more pronounced way than being anchored to the ferrocenyl unit via an organic spacer. With their low absorbance in the visible light and reversible, tunable redox potential, these room temperature ILs open perspectives as redox mediators in dye sensetized solar cells (DSSCs), as redox electrolytes in supercapacitors or as overcharge protection additives in batteries.

Introduction

In recent years a number of ferrocene-based ionic liquids were reported. The synthetically most simple way to combine the robust, fully reversible organometallic redox group, ferrocene, with the functionality of an ionic liquid or salt is to anchor the ferrocenyl substituent via an organic linker to an anion[1,2] or more often to a cation.[3–10] Spacer-free ionic liquids where the anion[11] or cation[4,10] is directly bonded to the ferrocenyl redox unit are much less investigated. Recently we reported a number of such ferrocenylphosphonium ILs.[4] Their potential could be tuned in a broad range due to direct influence of differently substituted electron withdrawing phosphonium substituents [FcPR'R$_2$]TFSI to the redox center. In this context, we became interested in corresponding ferrocenylsulfonium ILs [FcSR'R]TFSI. In contrast to literature known ferrocenyl-based ionic liquids, these ILs do not contain linker groups such as keto or ester functionalities between the ionic tag and the ferrocenyl group, which are not stable under very reductive conditions or alkyl spacers which are prone to be oxidized and cleaved with loss of stabilized cation [FcCHR]$^+$.

Fundamental and application oriented studies on ferrocene based ILs include mass transport and electrochemical properties[12,13] as well as the modification of platinum electrode surfaces.[14] Furthermore ferrocene based ionic liquids were tested for their application as redox active species in electrolytes for lithium ion batteries[13,15] or as redox-active electrolyte supercapacitors.[16] Recently, a ferrocene viologen linked ionic liquid was published as an electrochromic material[17] which could be interesting for its application in optical sensors or electronic displays. Free ferrocenium ion based ionic liquids were prepared due to their interesting magnetic properties.[18]

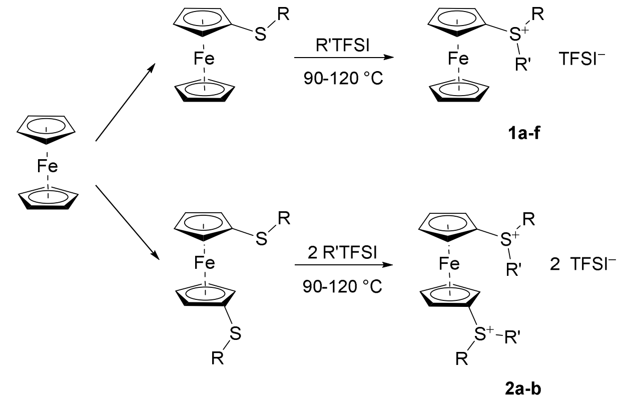
While trialkylsulfonium dicyanamides, bis(fluorosulfonyl)imides and TFSI salts are described as ionic liquids with low melting points and low viscosity,[19–21] ferrocenyl substituted sulfonium ILs have not yet been thoroughly investigated with respect to their thermal and electrochemical ILs properties. Early reports of Knox et al. describe ferrocenyldimethylsulfonium iodide, which is only stable in solid state. Attempts to recrystallize this salt lead to dealkylation of the cation.[22] The critical role of nucleophilic iodide was recognized and a thermally more stable ferrocenyldimethylsulfonium salt involving a methyl sulfate counter anion was published later.[23] Finally, a ferrocene with two dimethylsulfonium substituents, one at each ring, has been described as tetrachloroferrate(II) salt, however, it could not be recrystallized due to its instability in solution.[24] Its synthesis involved the reaction of dimethylsulfonium cyclopentadienylide with FeCl$_2$. Deprotonation of such ferrocenyl sulfonium salts generates S-ylides that were used for stereoselective syntheses of epoxides from carbonyl compounds.[25,26]

---

[a] A. Venker, Tobias Vollgraff, Prof. Dr. J. Sundermeyer
Fachbereich Chemie und Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg
Hans-Meerwein-Str. 4, 35043 Marburg, Germany
E-mail: JSU@staff.uni-marburg.de.

Electronic Supplementary Information (ESI) available: [Crystallographic data and refinement details, NMR spectra of the isolated compounds]. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C7DT04139J



Scheme 1. Alkylation of ferrocenyl thioethers with N-methyl- and N-n-butylbis(trifluoromethansulfonyl)imide. For **1**: R′ = Me, R = Me (**a**), n-Bu (**b**), Ph (**c**), Fc (**d**); R′ = n-Bu, R = n-Bu (**e**), Ph (**f**). For **2**: R′ = Me, R = Me (**a**), n-Bu (**b**).

Herein we present the preparation of comparatively stable ferrocenylsulfonium based ionic liquids containing S-alkyl and S-phenyl substituents and a TFSI anion. Their synthesis is accomplished by simple alkylation of mono- and bisferrocenyl substituted sulfides with N-alkylbis(trifluoromethane-sulfonyl)imides. Their redox potentials, absorption spectra and thermal stabilities are discussed.

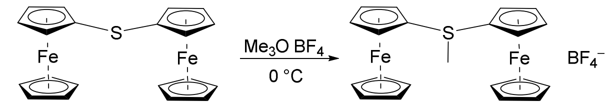
Results and discussion

Preparation of Redoxactive Sulfonium Ionic Liquids.

Due of the instability of the ferrocenyldimethylsulfonium iodide,[22] we followed a synthetic strategy avoiding any anion exchange and any electrochemically active water or halide impurities in the IL product. The advantage of using N-methyl- and N-n-butylbis(trifluoromethanesulfonyl)imide as alkylating agent has been laid out by our recent report on ferrocenylphosphonium ILs with non-nucleophilic TFSI counter ions.[4]

The alkyl ferrocenyl sulfides were prepared via a slightly modified procedure originally described by Minière et al..[25] A monolithoferrocene solution obtained by lithiation of ferrocene with *tert*-butyllithium and potassium *tert*-butanolate at −78 °C in THF[27] was treated with dimethyl disulfide. After separation of ionic thiolates, ferrocenyl methyl sulfide can be isolated by distillation in yields up to 77% at higher reaction scales. The preparation of di(butylthio)ferrocene was carried out by the reaction of dilithioferrocene · TMEDA and dibutyl disulfide.

The subsequent alkylation of the precursor molecules was performed without any solvent applying an excess of alkylbis(trifluoromethanesulfonyl)imide R'TFSI at 90-120 °C (Scheme 1). After decoloration with charcoal in acetonitrile, the products can be isolated by evaporation of all volatiles at high vacuum. Compounds **1a, b, d** were obtained as orange to brown-yellow oils, while **1c** crystallized at rt after a certain time. Compounds **2a** and **b** were received as yellow to red-brown solids. For compounds with three different substituents at the sulfur atom, the racemic mixture was obtained. Butylation of ferrocenyl methyl sulfide surprisingly yielded a product mixture of dimethylsulfonium derivative **1a**, expected n-butylmethylsulfonium derivative **1b** and di-n-butylsulfonium compound **1c**. That means, product **1b** acted as methyl transfer reagent towards ferrocenyl methyl sulfide starting material. **1a** was also a side product in the synthesis of **1d** by reaction of Fc-S-Fc with Me-TFSI. According to ^{1}H NMR spectroscopy **1d** is contaminated by 2-3% of **1a**. Therefore, the high purity BF_4^- analogue of **1d**, complex **3** was prepared by methylation of Fc-S-Fc by more reactive trimethyloxonium tetrafluoroborate Meerwein salt in dichloromethane (Scheme 2). **3** was crystallized in form of orange needles containing one equivalent of acetonitrile.



3

Scheme 2. Methylation of diferrocenyl sulfide with trimethyloxonium tetrafluoroborate in dichloromethane.

