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(54) Title: COMPOUNDS CONTAINING ALKYL-CYANO-BORATE OR ALKYL-CYANO-FLUOROBORATE ANIONS

(57) Abstract: The invention relates to new compounds containing alkyl/alkenyl-cyano- borate or alkyl/alkenyl-cyano-fluoroborate anions, their preparation and their use, in particular as part of electrolyte formulations for electrochemical or optoelectronic devices.

Compounds containing alkyl-cyano-borate or alkyl-cyano-fluoroborate anions

The invention relates to new compounds containing alkyl/alkenyl-cyano-
5 borate or alkyl/alkenyl-cyano-fluoroborate anions, their preparation and
their use, in particular as part of electrolyte formulations for electrochemical
or optoelectronic devices.

The salts according to the invention can on the one hand be used for the
10 synthesis of ionic liquids, on the other hand the salts can be employed per
se as ionic liquid.

Ionic liquids or liquid salts are ionic species which consist of an organic
15 cation and a generally inorganic anion. They do not contain any neutral
molecules and usually have melting points below 373 K.

The area of ionic liquids is currently the subject of intensive research since
the potential applications are multifarious. Review articles on ionic liquids
are, for example, R. Sheldon "Catalytic reactions in ionic liquids", *Chem.*
20 *Commun.*, 2001, 2399-2407; M.J. Earle, K.R. Seddon "Ionic liquids. Green
solvent for the future", *Pure Appl. Chem.*, 72 (2000), 1391-1398; P.
Wasserscheid, W. Keim "Ionische Flüssigkeiten – neue Lösungen für die
Übergangsmetallkatalyse" [Ionic Liquids – Novel Solutions for Transition-
Metal Catalysis], *Angew. Chem.*, 112 (2000), 3926-3945; T. Welton "Room
25 temperature ionic liquids. Solvents for synthesis and catalysis", *Chem.*
Rev., 92 (1999), 2071-2083 or R. Hagiwara, Ya. Ito "Room temperature
ionic liquids of alkylimidazolium cations and fluoroanions", *J. Fluorine
Chem.*, 105 (2000), 221-227.

30 The properties of ionic liquids, for example melting point, thermal and
electrochemical stability, viscosity, are strongly influenced by the nature of
the anion.

E. Bernhardt et al, Z. Anorg. Allg. Chem. 2000, 626, 560, E. Bernhardt et al, Chem. Eur. J. 2001, 7, 4696 and E. Bernhardt et al, Z. Anorg. Allg. Chem. 2003, 629, 1229 disclose the novel chemically and electrochemically stable borate anions $[B(CN)_4]^-$, $[F_xB(CN)_{4-x}]^-$, where x = 1 to 3, and $[B(CF_3)_4]^-$.

5

EP 1205480 A1 describes tetrakisfluoroalkylborate salts and the use thereof as conductive salts or ionic liquids.

10

WO 2005/021661 describes cationic dyes having alkylcyanofluoroborate anions in which the dye is selected from the group of the azine, xanthene, polymethine, styryl, azo, tetrazolium, pyrylium, benzopyrylium, thiopyrylium, benzothiopyrylium, thiazine, oxazine, triarylmethane, diarylmethane, acridine, quinoline, isoquinoline or quaternised azafluorenone dyes.

15

Roland Köster et al, Chem. Ber. 1993, 126, 305 describes the synthesis of solvated $K[(C_2H_5)_3BCN]$ through reaction of KCN with $B(C_2H_5)_3$ in toluene.

20

H. Witte et al, Z. für Naturforschung, 22b (1967), 1083 presents the preparation of $K[(Alk)_3BCN]$ and $[(CH_3)_4N][(Alk)_3BCN]$ through reaction of KCN with $B(Alk)_3$ in diethyl ether in which Alk denotes CH_3 , C_2H_5 , $n-C_3H_7$ and $n-C_4H_9$.

25

Haijun Yao et al, Inorganic Chemistry (2005), 44(18), 6256-6264 describes the synthesis of potassium(18-crone-6) $[(n-C_8H_{17})_3B(CN)]$ -anion and tetraethylammonium $[(phenyl)_3B(CN)]$ for further application in coordination chemistry.

30

The object of the present invention was to provide alternative compounds which are novel, thermally and electrochemically stable which can be used for the synthesis of ionic liquids or as ionic liquids or as conductive salts, and which are in particular useful for the synthesis of ionic liquids or as ionic liquids or organic salts for application in electrochemical or

optoelectronic devices. The object of the present invention was furthermore to provide a method for the preparation of the alternative salts, especially the compounds of formula I, as described below, which can be produced in economical way on industrial scale.

5

The object is achieved by the salts of the formula I according to the invention with alkyl-cyano-, alkenyl-cyano-, alkenyl-cyano-fluoro- or alkyl-cyano-fluoro-borate anions and the described methods for their preparation.

10 The invention therefore relates to compounds of formula I



in which

R¹ each independently denotes

a straight-chain or branched alkyl group having 1 to 20 C atoms, which

15 optionally may contain at least one Cl, Br or I atom, at least one CN group and/or one or more oxygen or sulphur atoms,

a straight-chain or branched alkenyl group having 2 to 20 C atoms having one or more double bonds, which optionally may contain at least one Cl, Br or I atom and/or one or more oxygen or sulphur atoms,

20 a straight-chain or branched alkinyl group having 1 to 20 C atoms having one or more triple bonds, which optionally may contain at least one Cl, Br or I atom and/or one or more oxygen or sulphur atoms and optionally may have a double bond,

or unsubstituted phenyl,

25 z is 1, 2, 3 or 4, x is 1, 2 or 3, y is 0, 1 or 2, v is 0, 1 or 2 and the sum of x+y+v is 2 or 3 and

in which Kt^{z+} denotes

an inorganic cation selected from the group of NO⁺, H⁺, Li⁺, Na⁺, K⁺, Rb⁺,

30 Cs⁺, or Mg²⁺, Cu⁺, Cu²⁺, Zn²⁺, Ag⁺, Ca²⁺, Y⁺³, Yb⁺³, La⁺³, Sc⁺³, Ce⁺³, Nd⁺³, Tb⁺³, Sm⁺³ or complex (ligands containing) metal cations which include rare-earths, transitions or noble metals like rhodium, ruthenium, iridium,

palladium, platinum, osmium, cobalt, nickel, iron, chromium, molybdenum, tungsten, vanadium, titanium, zirconium, hafnium, thorium, uranium, gold,

or an organic cation selected from the group of

5

a tritylium cation, in which the phenyl groups may be substituted by straight-chain or branched alkyl groups having 1 to 20 C atoms, straight-chain or branched alkenyl having 2 to 20 C atoms and one or more double bonds or straight-chain or branched alkynyl having 2 to 20 C atoms and one or more triple bonds,

10

an oxonium cation of formula (1) or a sulfonium cation of formula (2)