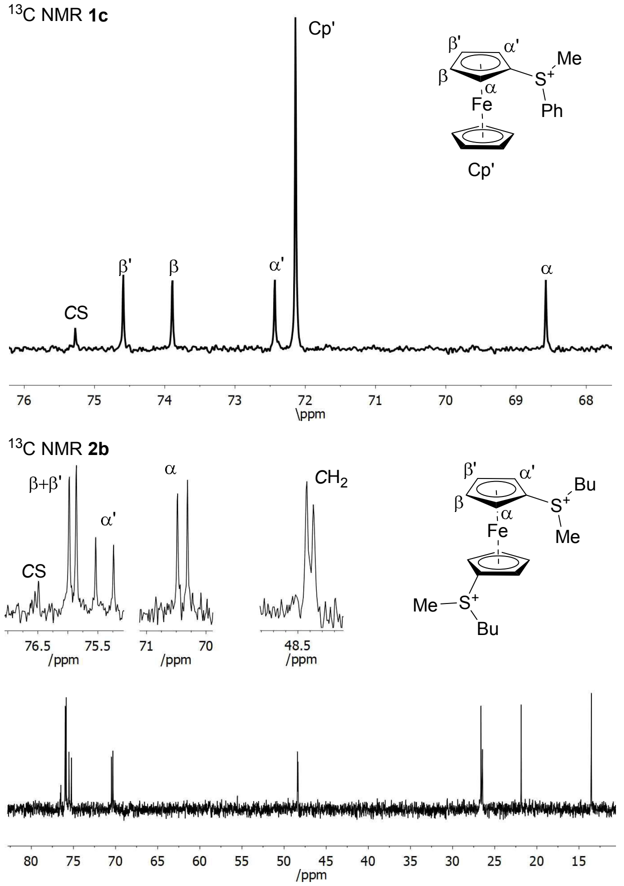


Figure 1. ^{13}C NMR (75.5 MHz, CD_3CN) spectra of ferrocenylmethylphenylsulfonium TFSI **1c** (top); α- and β-carbon signals split in the NMR spectra because of different substituents bonded to the sulfur atom. ^{13}C NMR (75.5 MHz, CD_3CN) spectra of 1,1'-bis(butylmethylsulfonium)ferrocene 2 TFSI **2b** (bottom); two pairs of stereoisomers, the *R,R* and *S,S* pair of enantiomers as well as the *R,S meso* compounds are formed.

View Article Online
DOI: 10.1039/C7DT04139J

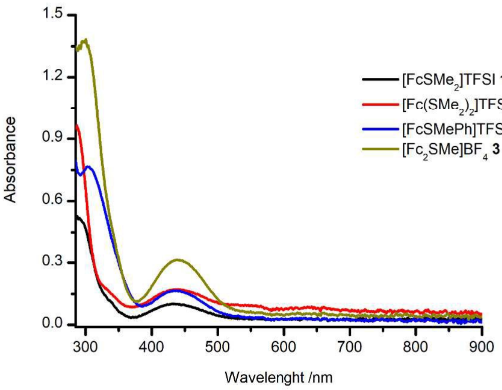


Figure 2. UV-Vis spectra of compounds **1a, 1c, 2a** and **3** in acetonitrile (c ≈ 0.5 mmol L^{-1}) at room temperature between 280 nm and 900 nm.

NMR Spectroscopy.

As anticipated alkylation of ferrocenyl sulfides leads to a down field shift of ^{1}H and ^{13}C signals in comparison to ferrocenyl thioether starting materials. An electron withdrawing sulfonium group is formed, their positive charge leads to a deshielding effect similar to corresponding phosphonium salts.[4] Similar trends of downfield shifts have been observed for ferrocenyl phenyl sulfide, -sulfoxide and -sulfone.[28]

Ionic liquids with three different substituents at pyramidal sulfur reveal a center of chirality. As a consequence a characteristic splitting of the Cp_α and Cp_β signals is observed in ^{1}H and ^{13}C NMR spectra. The ^{13}C NMR spectrum of **1c** is shown in Figure 1.

For 1,1'-bis(butylmethylsulfonium)ferrocene **2b** two pairs of diastereomers can be detected via NMR spectroscopy in an about 1:1 ratio. One set of signals belong to the *R,R* and *S,S* enantiomers. The other set is caused by the *R,S meso* compounds (Figure 1, bottom).

Table 1. Wavelength of maximal absorption of new ionic ferrocenylsulfonium ionic liquids and the corresponding molar absorption coefficient, measured in acetonitrile.

Compound	Wavelength of maximal absorption /nm	molar absorption coefficient /l mol^{-1} cm^{-1}
$[FcSMe_2]TFSI$ **1a**	431	177(2)
[FcSBuMe]TFSI **1b**	435	175(4)
[FcSMePh]TFSI **1c**	437	303(1)
$[FcSBu_2]TFSI$ **1e**	435	191(6)
[FcSBuPh]TFSI **1f**	434	305(5)
$[Fc(SMe_2)_2]TFSI_2$ **2a**	439	305(44)
$[Fc(SBuMe)_2]TFSI_2$ **2b**	424	319(5)
$[Fc_2SMe]BF_4$ **3**	439	549(4)

UV-Vis Spectra of Ferrocenyl-Sulfonium Ionic Liquids.

For the application as redox mediator in DSSCs, ionic liquids should show low absorbance of the terrestrial solar radiation - in contrast to the iodide/triiodide redox couple, they should not compete with the desired absorption of the dye. In order to evaluate their absorptivity UV-Vis spectra of the prepared compounds **1a, b, c, e, f, 2a, b** and **3** were recorded in acetonitrile. Representative spectra of **1a, c, 2a** and **3** in the range of 280 nm to 900 nm are shown in Figure 2. All compounds reveal a rather weak absorption at about 435 nm, which is responsible for their pale yellow solutions. Values for the absorption maximum for the local maximum and the corresponding molar absorption coefficient are listed in Table 1. The extinction coefficients of dialkyl substituted sulfonium ions are about 180 L mol^{-1} cm^{-1}. Compared to ferrocene (ε = 87 L mol^{-1} cm^{-1} in ethanol at 440 nm)[29], the absorption of the local maximum is higher, but weaker compared to ferrocenylmethyldiphenylphosphonium TFSI (ε = 241 L mol^{-1} cm^{-1} in dichloromethane at 447 nm).[4] Phenyl substituted and dicationic ferrocenylsulfonium ionic liquids have higher molar absorption coefficients of about ε = 305 L mol^{-1} cm^{-1}. Bisferrocenylmethylsulfonium tetrafluoroborate **3** shows the highest absorption coefficient with ε = 549(4) L mol^{-1} cm^{-1} caused by the second chromophoric ferrocene unit. All investigated compounds have high extinction coefficients in the range of 360 nm to 280 nm and lower wavelengths. Compound **1c** shows a second maximum absorption at 303 nm (ε = 1412(20) L mol^{-1} cm^{-1}). For compounds **1f** and **3** these absorbance maxima are indicated by shoulders. All prepared ionic compounds show much lower absorbance compared to the well-established $3I^-/I_3^-$ redox system, which is often used for DSSC. For $[Me_4N]I_3$ a molar absorption coefficient of ε = 25500 L mol^{-1} cm^{-1} at 360 nm in acetonitrile was determined.[30]

Table 2. Phase transitions, decomposition temperatures and equilibrium potentials of ferrocenylsulfonium compounds. Melting temperatures (T_m) were detected optical[a] or via differential scanning calorimetry[b] (DSC, heating rate: 10 K min^{-1}, values given as onset temperature). Decomposition temperatures (T_d) were measured via thermogravimetric analysis (TGA) and determined as 3% weight loss. Half-wave potentials ($E_{1/2}$, Fe^{2+}/Fe^{3+}) were recorded in [EMIM]TFSI at 10 mV s^{-1} against ferrocene/ferrocenium with an Ag/AgTFSI reference electrode. [c] measured at 50 mV s^{-1} because of better peak separation.

Compound	T_m (T_g) / °C	T_d / °C	$E_{1/2}$ / mV *vs.* Fc/Fc^+
$[FcSMe_2]TFSI$ **1a**	(–44.6)[b]	237	530
[FcSBuMe]TFSI **1b**			531
[FcSMePh]TFSI **1c**	55.1[a]		548
$[FcSBu_2]TFSI$ **1e**			525
[FcSBuPh]TFSI **1f**			538
$[Fc(SMe_2)_2]TFSI_2$ **2a**	83.7[a]	206	1001
$[Fc(SBuMe)_2]TFSI_2$ **2b**	93.0[b]	215	1005
$[Fc_2SMe]BF_4$ **3**	130.7[a]	234	499[c] 667[c]

View Article Online
DOI: 10.1039/C7DT04139J

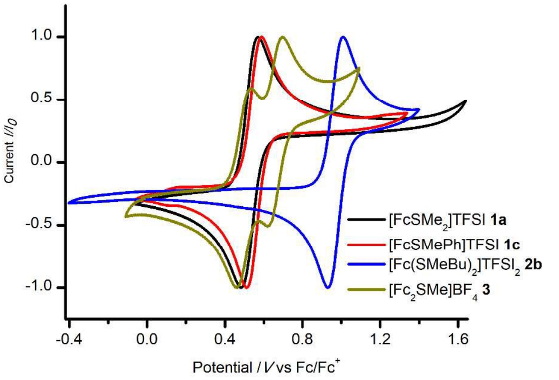


Figure 3. Cyclic voltammetry scans of selected new ferrocenylsulfonium compounds plotted against Fc/Fc$^+$. The measurements were performed in [EMIM]TFSI with an Ag/AgTFSI reference electrode with a scan rate of 10 mV s^{-1} for compounds **1a**, **1c**, **2b**. In case of compound **3** a scan rate of 50 mV s^{-1} was chosen because of better peak separation.