15

where R° each independently of one another denotes a straight-chain or branched alkyl group having 1-8 C atoms, non-substituted phenyl or phenyl which is substituted by R^{1*} , OR' , $N(R')_2$, CN or halogen and in case of sulfonium cations of formula (2) additionally denotes each independently $(R''')_2N$ and R' is independently of each other H, non-fluorinated, partially fluorinated or perfluorinated straight-chain or branched C_1 - to C_{18} -alkyl, saturated C_3 - to C_7 -cycloalkyl, non-substituted or substituted phenyl, R^{1*} is independently of each other non-fluorinated, partially fluorinated or perfluorinated straight-chain or branched C_1 - to C_{18} -alkyl, saturated C_3 - to C_7 -cycloalkyl, non-substituted or substituted phenyl and R''' is independently of each other straight-chain or branched C_1 to C_6 alkyl;

20

25

an ammonium cation, which conforms to the formula (3)



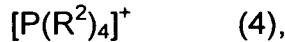
where

30

R in each case, independently of one another, denotes

H , OR' , $N(R')_2$, with the proviso that a maximum of one R in formula (3) is OR' or $N(R')_2$,

straight-chain or branched alkyl having 1-20 C atoms,
straight-chain or branched alkenyl having 2-20 C atoms and one or more
double bonds,
straight-chain or branched alkynyl having 2-20 C atoms and one or more
5 triple bonds,
saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms,
which may be substituted by straight-chain or branched alkyl groups having
1-6 C atoms, where one or two R may be fully substituted by halogens, in
particular -F and/or -Cl, and one or more of the substituents R may be
10 partially substituted by halogens, in particular -F and/or -Cl, and/or by -OH,
-OR', -CN, -N(R')₂, -C(O)OH, -C(O)OR', -C(O)R', -C(O)N(R')₂, -SO₂N(R')₂,
-C(O)X, -SO₂OH, -SO₂X, -NO₂, -SR', -S(O)R', -SO₂R' and where one or two
non-adjacent carbon atoms in R which are not in the α -position may be
replaced by atoms and/or atom groups selected from the group -O-, -S-,
15 -S(O)-, -SO₂-, -SO₂O-, -C(O)-, -C(O)O-, -N⁺(R')₂-, -P(O)R'O-, -C(O)NR'-,
-SO₂NR'-, -OP(O)R'O-, -P(O)(N(R')₂)NR'-, -P(R')₂=N- or -P(O)R'- where
R' each independently is H, non-fluorinated, partially fluorinated or
perfluorinated straight-chain or branched C₁- to C₁₈-alkyl, saturated C₃- to
C₇-cycloalkyl, non-substituted or substituted phenyl and X each
20 independently is halogen;
a phosphonium cation, which conforms to the formula (4)



where

R² in each case, independently of one another, denotes

25 H, OR' or N(R')₂,
straight-chain or branched alkyl having 1-20 C atoms,
straight-chain or branched alkenyl having 2-20 C atoms and one or more
double bonds,
straight-chain or branched alkynyl having 2-20 C atoms and one or more
30 triple bonds,

saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by straight-chain or branched alkyl groups having 1-6 C atoms,

where one or two R² may be fully substituted by halogens, in particular -F

5 and/or -Cl, and one or more of the substituents R² may be partially substituted by halogens, in particular -F and/or -Cl, and/or by -OH, -OR', -CN, -N(R')₂, -C(O)OH, -C(O)OR', -C(O)R', -C(O)N(R')₂, -SO₂N(R')₂, -C(O)X, -SO₂OH, -SO₂X, -NO₂, -SR', -S(O)R', -SO₂R' and where one or two non-adjacent carbon atoms in R² which are not in the α -position may be replaced by atoms and/or atom groups selected from the group -O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -C(O)-, -C(O)O-, -N⁺(R')₂-, -P(O)R'O-, -C(O)NR'-, -SO₂NR'-, -OP(O)R'O-, -P(O)(N(R')₂)NR'-, -P(R')₂=N- or -P(O)R'- where R' each independently is H, non-fluorinated, partially fluorinated or perfluorinated straight-chain or branched C₁- to C₁₈-alkyl, saturated C₃- to C₇-cycloalkyl, non-substituted or substituted phenyl and X each independently is halogen;

10 a uronium cation, which conforms to the formula (5)



15 where

R³ to R⁷ each, independently of one another, denote

H, where H is excluded for R⁵,

straight-chain or branched alkyl having 1 to 20 C atoms,

straight-chain or branched alkenyl having 2-20 C atoms and one or more

20 double bonds,

straight-chain or branched alkynyl having 2-20 C atoms and one or more

triple bonds,

saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms,

which may be substituted by straight-chain or branched alkyl groups having

25 1-6 C atoms, where one or two of the substituents R³ to R⁷ may be fully

substituted by halogens, in particular -F and/or -Cl, and one or more of the

30 substituents R³ to R⁷ may be partially substituted by halogens, in particular

-F and/or -Cl, and/or by -OH, -OR', -N(R')₂, -CN, -C(O)OH, -C(O)OR', -C(O)R', -C(O)N(R')₂, -SO₂N(R')₂, -C(O)X, -SO₂OH, -SO₂X, -SR', -S(O)R', -SO₂R', -NO₂ and where one or two non-adjacent carbon atoms in R³ to R⁷ which are not in the α -position may be replaced by atoms and/or atom groups selected from the group -O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -C(O)-, -C(O)O-, -N⁺(R')₂-, -P(O)R'O-, -C(O)NR'-, -SO₂NR'-, -OP(O)R'O-, -P(O)(N(R')₂)NR'-, -P(R')₂=N- or -P(O)R'- where R' each independently is H, non-fluorinated, partially fluorinated or perfluorinated straight-chain or branched C₁- to C₁₈-alkyl, saturated C₃- to C₇-cycloalkyl, non-substituted or substituted phenyl and X each independently is halogen;

a thiuronium cation, which conforms to the formula (6)



where

R³ to R⁷ each, independently of one another, denote H, where H is excluded for R⁵, straight-chain or branched alkyl having 1 to 20 C atoms, straight-chain or branched alkenyl having 2-20 C atoms and one or more double bonds,

20 straight-chain or branched alkynyl having 2-20 C atoms and one or more triple bonds, saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by straight-chain or branched alkyl groups having 1-6 C atoms, where one or two of the substituents R³ to R⁷ may be fully substituted by halogens, in particular -F and/or -Cl, and one or more of the substituents R³ to R⁷ may be partially substituted by halogens, in particular -F and/or -Cl, and/or by -OH, -OR', -N(R')₂, -CN, -C(O)OH, -C(O)OR', -C(O)R', -C(O)N(R')₂, -SO₂N(R')₂, -C(O)X, -SO₂OH, -SO₂X, -SR', -S(O)R', -SO₂R', -NO₂ and where one or two non-adjacent carbon atoms in R³ to R⁷ which are not in the α -position may be replaced by atoms and/or atom groups selected from the group -O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -C(O)-,