Thermal Analysis of Ferrocenyl-Sulfonium Ionic Liquids.

The solid compounds **1c**, **2a**, **2b** and **3** as well as the oil **1a** were investigated regarding their melting and decomposition temperatures (T_m and T_d, respectively). Measured temperatures are listed in Table 2. All ionic compounds are stable up to temperatures of about 200 °C. The dicationic salts bis(dimethylsulfonium)ferrocene **2a** and bis(butylmethylsulfonium)ferrocene **2b** reveal higher melting points of 83.7 and 93.0 °C, nevertheless they can be regarded as ionic liquids with unusually low lattice energy. Only for diferrocenylmethylsulfonium tetrafluoroborate **3** a melting point of 130.7 °C, higher than the formal 100 °C limit for ILs, is observed. The TFSI salts **1a, 1b, 1e** and **1f** are obtained as oils. For **1a** as a representative example, differential scanning calorimetry was performed, but no melting point could be observed due to the formation of a supercooled glass.

Cyclic Voltammetry of Ferrocenyl-Sulfonium Salts.

It is known, that electron withdrawing substituents cause a positive shift of the Fe^{II}/Fe^{III} ferrocene redox potential.[31] This behavior was also observed for the prepared ferrocene-based ionic liquids. In dependence of the ferrocene substituents, equilibrium potential of the compounds is shifted (Table 2, Figure 3).

The positive charge of the sulfonium group leads to a half-wave potential for [FcSMe$_2$]TFSI **1a** of 530 mV versus ferrocene/ferrocenium redox couple in electrochemically innocent 1-ethyl-3-methylimidazolium ([EMIM]) TFSI as solvent. Longer alkyl chains do not show a strong influence on the potential while a phenyl group leads to an additional shift of 18 mV for ferrocenylmethylphenylsulfonium TFSI **1c**. The incorporation of an additional sulfonium group affects an almost doubled raise of the potential up to 1.001 V for bis(dimethylsulfonium)ferrocene **2a** in comparison to the unsubstituted ferrocene. Compared to corresponding ferrocenylphosphonium ILs, the redox potential of sulfonium ILs is shifted by 56 mV to higher potentials, e.g. for [FcSMe$_2$]TFSI **1a** in comparison to [FcPMe$_3$]TFSI and 18 mV for [Fc(SMe$_2$)$_2$]TFSI$_2$ **2a** in comparison to [Fc(PMePh$_2$)$_2$]TFSI$_2$, despite of the phenyl substituents, respectively.[4]

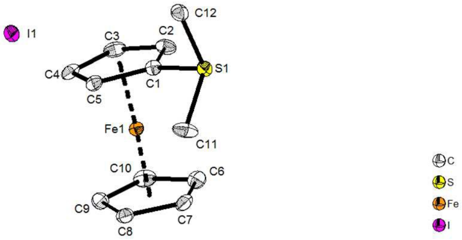


Figure 4. Molecular structure of **4**, hydrogen atoms omitted for clarity. Relevant bond distances per Å and angels per °: S1-C1: 1.754(2), S1-C11: 1.793(3), S1-C12: 1.796(2), C1-C2: 1.433(3), C2-C3: 1.413(3), C3-C4: 1.427(3), C4-C5, 1.413(3), C1-C5: 1.435(3), S1-C1-C2: 122.96(16), S1-C1-C5: 128.16(15), Fe1-Cp(SMe$_2$): 1.6642(3), Fe1-Cp': 1.6558(3).

For diferrocenylmethylsulfonium BF$_4$ **3** a second redox potential could be measured. The first one was detected at a lower potential compared to the other investigated sulfonium ionic liquids (499 mV), while the second one falls into the range of the mono- and the disubstituted ferrocenes (667 mV). For [FcSMe$_2$]TFSI **1a** the reductive stability was investigated in the neat IL. No decomposition of **1a** was noticed up to a reduction potential of −2.0 V versus ferrocene/ferrocenium. However, we observed, that some ferrocenylsulfonium compounds start to decompose to some extent while standing after CV measurement in the electrochemical cell over several hours. This decomposition was not observed in glass tubes and is probably induced by the large platinum surface of the 1000 µL microcell crucible and electrode.

Crystal Structures of Ferrocenyl-Sulfonium Salts.

For the first time it was possible to investigate two ferrocenylsulfonium compounds by X-ray crystallography. Crystals suitable for XRD of ferrocenyldimethylsulfonium iodide were obtained by the reaction of ferrocenyl methyl sulfide with an excess of neat iodomethane by slow cooling. The molecular structure is depicted in Figure 4. Ferrocenyldimethylsulfonium iodide **4** crystallizes in the space group $P2_1/c$ with four molecules per unit cell.[32] The bis(dimethylsulfonium)ferrocen cation was crystallized after an exchange of the TFSI anion by sodium tetraphenylborate from an acetonitrile/THF/diethyl ether mixture. The resulting bis(dimethylsulfonium)ferrocene ditetraphenylborate **5** crystallizes in the triclinic space group $P\overline{1}$ with one equivalent THF (Figure 5).[33] In both compounds a nearly eclipsed conformation of the Cp rings is found: The deviation from ideal conformation is 0.7° for monocationic **4** and 10.8° for dicationic **5**.

The sulfur atom of **4** reveals a pyramidal configuration. It is surrounded by one ferrocenyl unit and two methyl groups. In first approximation the non-bonding S-electron pair is coplanar to the cyclopentadienyl plain. For C1-S1 a distance of 1.754(2) Å is observed, whereas S1-C11 and S1-C12 are 1.793(3) Å and 1.796(2) Å, respectively. As expected, the S1-

View Article Online
DOI: 10.1039/C7DT04139J

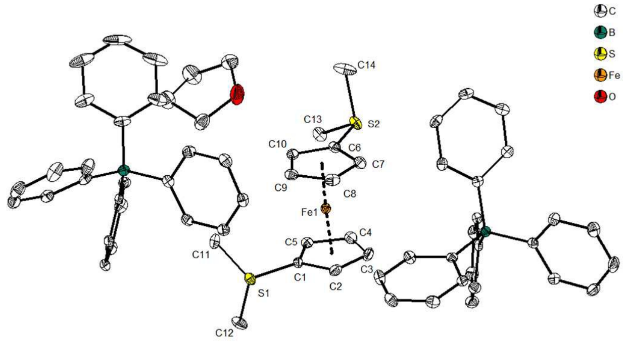


Figure 5. Molecular structure of **5**·THF, hydrogen atoms omitted for clarity. Relevant bond distances per Å and angels per °: S1-C1: 1.749(2), S1-C11: 1.790(2), S1-C12: 1.797(2), C1-C2: 1.433(3), C2-C3: 1.415(2), C3-C4: 1.422(3), C4-C5, 1.424(3), C1-C5: 1.431(2), S2-C6: 1.756(2), S2-C13: 1.788(2), S2-C14: 1.794(3); C6-C7: 1.436(3), C7-C8: 1.421(2), C8-C9: 1.425(3), C9-C10: 1.414(2), C10-C6: 1.426(3), S1-C1-C2: 122.02(11), S1-C1-C5: 128.49(11), S2-C6-C7: 122.64(12), S2-C6-C10: 128.01(11), Fe-Cp: 1.6522(3), 1.6504(3).

C1(sp^2) bond distance is a bit shorter than distances to methyl groups. Similar orientation of the sulfur lone pair and similar bond distances are detected for compound **5**, as well as for $[Cr(CpSMe_2)(CO)_3]$.[34] S1-C(sp^2) bond distances in the same range were observed in non-ionic ferrocenyl phenyl sulfide with 1.749(5) Å or bis(phenylthio)ferrocene with 1.753(2) Å;[35] S1–C(sp^2) of non-coordinated dimethylsulfonium cyclopentadienylide is slightly shorter: 1.712(8) Å.[36] A similar trend was observed for alkylferrocenylposphonium ions and ylids.[4] Within the S-functionalized ring of **4** the pair of distances C1-C2 (1.433(3) Å and C1-C5 (1.435(3) Å) adjacent to the onium substituent is slightly elongated in comparison to the pair C2-C3 (1.413(3) Å) and C4-C5 (1.413(3) Å) while C3-C4, most remote to the S-substituent, is 1.427(3) Å. In **5** the average C-C bond adjacent to S is 1.425 Å.

Conclusions

Several unprecedented ferrocenylsulfonium ionic liquids were prepared by an atom economic alkylation with alkyl bis(trifluoromethanesulfonyl)imides and release of the TFSI anion. This synthetic strategy requires relatively cheap starting materials and guarantees high purity ILs free from electroactive water, metal and halogen ion impurities even at large scales. Both, room temperature ILs as well as crystal structures of ferrocenylsulfonium salts, are presented and discussed.

The influence of the substituents at the sulfur atom on its electrochemical, thermal and absorption behavior was investigated. Due to the positive charge located at the sulfonium ion and its electron withdrawing effect, the potentials of the prepared ionic liquids are shifted by about 0.53 V (av.) to higher values versus ferrocene standard. The shift is more pronounced than in corresponding alkylphosphonium substituted ferrocenes. For 1,1'-disubstituted ferrocenes, this effect is almost doubled. With respect to this tunable potential, a low absorbance in the visible light, low melting points and enhanced thermal stabilities compared to state of the art ferrocenylsulfonium salts, this class of room temperature ionic liquids might be useful as redox mediators for DSSCs, as redox electrolytes in supercapacitors or as overcharge protection additives in batteries. In contrast to literature known ferrocenyl-based ionic liquids, the ILs described here do not contain linker groups such as keto or ester functionalities between the ionic tag and the ferrocenyl group, which are not stable under very reductive conditions or alkyl spacers, which are prone to be oxidized and cleaved with loss of stabilized cation $[FcCHR]^+$.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the Hessisches Graduiertenprogramm für wissenschaftlich-technologische Grundlagen der Elektromobilität – HGP-E for financial support.

Experimental Section

Methods and Devices.

All synthetic steps, expect of the extraction with water and column chromatography, were conducted using standard Schlenk techniques. Elemental analyses (C, N, H, S) were carried out by the service department for routine analysis and mass spectrometry with a vario MICRO cube (Elementar). The samples were weighted into tin capsules inside a nitrogen filled glove box. Melting points and decomposition temperatures were determined with a Büchi Melting Point B540, a METTLER TOLEDO TGA/DSC 3+ and a METTLER TOLEDO DSC 1, respectively. ^{1}H, proton decoupled ^{13}C and ^{19}F NMR spectra were recorded at 300 K in automation with a Bruker Avance III 300 spectrometer and were calibrated using residual proton and solvent signals (CD_3CN: δ_H 1.94 ppm, δ_C 1.32 ppm, C_6D_6: δ_H 7.16 ppm, δ_C 128.06 ppm; $CDCl_3$: δ_H 7.26 ppm, δ_C 77.16 ppm)[37] or externally against $CFCl_3$. IR spectra were recorded on a Bruker APLPHA FT-IR spectrometer with Platinum ATR-sampling (diamond single crystal). HR-ESI mass spectra were acquired with a LTQ-FT Ultra mass spectrometer (Thermo Fischer Scientific). The resolution was set to 100.000.

UV-Vis spectroscopy was performed with an Avantes AvaSpec-2048 photometer in a glovebox. The probes were dissolved in acetonitrile and measured at room temperature.

Cyclic voltammetry experiments were carried out with a RHD Instruments Microcell HC and a Metrohm Autolab PG Stat 204 in a nitrogen flushed glove box at 24.5 ± 0.7 °C. The ionic compounds were solved in [EMIM]TFSI (c = 3.6-11.7 mmol L^{-1}) and the resulting solutions were placed in a platinum crucible, which acted as counter electrode. As working electrode a platinum wire (ø = 0.25 mm) was used and as reference electrode a 100 mM Ag/AgTFSI in [EMIM]TFSI.[38] Both platinum electrodes were polished with Kemet diamond paste (0.25 µm)

View Article Online
DOI: 10.1039/C7DT04139J

prior use. The potentials were calibrated against ferrocene/ferrocenium by addition of small amounts of ferrocene to the solution or by measurement of a ferrocene solution in [EMIM]TFSI after measurement. All data were detected at a scan rate of 10 mV s^{-1} unless mentioned otherwise.

The data collection for the single crystal structure determinations was performed on a Bruker D8 QUEST diffractometer. Bruker software (APEX2, SAINT)[39] was used for data collection, cell refinement and data reduction. The structures were solved with SIR2014[40] refined with SHELXL-2014[41] and finally validated using PLATON[42] software, all within the WinGX[43] software bundle. Absorption corrections were applied beforehand within the APEX2 software (multi-scan).[44] Graphic representations were created using Diamond 4.[45] H-atoms were constrained to parent site. In all graphics the ellipsoids are shown for the 50% probability level. Crystallographic data for the structures reported in this paper are supplied as supporting information and have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1583349 and 1583350).

Starting Materials.

All solvents were dried according to common procedures[46] and passed through columns of aluminum oxide, 3 Å molecular sieve and R3-11G-catalyst (BASF) or stored over molecular sieve (3 or 4 Å) until use. n-Butyl- and methylbis(trifluoromethanesulfonyl)imides R'TFSI,[4,47] 1,1'-bis(methylthio)ferrocene,[25] phenyl ferrocenyl sulfide,[25] butyl ferrocenyl sulfide,[48] bis(phenylthio)ferrocene[25] and bromoferrocene[51] were synthesized according to literature procedures. For ferrocenyl methyl sulfide[25] and diferrocenyl sulfide[49] modified procedures are described. Literature known 1,1'-di(butylthio)ferrocene[50] was prepared by a method reported for 1,1'-bis(methylthio)ferrocene. Details for these starting materials are given in the supporting information.

X-Ray suitable crystals of ferrocenyldimethylsulfonium iodide were obtained by the synthesis according to Watts.[22]

Synthetic Procedures.

Preparation of dimethylferrocenylsulfonium bis(trifluoromethanesulfonyl)imide 1a. To 1.5 equivalents of Me-TFSI, 1.0 equivalents of ferrocenyl methyl sulfide were added and the resulting mixture was stirred for 18 h at 90 °C. The crude product was washed with 10 mL pentane and afterwards it was dissolved in 10 mL of acetonitrile. After addition of charcoal, the suspension was stirred for 1 h, filtered and the solvent was removed at 60 °C in vacuum (10^{-4} mbar). **1a** (81%) was obtained as yellow oil. Elem. anal. found C, 31.8; H, 2.8; N, 2.9: S 18.55: $C_{14}H_{15}F_6FeNO_4S_3$ (512.27 g mol^{-1}) requires C, 31.9; H, 2.9; N; 2.7; S, 18.2. **IR** (liquid film): $\tilde{\nu}$ /cm^{-1} = 3110 vw, 3029 vw, 2937 vw, 1415 w, 1346 s, 1327 m, 1225 w, 1176 vs, 1132 vs, 1107 w, 1050 vs, 998 m, 885 w, 825 m, 787 m, 762 w, 739 m, 653 w, 611 s, 599 s, 569 s, 504 s, 490 s, 442 m, 408 vw. **^{1}H NMR** (CD_3CN): δ = 3.03 (s, 6H, CH_3), 4.47 (s, 5H, C$H_{Cp'}$), 4.72 (t, 2H, $^3J_{HH}$ = 2.0 Hz, CH_β), 4.81 (t, 2H, $^3J_{HH}$ = 2.0 Hz, CH_α) ppm. **^{13}C NMR** (CD_3CN): δ = 31.0 (CH_3), 70.0 (C_α), 71.8 (Cp'), 73.6 (C_β), 75.1 (CS), 121.0 (q, $^1J_{CF}$ = 308.7 Hz, CF_3) ppm. **^{19}F NMR** (CD_3CN): δ = −81.0 ppm. **ESI-HRMS(+):** $m{\cdot}z^{-1}$ calculated for $C_{12}H_{15}FeS^+$: 247.0239, found: 247.0240. **ESI-HRMS(–):** $m{\cdot}z^{-1}$ calculated for $C_2F_6S_2O_4N^-$: 279.9178, found: 279.9178.