-C(O)O-, -N⁺(R')₂-, -P(O)R'O-, -C(O)NR'-, -SO₂NR'-, -OP(O)R'O-,
-P(O)(N(R')₂)NR'-, -P(R')₂=N- or -P(O)R'- where R' each independently
is H, non-fluorinated, partially fluorinated or perfluorinated straight-chain or
branched C₁- to C₁₈-alkyl, saturated C₃- to C₇-cycloalkyl, non-substituted or
5 substituted phenyl and X each independently is halogen;

a guanidinium cation, which conforms to the formula (7)



where

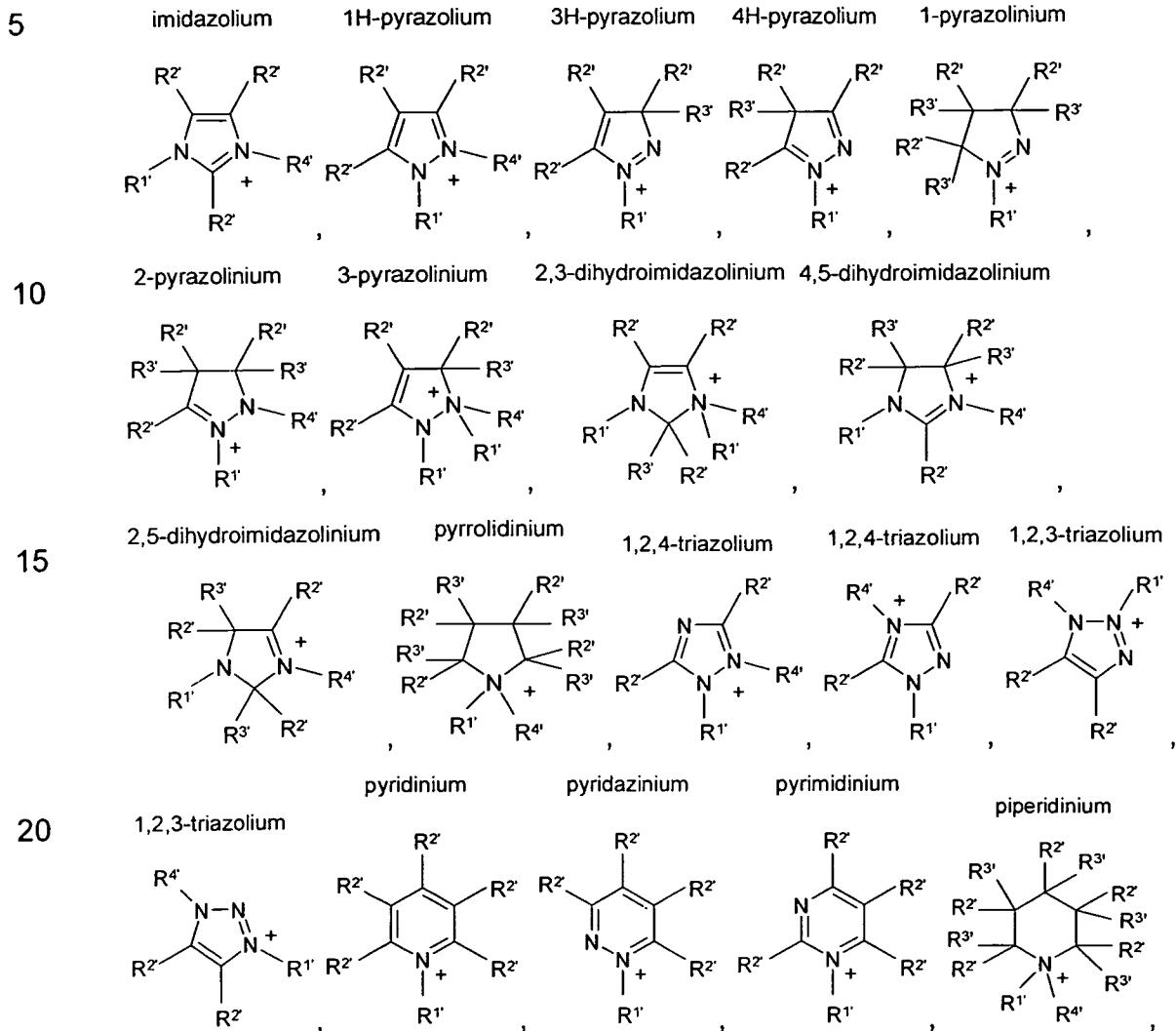
10 R⁸ to R¹³ each, independently of one another, denote
H, -CN, N(R')₂, -OR',
straight-chain or branched alkyl having 1 to 20 C atoms,
straight-chain or branched alkenyl having 2-20 C atoms and one or more
double bonds,
15 straight-chain or branched alkynyl having 2-20 C atoms and one or more
triple bonds,
saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms,
which may be substituted by straight-chain or branched alkyl groups having
1-6 C atoms, where one or two of the substituents R⁸ to R¹³ may be fully
20 substituted by halogens, in particular -F and/or -Cl, and one or more of the
substituents R⁸ to R¹³ may be partially substituted by halogens, in particular
-F and/or -Cl, and/or by -OH, -OR', -N(R')₂, -CN, -C(O)OH, -C(O)OR', -
C(O)R', -C(O)N(R')₂, -SO₂N(R')₂, -C(O)X, -SO₂OH, -SO₂X, -SR', -S(O)R', -
SO₂R', -NO₂ and where one or two non-adjacent carbon atoms in R⁸ to R¹³
25 which are not in the α -position may be replaced by atoms and/or atom
groups selected from the group -O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -C(O)-, -
C(O)O-, -N⁺(R')₂-, -P(O)R'O-, -C(O)NR'-, -SO₂NR'-, -OP(O)R'O-,
-P(O)(N(R')₂)NR'-, -P(R')₂=N- or -P(O)R'-, where R' each independently
is H, non-fluorinated, partially fluorinated or perfluorinated straight-chain or
30 branched C₁- to C₁₈-alkyl, saturated C₃- to C₇-cycloalkyl, non-substituted or
substituted phenyl and X each independently is halogen;

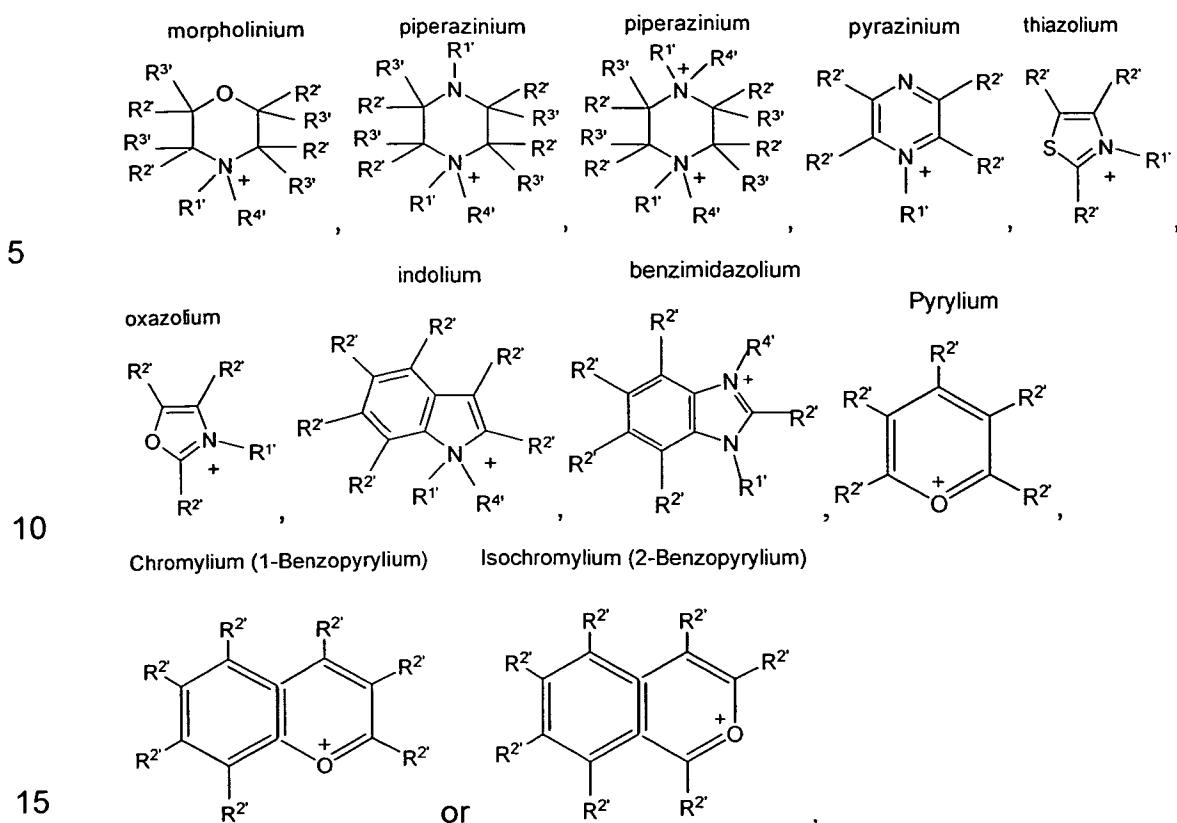
a heterocyclic cation which conforms to the formula (8)



where

HetN^{2+} denotes a heterocyclic cation selected from the group





where the substituents

R^1 , to R^4 , each, independently of one another, denote

H,

20 straight-chain or branched alkyl having 1-20 C atoms,

straight-chain or branched alkenyl having 2-20 C atoms and one or more double bonds,

straight-chain or branched alkynyl having 2-20 C atoms and one or more triple bonds,

25 and

R^2 denote additionally F, Cl, Br, I, -CN, -OR', -N(R')₂, -P(O)(R')₂, -

$P(O)(OR')_2$, $-P(O)(N(R')_2)_2$, $-C(O)R'$, $-C(O)OR'$, $-C(O)X$, $-C(O)N(R')_2$, -

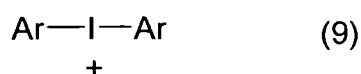
$\text{SO}_2\text{N}(\text{R}')_2$, $-\text{SO}_2\text{OH}$, $-\text{SO}_2\text{X}$, $-\text{SR}'$, $-\text{S(O)R}'$, $-\text{SO}_2\text{R}'$ and/or NO_2 , with the

proviso that R^1 , R^3 , R^4 are in this case independently of each other H

30 and/or a straight-chain or branched alkyl having 1-20 C atoms, straight-

chain or branched aikanyl having 2-20 C atoms and one or more double bonds,

where one to three substituents R¹ to R⁴ may be fully substituted by
 5 halogens, in particular -F and/or -Cl, and one or more substituents R¹ to R⁴
 may be partially substituted by halogens, in particular -F and/or -Cl, and/or
 by -OH, -OR', N(R')₂, -CN, -C(O)OH, -C(O)OR', -C(O)R', -C(O)N(R')₂, -
 SO₂N(R')₂, -C(O)X, -SO₂OH, -SO₂X, -SR', -S(O)R', -SO₂R', -NO₂, but
 where R¹ and R⁴ cannot simultaneously be fully substituted by halogens
 10 and where, in the substituents R¹ to R⁴, one or two non-adjacent carbon
 atoms which are not bonded to the heteroatom may be replaced by atoms
 and/or atom groups selected from the -O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -
 C(O)-, -C(O)O-, -N⁺(R')₂-, -P(O)R'O-, -C(O)NR'-, -SO₂NR'-, -OP(O)R'O-,
 -P(O)(N(R')₂)NR'-, -P(R')₂=N- or -P(O)R',
 15 where R' each independently is H, non-fluorinated, partially fluorinated or
 perfluorinated straight-chain or branched C₁- to C₁₈-alkyl, saturated C₃- to
 C₇-cycloalkyl, non-substituted or substituted phenyl and X each
 independently is halogen or
 20 a iodonium cation which conforms to the formula (9)



where

the aryl group Ar denotes each independently of each other aryl with 6 to
 25 30 C atoms which is non-substituted or substituted with at least a straight-
 chain or branched alkyl group having 1 to 20 C atoms, a straight-chain or
 branched alkenyl group having 2 to 20 C atoms and one or more double
 bonds, a straight-chain or branched alkynyl group having 2 to 20 C atoms
 and one or more triple bonds, R¹, NO₂, SR', N(R')₂, CN and/or halogen
 30 and

where R' each independently is H, non-fluorinated, partially fluorinated or perfluorinated straight-chain or branched C₁- to C₁₈-alkyl, saturated C₃- to C₇-cycloalkyl, non-substituted or substituted phenyl and

where R¹ each independently is non-fluorinated, partially fluorinated or

5 perfluorinated straight-chain or branched C₁- to C₁₈-alkyl, saturated C₃- to C₇-cycloalkyl, non-substituted or substituted phenyl

and halogen is F, Cl, Br or I,

10 with the proviso that potassium (18-crone-6) tricyano-*n*-octylborate and tetraethylammonium phenyl-tricyanoborate are excluded.

Halogen is preferably F, Cl or Br, particularly preferably F or Cl.

15 R¹ preferably each independently denotes a straight-chain or branched alkyl group having 1 to 4 C atoms, which optionally may contain at least one Br atom or at least one CN group or at least one oxygen atom or a straight-chain or branched alkenyl having 2 to 4 C atoms. R¹ is particularly preferably each independently methyl, ethyl, *n*-butyl, bromomethyl, cyanomethyl, methoxymethyl, ethoxymethyl, vinyl or allyl. R¹ is very particularly preferably each independently methyl, ethyl, *n*-butyl, vinyl or allyl or very particularly preferably methyl, ethyl, vinyl or allyl or very particularly preferably methyl, ethyl or vinyl.