Preparation of butylferrocenylmethylsulfonium bis(trifluoromethanesulfonyl)imide 1b. The preparation was performed analogous to **1a** with 175 mg (0.638 mmol, 1.00 eq.) butyl ferrocenyl sulfide and 628 mg (2.13 mmol, 3.33 eq.) Me-TFSI and a reaction time of 44 h. 363 mg (0.621 mmol, 97%) **1b** were obtained as orange oil. Elem. anal. found C, 35.7; H, 3.7; N, 2.6; S, 17.0; $C_{17}H_{24}F_6FeNO_4S_3$ (569.38 g mol^{-1}) requires C, 35.9; H, 3.7; N, 2.5; S, 16.9. **IR** (liquid film): $\tilde{\nu}$ /cm^{-1} = 3112 w, 3032 vw, 2967 w, 2938 w, 2879, w, 1468 vw, 1416 w, 1347 s, 1329 m, 1226 w, 1176 vs, 1132 vs, 1107 w, 1050 vs, 1003 m, 982 w, 919 vw, 885 w, 828 m, 787 m, 762 w, 739 m, 653 w, 612 s, 599 s, 569 s, 507 s, 490 s, 460 w, 444 m, 408 vw. **^{1}H NMR** (CD_3CN): δ = 0.90 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH_2CH_3), 1.41 (qt, 2H, $^3J_{HH}$ = 7.4, 7.4 Hz, CH_2CH_3), 1.53-1.64 (m, 2H, $CH_2CH_2CH_3$), 3.12 (s, 3H, SCH_3), 3.17 (dt, 1H, $^2J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 7.2 Hz, SCH_2), 3.35 (dt, 1H, $^2J_{HH}$ = 12.5 Hz, $^3J_{HH}$ = 7.8 Hz, SCH_2'), 4.47 (s, 5H, C$H_{Cp'}$), 4.72-4.77 (m, 3H, C$H_{\alpha+\beta+\beta'}$), 4.82-4.83 (m, 1H, CH_α) ppm. **^{13}C NMR** ($CDCl_3$): δ = 13.5 (CH_2CH_3), 21.3 (CH_2CH_3), 26.2 ($CH_2CH_2CH_3$), 26.8 (SCH_3), 48.4 (SCH_2), 66.4 (C_α), 71.1 (Cp'), 71.8 (CS), 72.4 (C_α'), 72.9 (C_β), 73.2 (C_β'), 119.9 (vq, $^1J_{CF}$ = 323.6 Hz, CF_3)[52] ppm. **^{13}C NMR** (CD_3CN): δ = 13.6 (CH_2CH_3), 21.9 (CH_2CH_3), 26.7 ($CH_2CH_2CH_3$), 27.1 (SCH_3), 48.4 (SCH_2), 67.8 (C_α), 71.9 (Cp'), 73.1 (CS), 73.2 ($C_{\alpha'}$), 73.8 ($C_{\beta+\beta'}$), 121.0 (vq, $^1J_{CF}$ = 321.2 Hz, CF_3)[52] ppm. **^{19}F NMR** (CD_3CN): δ = −78.9 ppm. **ESI-HRMS(+):** $m{\cdot}z^{-1}$ calculated for $C_{15}H_{21}FeS^+$: 289.0709, found: 289.0708. **ESI-HRMS(–):** $m{\cdot}z^{-1}$ calculated for $C_2F_6S_2O_4N^-$: 279.9178, found: 279.9178.

Preparation of ferrocenylmethylphenylsulfonium bis(trifluoromethanesulfonyl)imide 1c. The preparation was performed analogous to **1a** with 212 mg (0.721 mmol 1.00 eqn.) ferrocenyl phenyl sulfide and 558 mg (1.89 mmol, 2.62 eq.) Me-TFSI. 283 mg (0.48 mmol, 67%) **1c** were obtained as yellow oil, which crystallized after a period of several months. **Mp:** 55.1 °C (1.0 K min^{-1}). Elem. anal. found C, 38.8; H, 2.8; N, 2.5; S, 16.9; $C_{19}H_{17}F_6FeNO_4S_3$ (589.37 g mol^{-1}) requires: C 38.7, H 2.9, N 2.4, S 16.3. **IR** (liquid film): $\tilde{\nu}$ /cm^{-1} = 3112 w, 3032 vw, 2942 vw, 1478 vw, 1447 w, 1414 w, 1347 s, 1328 s, 1226 w, 1175 vs, 1131 vs, 1108 w, 1049 vs, 1000 w, 976 m, 883 w, 835 m, 787 m, 748 m, 739 m, 713 vw, 684 m, 652 w, 610 s, 598 s, 569 s, 498 ssh, 477 s, 448 w, 433 m, 405 vw. **^{1}H NMR** ($CDCl_3$): δ = 3.49 (s, 3H, CH_3), 4.46 (s, 5H, C$H_{Cp'}$), 4,72 (br, 2H, CH_β), 4.78 (br, 1H, CH_α), 4.99 (br, 1H, CH_α), 7.62 (t, 2H, $^3J_{HH}$ = 7.4 Hz, H_{meta}), 7.68-7.74 (m, 3H, H_{ortho}, H_{para}) ppm. **^{1}H NMR** (CD_3CN): δ = 3.46 (s, 3H, CH_3), 4.44 (s, 5H, C$H_{Cp'}$), 4.75 (dt, 1H, $^3J_{HH}$ = 1.3, 2.6 Hz, CH_β), 4.79 (dt, 1H, $^3J_{HH}$ = 1.3, 2.7 Hz, CH_β), 4.81 (dt, 1H, $^3J_{HH}$ = 1.3, 2.6 Hz, CH_α), 4.96 (dt, 1H, $^3J_{HH}$ = 1.3, 2.6 Hz, CH_α), 7.62-7.68 (m, 2H, H_{meta}), 7.71-7.78 (m, 3H, H_{ortho},

View Article Online
DOI: 10.1039/C7DT04139J

H_{para}) ppm. **^{13}C NMR** (CD_3CN): δ = 30.9 (CH_3), 68.5 (Cp_α), 72.1 (Cp'), 72.4 ($Cp_{\alpha'}$), 73.9 (Cp_β), 74.6 ($Cp_{\beta'}$), 75.3 (CS), 121,0 (vq, $^1J_{CF}$ = 320.9 Hz, CF_3),[52] 129.6 (C_{ipso}), 130.1 (C_{meta}), 131.9 (C_{ortho}), 135.2 (C_{para}) ppm. **^{19}F NMR** (CD_3CN): δ = –80.1 ppm. **ESI-HRMS**(+): $m{\cdot}z^{-1}$ calculated for $C_{17}H_{17}FeS^+$: 309.0395, found: 309.0395. **ESI-HRMS(–):** $m{\cdot}z^{-1}$ calculated for $C_2F_6S_2O_4N^-$: 279.9178, found: 279.9173.

Preparation of diferrocenylmethylsulfonium bis(trifluoromethanesulfonyl)imide 1d The preparation of **1d** was performed analogous to **1a** with 123 mg (0.306 mmol 1.00 eq.) diferrocenyl sulfide and 286 mg (0.969 mmol, 3.17 eq.) Me-TFSI and a reaction time of 3 d. 142 mg (0.204 mmol, 67%) **1d** were obtained as dark orange oil. Elem. anal. found C, 39.2; H, 3.0; N, 2.1; S, 14.1; $C_{23}H_{21}F_6Fe_2NO_4S_3$ (697.29 g mol^{-1}) requires C, 39.6; H, 3.0; N, 2.0; S, 13.8. **IR** (liquid film): $\tilde{\nu}$ /cm^{-1} = 3109 w, 2942 vw, 1414 w, 1394 vw, 1347 s, 1329 s, 1225 w, 1176 vs, 1132 vs, 1107 w, 1049 vs, 1004 w, 972 m, 881 w, 827s, 787 m, 761 w, 738 m, 652 m, 612 s, 598 s, 568 s, 506 s, 487 s, 447 s, 404 vw. **^{1}H NMR** (CD_3CN): δ = 3.39 (s, 3H, CH_3), 4.40 (s, 10H, Cp'), 4.69-4.73 (m, 4H, $CH_{\beta+\beta'}$), 4.74 (dt, 2H, J_{HH} = 1.3, J_{HH} = 2.6 Hz, CH_α), 4.82 (dt, 2H, J_{HH} = 1.2, J_{HH} = 2.5 Hz, CH_α) ppm. **^{13}C NMR** (CD_3CN): δ /ppm = 32.5 (CH_3), 68.6 (Cp_α), 71.5 (Cp_α), 71.9 (Cp'), 73.5 (Cp_β), 73.5 (Cp_β), 78.6(CS), 121.1 (vq, $^1J_{CF}$ = 321.5 Hz, CF_3)[52] ppm. **^{19}F NMR** (CD_3CN): δ = –79.5 ppm. **ESI-HRMS**(+): $m{\cdot}z^{-1}$ calculated for $C_{21}H_{21}Fe_2S$: 417.0058, found: 417.0048. **ESI-HRMS**(–): $m{\cdot}z^{-1}$ calculated for $C_2F_6NO_4S_2^-$: 279.9178, found: 279.9173.