20 25 Particularly preferred compounds are compounds of formula IA, in which v is 1, y is 0 and x is 2



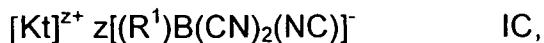
in which [Kt]^{z+}, z and R¹ has a meaning as defined above;

30 formula IB, in which v is 0, y is 0 and x is 3



in which [Kt]^{z+}, z and R¹ has a meaning as defined above;

formula IC, in which v is 0, y is 1 and x is 2



in which $[Kt]^{z+}$, z and R^1 has a meaning as defined above;

5

formula ID, in which v is 2, y is 0 and x is 1



in which $[Kt]^{z+}$, z and R^1 has a meaning as defined above or

10

formula IE, in which v is 0, y is 0 and x is 2



in which $[Kt]^{z+}$, z and R^1 has a meaning as defined above.

15

R^1 in a compound of formula IA preferably denotes an alkyl group having 1 to 4 C atoms which optionally may contain at least one Br atom or at least one CN group or at least one oxygen atom, particularly preferably methyl, ethyl, *n*-butyl, bromomethyl, cyanomethyl, methoxymethyl or ethoxymethyl, very particularly preferably methyl.

20

In another embodiment, R^1 in compound of formula IA preferably denotes an alkenyl group having 2 to 4 C atoms, particularly preferably vinyl or allyl.

25

R^1 in a compound of formula IB preferably denotes an alkyl group having 1 to 4 C atoms which optionally may contain at least one Br atom or at least one CN group or at least one oxygen atom or an alkenyl group having 2 to 4 C atoms, particularly preferably methyl, ethyl, *n*-butyl, bromomethyl, cyanomethyl, methoxymethyl, ethoxymethyl, vinyl or allyl, very particularly preferably methyl, ethyl or allyl or very particularly preferably methyl or allyl.

30

R^1 in a compound of formula IC preferably denotes an alkyl group having 1 to 4 C atoms or an alkenyl group having 2 to 4 C atoms, particularly preferably methyl, ethyl, *n*-butyl, vinyl or allyl, very particularly preferably

methyl, *n*-butyl or vinyl or very particularly preferably methyl, ethyl, vinyl or allyl.

R^1 in a compound of formula ID preferably denotes an alkyl group having 1 to 4 C atoms which optionally may contain at least one Br atom or at least one CN group or at least one oxygen atom, particularly preferably methyl, ethyl, *n*-butyl, bromomethyl, cyanomethyl, methoxymethyl or ethoxymethyl, very particularly preferably methyl or ethyl or very particularly preferably methyl.

10

R^1 in a compound of formula IE preferably denotes an alkyl group having 1 to 4 C atoms which optionally may contain at least one Br atom or at least one CN group or at least one oxygen atom, particularly preferably methyl, ethyl, *n*-butyl, bromomethyl, cyanomethyl, methoxymethyl or ethoxymethyl, very particularly preferably methyl and ethyl or methyl or ethyl.

15

In another embodiment, R^1 in compound of formula IE preferably denotes an alkenyl group having 2 to 4 C atoms, particularly preferably vinyl or allyl.

20

Preferred anions according to the invention are methyltricyanoborate, ethyltricyanoborate, allyltricyanoborate, methylethyldicyanoborate, dimethyldicyanoborate and diethyldicyanoborate.

25

The compounds of formula I, preferably the compounds of formula IA to IE having organic cations are possessing good thermal and electrochemical stabilities and are of interest for practical applications, for example in dye or quantum dot sensitized solar cells (DSSCs). Some compounds of formula IA to IE having organic cations are even less viscous compared to the corresponding tetracyanoborates having the same organic cation. For example, 1-ethyl-3-methyl-imidazolium tetracyanoborate (emim TCB) has the dynamic viscosity of 22 mPas (at 20°C) and the corresponding 1-ethyl-3-methyl-imidazolium methyl-tricyano-borate has a viscosity of 21.1 mPas (at 20°C). The positive influence of the replacement of one cyano-group

30

with an alkyl group on the viscosity of compounds of formula I having organic cations compared to the compounds with tetracyanoborate anions having the same organic cation is unexpected. In comparison to electron-withdrawing groups like fluor, perfluoroalkyl or cyano groups which are able 5 to effectively delocalise the negative charge of borate anions, an alkyl group practically does not participate in the stabilization of the borate-anion. The introduction of one alkyl group to Boron should increase the coordination ability of the alkyl-tricyano borate anion, causing increase in the viscosity of ionic liquids with this anion. But the experimental results are 10 totally opposite from the theoretical point of view.

Not being bound by that theory, it seems that the introduction of one alkyl group to Boron breaks the symmetry of tetracyano-borate anion resulting in decreasing of ionic liquids viscosity.

15 Another advantage of compounds of formula I is that they can be prepared from commercially available starting materials via a simple reaction protocol.

Preferred inorganic cations $[Kt]^{z+}$ are metal cations, such as Li^+ , Na^+ , K^+ , 20 Rb^+ , Cs^+ , or Mg^{2+} , Cu^+ , Cu^{2+} , Zn^{2+} , Ag^+ , Ca^{2+} , wherein copper-tricyano-*n*-octylborate is excluded from the protection as a compound and *z* is 1 or 2. The alkali metal is preferably lithium which is preferably used as conducting salt and/or component of electrolytes for application in batteries, capacitors, sensors or for electrochemical processes, and sodium or potassium which 25 is preferably used for the synthesis of compounds of formula I as described above and below in which the cation $[Kt]^{z+}$ is a cation other than the used sodium or the used potassium, especially preferably for compounds of formula I in which the cation $[Kt]^{z+}$ is an organic cation.

30 If $[Kt]^{z+}$ is an organic cation, the organic cation is preferably selected from the group comprising iodonium, tritylium, sulfonium, oxonium, ammonium,

phosphonium, uronium, thiouronium, guanidinium cations or heterocyclic cations.

5 Examples of organic cations are also polyammonium ions having a degree of charging of 4 which means z denotes 4.

For organic cations, the following apply:

10 R^0 of the $[(R^0)_3O]^+$ cation (formula (1)) is preferably straight-chain alkyl having 1-8 C atoms, preferably having 1-4 C atoms, in particular methyl or ethyl, very particularly preferably ethyl.

15 R^0 of the $[(R^0)_3S]^+$ cation (formula (2)) is preferably straight-chain alkyl having 1-8 C atoms, preferably having 1-4 C atoms, in particular methyl or ethyl, very particularly preferably ethyl. This definition is preferably for the technical application as component of an electrolyte, e.g. for DSSC. Preferred cations for this application are diethyl-methylsulfonium and triethylsulfonium.

20 At least one substituent R^0 within the sulfonium cations of formula (2) is preferably phenyl or substituted phenyl in case the sulfonium cation is chosen together with the inventive anion as cationic polymerization initiator, photo-polymerization initiator or photo-acid generator. Particularly preferably all substituents R^0 in formula (2) are for this application each independently phenyl and/or phenyl substituted with SR' where R' has a meaning as described before.

25 Preferred cations of formula (2) for this application are triphenylsulfonium, diphenyltolylsulfonium, diphenylethylsulfonium, diphenyl-2,2,2-trifluorethyl sulfonium, diphenyl-2-ethoxy-ethylsulfonium, diphenyl-2-chlorethylsulfonium, diphenyl-3-brompropylsulfonium, diphenyl-3-chlorpropylsulfonium, diphenyl-3-cyanopropylsulfonium, diphenylallylsulfonium, diphenyl-4-pentenylsulfonium,

diphenylpropargylsulfonium, diphenylbenzylsulfonium, diphenyl(*p*-cyanobenzyl)sulfonium, diphenyl(*p*-methylbenzyl)sulfonium, diphenyl(*p*-phenylthiobenzyl)sulfonium, diphenyl(3,3-dicyano-2-phenyl-2-propenyl)sulfonium, diphenyl(*p*-methylphenacyl)sulfonium,

5 diphenyl(ethylcarboxy)methylsulfonium, diphenyl(*n*-octyl)sulfonium, diphenyl(*n*-octadecyl)sulfonium, diphenyl(ω -carboxytridecyl)sulfonium, diphenyl(3-oxypropyl)sulfonium, diphenyl(ω -carboxydodecyl)sulfonium, dihexyl-phenylsulfonium, ditolylphenylsulfonium, tritolylsulfonium, *m*- or *p*-(*tert*-butyl)phenyl-diphenylsulfonium, *m*- or *p*-methoxyphenyl-diphenylsulfonium, *m*- or *p*-CN-phenyl-diphenylsulfonium, *m*- or *p*-C₆H₁₃S-phenyl-diphenylsulfonium, *m*- or *p*-C₆H₅S-phenyl-diphenylsulfonium, Tri(*p*-methoxyphenyl)sulfonium, tri[4-(4-acetyl-phenylsulfanyl)phenyl]sulfonium, tri(4-*tert*-butylphenyl)sulfonium.

15 For the purposes of the present invention, fully unsaturated cycloalkyl substituents are also taken to mean aromatic substituents.

In accordance with the invention, suitable substituents R and R² to R¹³ of the compounds of the formulae (3) to (7) are preferably: H, C₁- to C₂₀-, in particular C₁- to C₁₄-alkyl groups, and saturated or unsaturated, i.e. also aromatic C₃- to C₇-cycloalkyl groups, which may be substituted by C₁- to C₆-alkyl groups, in particular phenyl which may be substituted by C₁- to C₆-alkyl groups.

25 The substituents R and R² in the compounds of the formula (3) or (4) may be identical or different. The substituents R and R² are preferably different.

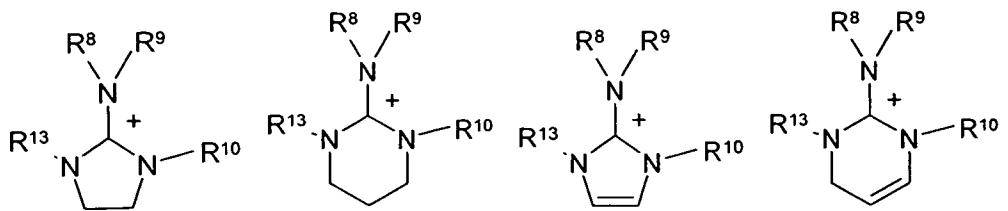
The substituents R and R² are particularly preferably methyl, ethyl, *iso*-propyl, propyl, *n*-butyl, *sec*-butyl, pentyl, hexyl, octyl, decyl or tetradecyl.

Up to four substituents of the guanidinium cation

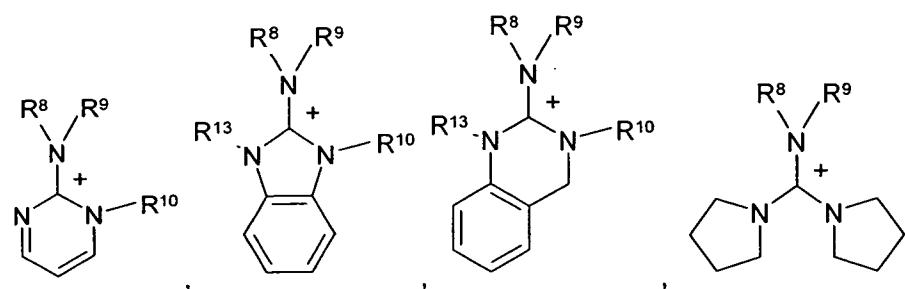
$[\text{C}(\text{NR}^8\text{R}^9)(\text{NR}^{10}\text{R}^{11})(\text{NR}^{12}\text{R}^{13})]^+$ may also be bonded in pairs in such a way that mono-, bi- or polycyclic cations are formed.

Without restricting generality, examples of such guanidinium cations are:

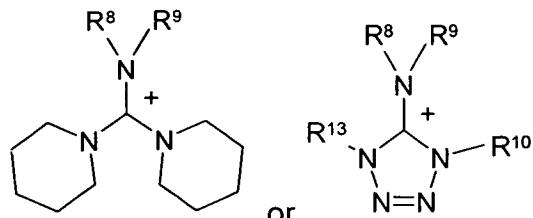
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where the substituents R^8 to R^{10} and R^{13} can have a meaning or particularly preferred meaning indicated above.