Preparation of dibutylferrocenylsulfonium bis(trifluoromethanesulfonyl)imide 1e The preparation of **1e** was performed analogous to **1a** with 158 mg (0.577 mmol 1.00 eqn.) butyl ferrocenyl sulfide and 448 mg (1.33 mmol, 2.30 eqn.) nBu-TFSI and a reaction time of 44 h. 328 mg (0.536 mmol, 93%) **1e** were obtained as yellow orange oil. Elem. anal. found C, 38.8; H, 4.4; N, 2.5; S, 16.1; $C_{20}H_{27}F_6FeNO_4S_3$ (611.46 g mol^{-1}) requires C, 39.3; H, 4.45; N, 2.3; S, 15.7. **IR** (liquid film): $\tilde{\nu}$ /cm^{-1} = 3109 vw, 2966 w, 2937 w, 2878 vw, 1467 w, 1415 w, 1346 s, 1329 m, 1225 w, 1177 vs, 1133 vs, 1108 w, 1051 vs, 1005 w, 920 vw, 885 vw, 835 m, 787 m, 761 w, 738 m, 652 m, 613 s, 599 s, 569 s, 508 ssh, 461 w, 443 vw, 405 vw. **^{1}H NMR** (CD_3CN): δ = 0.95 (t, 6H, $^3J_{HH}$ = 7.3 Hz, CH_3), 1.48 (tq, 4H, $^3J_{HH}$ = 7.4, 7.4 Hz, CH_2CH_3), 1.64-1.75 (m, 4H, $CH_2CH_2CH_3$), 3.30 (dt, 2H, $^2J_{HH}$ =12.9 Hz, $^3J_{HH}$ = 7.8 Hz, SCH_2), 3.47 (dt, 2H, $^3J_{HH}$ = 7.6 Hz, $^2J_{HH}$ = 12.9 Hz, SCH_2'), 4.46 (s, 5H, Cp'), 4.74 (s br, 4H, $Cp_{\alpha+\beta}$) ppm. **^{13}C NMR** (CD_3CN): δ = 13.6 (CH_3), 22.1 (CH_2CH_3), 27.0 ($CH_2CH_2CH_3$), 45.0 (SCH_2), 70.7 ($Cp_{\alpha\text{ or }\beta}$), 71.9 (Cp'), 72.8 (CS), 73.7 ($Cp_{\alpha\text{ or }\beta}$), 121.0 (vq, $^1J_{CF}$ = 320.0 Hz, CF_3)[52] ppm. **^{19}F NMR** (CD_3CN): δ = –80.2 ppm. **ESI-HRMS(+):** $m{\cdot}z^{-1}$ calculated for $C_{18}H_{27}FeS^+$: 331.1178, found: 331.1171. **ESI-HRMS(–):** $m{\cdot}z^{-1}$ calculated for $C_2F_6NO_4S_2^-$: 279.9178, found: 279.9174.

Preparation of butylferrocenylphenylsulfonium bis(trifluoromethanesulfonyl)imide 1f. The preparation of **1f** was performed analogous to **1a** with 225 mg (0.765 mmol 1.00 eq.) ferrocenyl phenyl sulfide and 472 mg (1.40 mmol, 1.83 eq.) nBu-TFSI. 150 mg (0.238 mmol, 31%) **1f** were obtained as yellow orange oil. Elem. anal. found C, 41.0; H, 3.6; N, 2.7; S, 15.4; $C_{22}H_{23}F_6FeNO_4S_3$ (631.45 g mol^{-1}) requires C, 41.85; H 3.7; N, 2.2; S, 15.2. **IR** (liquid film): $\tilde{\nu}$ /cm^{-1} = 3112 vw (CH), 2965 w (CH), 2937 vw (CH), 2878 vw (CH), 1467 vw, 1447 w, 1416 vw, 1347 s, 1329 m, 1226 m, 1176 vs, 1132 s, 1108 w, 1050 s, 1022 w, 1000 w, 922 vw, 883 vw, 833 m, 787 m, 750 w, 739 m, 686 m, 652 w, 611 s, 598, s, 569 s, 499 m, 480 m, 433 vw, 405 vw. **^{1}H NMR** (CD_3CN): δ = 0.91 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH_3), 1.44-1.60 (m, 2H, CH_2CH_3), 1.64-1.72 (m, 2H, $CH_2CH_2CH_3$), 3.74-3.83 (m, 2H, SCH_2), 4.30 (s, 5H, Cp'), 4.72-4.75 (m, 2H, $CH_{\alpha Ph+\beta Ph}$), 4.77 (dt, 1H, $^3J_{HH}$ = 1.3, 2.6 Hz, $CH_{\beta Bu}$), 4.97 (dt, 1H, $^3J_{HH}$ = 1.2, 2.6 Hz, $CH_{\alpha Bu}$), 7.72 (t, 2H, $^3J_{HH}$ = 7.9, H_{ortho}), 7.82 (tt, 1H, $^3J_{HH}$ = 7.5, $^5J_{HH}$ = 1.2, H_{para}), 7.88 (dd, 2H, $^3J_{HH}$ = 8.4, $^5J_{HH}$ = 1.0, H_{meta}) ppm. **^{13}C NMR** (CD_3CN): δ = 13.6 (CH_3), 21.9 (CH_2CH_3), 27.4 ($CH_2CH_2CH_3$), 48.0 (SCH_2), 70.8 ($Cp_{\alpha Ph}$), 71.0 ($Cp_{\alpha Bu}$), 72.1 (Cp'), 73.6 ($Cp_{\beta Bu}$), 74.4 ($Cp_{\beta Ph}$), 75.0 (CS), 126.8 (C_{ipso}), 131.6 (C_{meta}), 132.1 (C_{ortho}), 135.8 (C_{para}) ppm.[53] **^{19}F NMR** (CD_3CN): δ = –80.2 ppm. **ESI-HRMS(+):** $m{\cdot}z^{-1}$ calculated for $C_{20}H_{23}FeS^+$: 351.0865, found: 351.0864. **ESI-HRMS(–):** $m{\cdot}z^{-1}$ calculated for $C_2F_6S_2O_4N^-$: 279.9178, found: 279.9173.

Preparation of diferrocenylmethylsulfonium tetrafluoroborate 3. 195 mg (0.485 mmol, 1.0 eq.) diferrocenyl sulfide were solved in 3 mL dichloromethane and the solution was cooled to 0°C. A solution of 73 mg (0.49 mmol, 1.0 eq.) trimethyloxonium tetrafluoroborate in 2 mL dichloromethane were added dropwise over 10 min. The solution was stirred for 18 h while it warmed up to room temperature. The solvent was removed in vacuum, the residue was solved in acetonitrile and the product was crystallized by layering with THF and diethyl ether. 85 mg (0.16 mmol, 32%) **3** containing one equivalent of acetonitrile were obtained as orange needles. **Mp:** 130.7 °C (2.0 K min^{-1}). **IR** (neat): $\tilde{\nu}$ /cm^{-1} = 3097 w, 3030 vw, 1413 m, 1390 w, 1368 vw, 1322 w, 1283 w, 1215 w, 1162 m, 1025 vssh, 974 w, 889 w, 829 ssh, 738 w, 638 vw, 487 vs, 447 vs. **^{1}H NMR** (CD_3CN): δ = 3.40 (s, 3H, CH_3), 4.40 (s, 10H, Cp'), 4.69-4.72 (m, 4H, $CH_{\beta+\beta'}$), 4.74-4.76 (m, CH_α), 4.82-4.84 (m, 2H, CH_α') ppm. **^{13}C NMR** (CD_3CN): δ = 32.4 (CH_3), 68.6 (Cp_α), 71.5 ($Cp_{\alpha'}$), 71.9 (Cp'), 73.5 (Cp_β), 73.5 ($Cp_{\beta'}$), 78.7 (CS) ppm. **^{19}F NMR** (CD_3CN): δ = –152.4 ppm. **ESI-HRMS**(+): $m{\cdot}z^{-1}$ calculated for $C_{20}H_{18}Fe_2S$: 417.0058, found: 417.0058.

Preparation of 1,1'-bis(dimethylsulfonium)ferrocene di{bis(trifluoromethanesulfonyl)imide} 2a. The preparation of **2a** was performed analogous to **1a** with 147 mg (0.529 mmol 1.00 eq.) 1,1'-di(methylthio)ferrocene and 569 mg (1.93 mmol, 3.65 eq.) Me-TFSI. 318 mg (0.366 mmol, 69%) **2a** were obtained as yellow orange solid. **Mp:** 83.7 °C (1.0 K min^{-1}). Elem. anal. found C, 24.9; H, 2.4; N, 3.25; S, 22.6; $C_{18}H_{20}F_{12}FeN_2O_8S_6$ (868.58 g mol^{-1}) requires C, 24.9, H 2.3, N 3.2, S 22.15. **IR** (neat): $\tilde{\nu}$ /cm^{-1} = 3117 w, 3033 w, 2943 vw, 1419 w, 1344 s, 1327 w, 1223 vw, 1172 vs, 1135 s, 1049 vs, 1000 m, 891 w, 871 w, 837 m, 790 m, 763 w, 740 m, 609 s, 569 s, 513 s, 438 vw, 409 vw. **^{1}H NMR** (CD_3CN): δ = 3.07 (s, 12H, CH_3), 4.98 (t, 4H, $^3J_{HH}$ = 2.0 Hz, CH_β), 5.09 (t, 4H, $^3J_{HH}$ = 2.0 Hz, CH_α) ppm. **^{13}C NMR** (CD_3CN): δ = 30.6 (CH_3), 72.5 (Cp_α), 75.7 (Cp_β), 78.3 (CS), 120,9 (vq, $^1J_{CF}$ = 322.2 Hz, CF_3)[52] ppm. **^{19}F NMR** (CD_3CN): δ = –80.7 ppm. **ESI-HRMS**(+): $m{\cdot}z^{-1}$

DOI: 10.1039/C7DT04139J

calculated for $C_{16}H_{20}F_6FeNO_4S_4^+$: 587.9524, found: 587.9523. **ESI-HRMS**(–): *m·z*$^{-1}$ calculated for $C_2F_6NO_4S_2^-$: 279.9178, found: 279.9172.

Preparation of 1,1'-bis(dimethylsulfonium)ferrocene di(tetraphenylborate) · THF 5.

353 mg (1.19 mmol, 3.25) Me-TFSI were added to 102 mg (0.367 mmol, 1.00 eq.) 1,1'-di(methylthio)ferrocene, and the solution was stirred for 18 h at 100 °C. After cooling, the mixture was washed with 10 mL pentane and dried in vacuum at 90 °C. The residual oil was dissolved in THF and 252 mg (0.734 mmol, 2.00 eq.) of sodium tetraphenylborate were added. The solution was stirred for 1 h. After removing the solvent in vacuum the residue was washed with 2 mL nitrogen saturated water and all volatile compounds were removed in vacuum. 72 mg (71 µmol, 19%) **5** were obtained as X-ray suitable crystals by crystallization from acetonitrile/ THF/diethyl ether. Elem. anal. found C, 77.15; H, 6.5; S, 6.9; $C_{66}H_{68}B_2FeOS_2$ (1018.84 g mol^{-1}) requires C, 77.8; H, 6.7; S, 6.3. **IR** (neat): $\tilde{\nu}$ /cm^{-1} = 3107 vw, 3078 vw, 3052 m, 3000 m, sh, 2916 vw, 1578 w, 1476 m, 1415 m, 1396 m, 1325 vw, 1303 vw, 1261 w, 1175 w, 1123 w, 1063 w, 1032 m, 987 w, 918 vw, 887 vw, 833 w, 811 vw, 750 m, 731 s, 707 vs, 624 vw, 611 s, 510 m, 495 m, 469 w, 453 vw, 442 w. **^{1}H NMR** (CD_3CN): δ = 1.81 (t, 4H, $^3J_{HH}$ = 6.0 Hz, THF 2/3 CH_2), 2.98 (s, 12H, CH_3), 3.65 (t, 4H, $^3J_{HH}$ = 5.7 Hz, THF 1/4 CH_2), 4.92 (sbr, 4H, CH_β), 5.01 (sbr, 4H, CH_α), 6.85 (t, 8H, $^3J_{HH}$ = 6.4 Hz, CH_{para}), 7.00 (t, 16H, $^3J_{HH}$ = 6.8 Hz, CH_{meta}), 7.28 (sbr, 16H, CH_{ortho}) ppm. **^{13}C NMR** (CD_3CN): = 30.6 (CH_3), 72.4 (Cp_α), 75.7 (Cp_β), 78.3 (*C*S), 122.8 (C_{para}), 126.7 (C_{meta}), 136.8 (C_{ortho}).[54] **ESI-HRMS**(+): *m·z*$^{-1}$ calculated for $C_{14}H_{20}FeS_2^{2+}$: 154.0172, found: 154.0169. **ESI-HRMS**(–): *m·z*$^{-1}$ calculated for $C_{24}H_{20}B$: 319.1668, found: 319.1657.

Preparation of 1,1'-di(butylmethylsulfonium)ferrocene di{bis(trifluoromethanesulfonyl)imide} 2b. The preparation was performed analogous to **1a** with 187 mg (0.516 mmol, 1.00 eq.) 1,1'-di(butylthio)ferrocene and 406 mg (1.37 mmol, 2.66 eq.) Me-TFSI. 372 mg (0.391 mmol, 76%) **2b** were obtained as dark red solid. A further purification can be accomplished by solving the product in dichloromethane and precipitation with hexane. **Mp:** 93.0 °C (10 K min^{-1}). Elem. anal. found C, 30.5; H, 3.4; N, 3.1: S, 20.25; $C_{24}H_{32}F_{12}FeN_2O_8S_6$ (952.74 g mol^{-1}) requires C, 30.3; H, 3.4; N, 2.9; S, 20.2. **IR** (neat): $\tilde{\nu}$ /cm^{-1} = 3117 vw, 3023 vw, 2969 w, 2940 w, 2880 vw, 1469 vw, 1423 w, 1344 s, 1329 w, 1181 vs br, 1134 s, 1047 vs, 985 w, 892 w, 872 vw, 836 m, 791 m, 763 w, 739 m, 654 vw, 610 vs, 569 s, 511 s, 438 vw, 408 w. **^{1}H NMR** (CD_3CN): δ = 0.91 (t, 6H, $^3J_{HH}$ = 7.1 Hz, CH_3), 1.42 (tq, 4H, $^3J_{HH}$ = 7.2, 7.2 Hz, CH_2CH$_3$), 1.53-1.65 (m br, 4H, CH_2CH$_2$CH$_3$), 3.14 (s, 6H, SCH_3), 3.22 (m, 2H, SCH_2), 3.39 (dt, 2H, $^3J_{HH}$ = 7.8 Hz, $^2J_{HH}$ = 12.2 Hz, SCH_2'), 4.99 (s, 4H, Cp), 5.03 (s br, 2H, Cp), 5.11 (s br, 2H, Cp) ppm. **^{13}C NMR** (CD_3CN): δ = 13.5 (CH$_2$*C*H$_3$), 21.9 (*C*H$_2$CH$_3$), 26.5 (S*C*H$_3$ or *C*H$_2$CH$_2$CH$_3$), 26.5 (S*C*H$_3$ or *C*H$_2$CH$_2$CH$_3$), 26.6 (S*C*H$_3$ or *C*H$_2$CH$_2$CH$_3$), 48.4 (S*C*H$_2$), 48.4 (S*C'*H$_2$), 70.3 (Cp_α), 70.5 (Cp_α), 75.2 (Cp_α), 75.5 (Cp_α), 75.9 (Cp_β), 76.0 (Cp_β), 76.5 (*C*S), 76.5 (*C*S), 121,0 (vq, $^1J_{CF}$ = 322.4 Hz, *C*F$_3$)[52] ppm. **^{19}F NMR** (CD_3CN): δ = –79.0 ppm. **ESI-HRMS**(+): *m·z*$^{-1}$ calculated for $C_{22}H_{32}FeNO_4S_4^+$: 672.0463, found: 672.0456. **ESI-HRMS**(–): *m·z*$^{-1}$ calculated for $C_2F_6S_2O_4N^-$: 279.9178, found: 279.9172.

Notes and references

1 L. S. Hernández-Muñoz and F. J. González, *Electrochem. Commun.*, 2011, **13**, 701–703.

2 M. Armand, Y. Choquette, M. Gauthier and C. Michot, EP 0 850 920 A2, 1998.

3 C. B. Bouvet and H. Krautscheid, *Eur. J. Inorg. Chem.*, 2016, **2016**, 4573–4580.

4 P. Kübler and J. Sundermeyer, *Dalt. Trans.*, 2014, **43**, 3750–3766.

5 B. Gelinas, J. C. Forgie, D. Rochefort, G. Bruno, J. C. Forgie and D. Rochefort, *J. Electrochem. Soc.*, 2014, **161**, H161–H165.

6 Y. Gao, B. Twamley and J. M. Shreeve, *Inorg. Chem.*, 2004, **43**, 3406–3412.

7 J. E. F. Weaver, D. Breadner, F. Deng, B. Ramjee, P. J. Ragogna and R. W. Murray, *J. Phys. Chem. C*, 2011, **115**, 19379–19385.