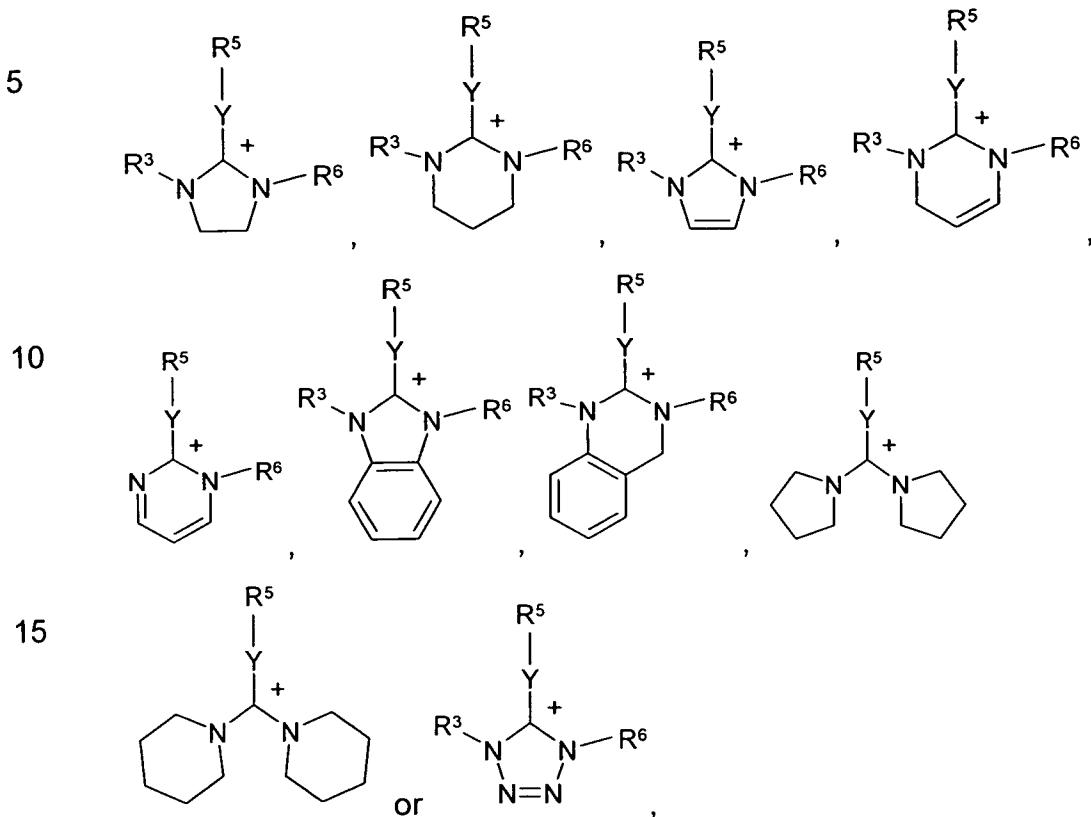
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If desired, the carbocycles or heterocycles of the guanidinium cations indicated above may also be substituted by straight-chain or branched C_1 - to C_6 -alkyl, straight-chain or branched C_1 - to C_6 -alkenyl, $-\text{CN}$, $-\text{NO}_2$, F , Cl , Br , I , OH , straight-chain or branched C_1 - C_6 -alkoxy, $-\text{N}(\text{R}')_2$, $-\text{SR}'$, $-\text{S}(\text{O})\text{R}'$, $-\text{SO}_2\text{R}'$, $-\text{COOH}$, $-\text{C}(\text{O})\text{OR}'$, $-\text{C}(\text{O})\text{R}'$, $-\text{C}(\text{O})\text{N}(\text{R}')_2$, $-\text{SO}_2\text{N}(\text{R}')_2$, $-\text{C}(\text{O})\text{X}$, $-\text{SO}_2\text{X}$, $-\text{SO}_3\text{H}$, substituted or non-substituted phenyl or a non-substituted or substituted heterocycle, where X and R' have a meaning indicated above.

30

Up to four substituents of the uronium cation $[\text{C}(\text{NR}^3\text{R}^4)(\text{OR}^5)(\text{NR}^6\text{R}^7)]^+$ or thiouronium cation $[\text{C}(\text{NR}^3\text{R}^4)(\text{SR}^5)(\text{NR}^6\text{R}^7)]^+$ may also be bonded in pairs in such a way that mono-, bi- or polycyclic cations are formed.

Without restricting generality, examples of such cations are indicated below, where Y = O or S:



where the substituents R³, R⁵ and R⁶ can have a meaning or particularly preferred meaning indicated above.

If desired, the carbocycles or heterocycles of the cations indicated above may also be substituted by straight-chain or branched C₁- to C₆-alkyl, straight-chain or branched C₁- to C₆-alkenyl, -CN, -NO₂, F, Cl, Br, I, OH, straight-chain or branched C₁-C₆-alkoxy, -N(R')₂, -SR', -S(O)R', -SO₂R', -COOH, -C(O)OR', -C(O)R', -C(O)N(R')₂, -SO₂N(R')₂, -C(O)X, -SO₂X, -SO₃H, substituted or non-substituted phenyl or a non-substituted or substituted heterocycle, where X and R' have a meaning indicated above.

The substituents R³ to R¹³ are each, independently of one another, preferably a straight-chain or branched alkyl group having 1 to 16 C atoms. The substituents R³ and R⁴, R⁶ and R⁷, R⁸ and R⁹, R¹⁰ and R¹¹ and R¹² and R¹³

in compounds of the formula (5) to (7) may be identical or different. R³ to R¹³ are particularly preferably each, independently of one another, methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *tert*-butyl, *sec*-butyl, phenyl, hexyl or cyclohexyl, very particularly preferably methyl, ethyl, *n*-propyl, *iso*-propyl, 5 *n*-butyl or hexyl.

In accordance with the invention, suitable substituents R¹ to R⁴ of compounds of the formula (8) are each, independently of one another, preferably,

10 H,
straight-chain or branched alkyl having 1 to 20 C atoms, which optionally may be fluorinated or perfluorinated,
straight-chain or branched alkenyl having 2 to 20 C atoms and one or more double bonds, which optionally may be fluorinated,
15 straight-chain or branched alkynyl having 2 to 20 C atoms and one or more triple bonds which optionally may be fluorinated or
straight-chain or branched alkoxyalkyl having 2 to 8 C atoms,
with the assumption that R¹ and R⁴ are not simultaneously be
perfluorinated.

20 The substituents R¹ and R⁴ are each, independently of one another, particularly preferably straight-chain or branched alkyl having 1 to 20 C atoms, which optionally may be fluorinated or perfluorinated or straight-chain or branched alkoxyalkyl having 2 to 8 C atoms with the assumption
25 that R¹ and R⁴ are not perfluorinated at the same time.
The substituents R¹ and R⁴ are each, independently of one another, particularly preferably methyl, ethyl, allyl, *iso*-propyl, propyl, *n*-butyl, *sec*-butyl, *tert*-butyl, *n*-pentyl, *n*-hexyl, *n*-octyl, *n*-decyl, cyclohexyl, methoxyethyl, methoxymethyl, ethoxyethyl or ethoxymethyl. They are very particularly
30 preferably methyl, ethyl, propyl, *n*-butyl or methoxyethyl. In pyrrolidinium, piperidinium or indolinium compounds, the two substituents R¹ and R⁴ are preferably different.

In accordance with the invention, suitable substituents R² and R³ of compounds of formula (8) are particularly preferably: H, straight-chain or branched C₁- to C₂₀-, in particular C₁- to C₁₂-alkyl groups.

5

The substituent R² or R³ is in each case, independently of one another, in particular H, methyl, ethyl, *iso*-propyl, propyl, *n*-butyl, *sec*-butyl or *tert*-butyl. R² is particularly preferably H, methyl, ethyl, *iso*-propyl, propyl, *n*-butyl or *sec*-butyl. R³ is particularly preferably H. R² and R³ are very particularly preferably H.