8 V. O. Nyamori, M. Gumede and M. D. Bala, *J. Organomet. Chem.*, 2010, **695**, 1126–1132.

9 J.-L. Thomas, J. Howarth, K. Hanlon and D. McGuirk, *Tetrahedron Lett.*, 2000, **41**, 413–416.

10 Y. Miura, F. Shimizu and T. Mochida, *Inorg. Chem.*, 2010, **49**, 10032–10040.

11 B. Gélinas and D. Rochefort, *Electrochim. Acta*, 2015, **162**, 36–44.

12 O. Fontaine, C. Lagrost, J. Ghilane, P. Martin, G. Trippé, C. Fave, J. C. Lacroix, P. Hapiot and H. N. Randriamahazaka, *J. Electroanal. Chem.*, 2009, **632**, 88–96.

13 B. Gélinas, M. Natali, T. Bibienne, Q. P. Li, M. Dollé and D. Rochefort, *J. Phys. Chem. C*, 2016, **120**, 5315–5325.

14 J. Ghilane and J. C. Lacroix, *J. Am. Chem. Soc.*, 2013, **135**, 4722–4728.

15 J. C. Forgie, S. El Khakani, D. D. MacNeil and D. Rochefort, *Phys. Chem. Chem. Phys.*, 2013, **15**, 7713–7721.

16 H. J. Xie, B. Gélinas and D. Rochefort, *Electrochem. commun.*, 2016, **66**, 42–45.

17 H. Tahara, R. Baba, K. Iwanaga, T. Sagara and H. Murakami, *Chem. Commun.*, 2017, **53**, 2455–2458.

18 Y. Funasako, T. Inagaki, T. Mochida, T. Sakurai, H. Ohta, K. Furukawa and T. Nakamura, *Dalton Trans.*, 2013, **42**, 8317–8327.

19 D. Gerhard, S. C. Alpaslan, H. J. Gores, M. Uerdingen and P. Wasserscheid, *Chem. Commun.*, 2005, 5080–5082.

20 H. B. Han, J. Nie, K. Liu, W. K. Li, W. F. Feng, M. Armand, H. Matsumoto and Z.-B. Zhou, *Electrochim. Acta*, 2010, **55**, 1221–1226.

21 E. Coadou, P. Goodrich, A. R. Neale, L. Timperman, C. Hardacre, J. Jacquemin and M. Anouti, *ChemPhysChem*, 2016, **17**, 3992–4002.

22 G. R. Knox, I. G. Morrison, P. L. Pauson, M. A. Sandhu and W. E. Watts, *J. Chem. Soc. C*, 1967, 1853–1856.

23 G. Marr and M. T. White, *J. Chem. Soc. C*, 1970, 1789–1792.

24 N. L. Holy, T. Nalesnik, L. Warfield and M. Mojesky, *J. Coord. Chem.*, 1983, **12**, 157–162.

25 S. Minière, V. Reboul, R. G. Arrayás, P. Metzner and J. C.

View Article Online
DOI: 10.1039/C7DT04139J

Carretero, *Synthesis (Stuttg).*, 2003, 2249–2254.

26 L. Wang and Z. Huang, *J. Zhejiang Univ. Sci.*, 2005, **6A**, 636–639.

27 R. Sanders and U. T. Mueller-Westerhoff, *J. Organomet. Chem.*, 1996, **512**, 219–224.

28 T. E. Pickett and C. J. Richards, *Tetrahedron Lett.*, 1999, **40**, 5251–5254.

29 G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *J. Am. Chem. Soc.*, 1952, **74**, 2125–2126.

30 A. I. Popov and R. F. Swensen, *J. Am. Chem. Soc.*, 1955, **77**, 3724–3726.

31 S. Lu, V. V. Strelets, M. F. Ryan, W. J. Pietro and A. B. P. Lever, *Inorg. Chem.*, 1996, **35**, 1013–1023.

32 Crystal Data for **4**: $C_{12}H_{15}FeIS$, M=374.05, monoclinic, a = 15.4360(6) Å, b = 9.5323(4) Å, c = 8.8874(3) Å, α = 90°, β = 93.0790(10)°, γ = 90°, V = 1305.81(9) Å^3, T = 100(2) K, space group $P2_1/c$, Z = 4, 25189 reflections measured, 2890 reflections unique (R_{int} = 0.0583). R_1 = 0.0186, wR_2 = 0.0376, GoF = 1.045, CCDC: 1583350.

33 Crystal Data for **5**: $C_{66}H_{68}B_2FeOS_2$, M = 1018.79, triclinic, a = 11.0520(5) Å, b = 14.8221(6) Å, c = 18.5056(7) Å, α = 104.7890(13)°, β = 104.0025(14)°, γ = 105.4496(14)°, V = 2664.29(19) Å^3, T = 100(2) K, space group $P\bar{1}$, Z = 2, 76302 reflections measured, 11807 reflections unique (R_{int} = 0.0325). R_1 = 0.0321, wR_2 = 0.0766, GoF = 1.031, CCDC: 1583349.

34 V. G. Andrianov, Y. T. Struchkov, V. N. Setkina, A. Z. Zhakaeva and V. I. Zdanovitch, *J. Organomet. Chem.*, 1977, **140**, 169–175.

35 J. A. Adeleke, Y. W. Chen and L. K. Liu, *Organometallics*, 1992, **11**, 2543–2550.

36 V. G. Andrianov and Y. T. Struchkov, *Russ. Chem. Bull.*, 1977, **26**, 624–626.

37 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.

38 B. Huber and B. Roling, *Electrochim. Acta*, 2011, **56**, 6569–6572.

39 *Bruker Instrument Service v3.0.26, APEX2 v2012.10-0, SAINT v8.27B, Bruker AXS Inc.*, Madison, Wisconsin, USA.

40 M. C. Burla, R. Caliandro, B. Carrozzini, G. L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzone and G. Polidori, *J. Appl. Crystallogr.*, 2015, **48**, 306–309.

41 G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **A71**, 3–8.

42 A. L. Spek, *Acta Crystallogr. D*, 2009, **65**, 148–155.

43 L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849–854.

44 *SADABS v2012/1, Bruker AXS Inc.*, Madison, Wisconsin, USA.

45 *Diamond - Crystal and Molecular Structure Visualization, Crystal Impact - H. Putz & K. Brandenburg GbR*, Kreuzherrenstr. 102, 53227 Bonn, Germany, 2009.

46 W. L. F. Armarego and D. D. Perrin, *Purification of Laboratory Chemicals*, Elsevier, Burlington, 4th edn., 1996.

47 H. J. Kim, W. S. Lee, S. Won, and K. B. Park, WO 2007091817 A1, 2007.

48 M. Perseghini and A. Togni, in *Science of Synthesis*, ed. M. Lautens, Georg Thieme Verlag, Stuttgart, New York, 2001, pp. 889–929.

49 D. C. O'Connor Salazar and D. O. Cowan, *J. Organomet. Chem.*, 1991, **408**, 227–231.

50 M. Sato, M. Sekino, M. Katada and S. Akabori, *J. Organomet. Chem.*, 1989, **377**, 327–331.

51 D. A. Khobragade, S. G. Mahamulkar, L. Pospíšil, I. Císařcová, L. Rulíšek and U. Jahn, *Chem. Eur. J.*, 2012, **18**, 12267–12277.

52 Due to the low concentration, the ^{13}C CF_3 signal was only detected as doublet (part of quartet).

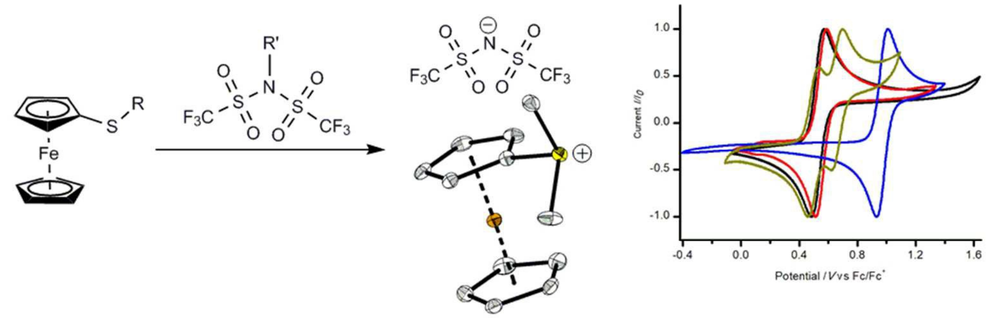
53 Due to the low concentration, the ^{13}C CF_3 signal of TFSI was not detected.

54 At low concentration, the ^{13}C Ph_{ipso} signal was not detected due to coupling with B^{11}.

View Article Online
DOI: 10.1039/C7DT04139J

Room temperature ferrocenylsulfonium ionic liquids are introduced.

Their tunable redox potential and thermal decay are investigated.



80x36mm (300 x 300 DPI)