10

A straight-chain or branched alkyl having 1-20 C atoms denotes an alkyl group having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 C atoms, for example methyl, ethyl, *iso*-propyl, *n*-propyl, *iso*-butyl, *n*-butyl, *tert*-butyl, *n*-pentyl, 1-, 2- or 3-methylbutyl, 1,1-, 1,2- or 2,2-dimethylpropyl, 1-ethylpropyl, *n*-hexyl, *n*-heptyl, *n*-octyl, ethylhexyl, *n*-nonyl, *n*-decyl, *n*-undecyl, *n*-dodecyl, *n*-tridecyl, *n*-tetradecyl, *n*-pentadecyl, *n*-hexadecyl, *n*-heptadecyl, *n*-octadecyl, *n*-nonadecyl or eicosyl, which optionally may be fluorinated or perfluorinated. The term "perfluorinated" means that all H atoms are substituted by F atoms in the given alkyl group. The term "fluorinated" means that at least one H atom of the given alkyl group is substituted by an F atom.

15

A straight-chain or branched alkenyl having 2 to 20 C atoms, in which a plurality of double bonds may also be present, is, for example, allyl, 2- or 3-butenyl, *iso*-butenyl, *sec*-butenyl, furthermore 4-pentenyl, *iso*-pentenyl, hexenyl, heptenyl, octenyl, -C₉H₁₇, -C₁₀H₁₉ to -C₂₀H₃₉, preferably allyl, 2- or 3-butenyl, *iso*-butenyl, *sec*-butenyl, furthermore preferably 4-pentenyl, *iso*-pentenyl or hexenyl, which may be optionally partially fluorinated.

20

A straight-chain or branched alkynyl having 2 to 20 C atoms, in which a plurality of triple bonds may also be present, is, for example, ethynyl, 1- or 2-

propynyl, 2- or 3-butynyl, furthermore 4-pentynyl, 3-pentynyl, hexynyl, heptynyl, octynyl, $-C_9H_{15}$, $-C_{10}H_{17}$ to $-C_{20}H_{37}$, preferably ethynyl, 1- or 2-propynyl, 2- or 3-butynyl, 4-pentynyl, 3-pentynyl or hexynyl, which may be optionally partially fluorinated.

5

A straight-chain or branched alkoxyalkyl having 2 to 12 C atoms is, for example, methoxymethyl, 1-methoxyethyl, 1-methoxypropyl, 1-methoxy-2-methyl-ethyl, 2-methoxy-propyl, 2-methoxy-2-methyl-propyl, 1-methoxybutyl, 1-methoxy-2,2-dimethyl-ethyl, 1-methoxy-pentyl, 1-

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methoxyhexyl, 1-methoxy-heptyl, ethoxymethyl, 1-ethoxyethyl, 1-ethoxypropyl, 1-ethoxy-2-methyl-ethyl, 1-ethoxybutyl, 1-ethoxy-2,2-dimethyl-ethyl, 1-ethoxypentyl, 1-ethoxyhexyl, 1-ethoxyheptyl,

propoxymethyl, 1-propoxyethyl, 1-propoxypropyl, 1-propoxy-2-methyl-ethyl, 1-propoxybutyl, 1-propoxy-2,2-dimethyl-ethyl, 1-propoxypentyl, butoxymethyl, 1-butoxyethyl, 1-butoxypropyl or 1-butoxybutyl. Particularly preferred is methoxymethyl, 1-methoxyethyl, 2-methoxy-propyl, 1-methoxypropyl, 2-methoxy-2-methyl-propyl or 1-methoxybutyl. The numeration begins from the last carbon in the alkyl chain.

20

Aryl with 6 to 30 C atoms denotes an aryl group with 6 to 30 C atoms and is an aromatic group with aromatic delocalized electrons, optionally substituted one or more times by R¹⁺, OR', N(R')₂, CN, NO₂ or halogen. An aryl group with 6 to 30 C atoms, preferably with 6 to 24 C atoms, is for example 1-2

25

or 8-phenanthrenyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-anthracyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11- or 12-tetracyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11- or 12-benzo[a]anthracyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-,

11-, 12-, 13- or 15-pentacenyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11- or 12-chrysenyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-pyrenyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11- or 12-benzo[a]pyrenyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- or 8-azulenyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-fluoranthenyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-,

30

, 8-, 9-, 10-, 11- or 12-benzo[a]pyrenyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- or 8-azulenyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-fluoranthenyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11- or 12-perylenyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-indenyl or 1-, 2-, 3-, 4-,

5-, 6-, 7-, 8- or 9-fluorenyl which is preferably non-substituted or substituted by R¹, OR', N(R')₂, CN or halogen. Preferably, aryl denotes 1-, 2-, 3-, 4-, 5- or 6-phenyl and 1-, 2-, 3-, 4-, 6-, 7- or 8-naphthyl which are non-substituted or substituted by R¹, OR', N(R')₂, CN or halogen. R¹ and R' have a meaning as described above.

5

Aryl-C₁-C₆-alkyl denotes, for example, benzyl, phenylethyl, phenylpropyl, phenylbutyl, phenylpentyl or phenylhexyl, where both the phenyl ring and also the alkylene chain may be partially or fully substituted, as described above, by halogens, in particular -F and/or -Cl, or partially by -OH, -OR', -N(R')₂, -CN, -C(O)OH, -C(O)N(R')₂, -SO₂N(R')₂, -C(O)X, -C(O)OR', -C(O)R', -SO₂OH, -SO₂X, -SR', -S(O)R', -SO₂R', -NO₂ and R' and X have a meaning as described above.

10

15 Non-substituted saturated or partially or fully unsaturated cycloalkyl groups having 3-7 C atoms are therefore cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclopentenyl, cyclopenta-1,3-dienyl, cyclohexenyl, cyclohexa-1,3-dienyl, cyclohexa-1,4-dienyl, phenyl, cycloheptenyl, cyclohepta-1,3-dienyl, cyclohepta-1,4-dienyl or cyclohepta-1,5-dienyl, each of 20 which may be substituted by straight-chain or branched C₁- to C₆-alkyl groups, where the cycloalkyl group or the cycloalkyl group substituted by straight-chain or branched C₁- to C₆-alkyl groups may in turn also be substituted by halogen atoms, such as F, Cl, Br or I, in particular F or Cl, or by -OH, -OR', -N(R')₂, -CN, -C(O)OH, -C(O)N(R')₂, -SO₂N(R')₂, -C(O)X, -C(O)OR', -C(O)R', -SO₂OH, -SO₂X, -SR', -S(O)R', -SO₂R', -NO₂ and R' and 25 X have a meaning as described above.

20

25

In the substituents R, R² to R¹³ or R¹' to R⁴', one or two non-adjacent carbon atoms which are not bonded in the α -position to the heteroatom may 30 also be replaced by atoms and/or atom groups selected from the group -O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -C(O)-, -C(O)O-, -N⁺R'₂-, -P(O)R'O-, -C(O)NR'-, -SO₂NR'-, -OP(O)R'O-, -P(O)(NR'₂)NR'-, -PR'₂=N- or -P(O)R'-, where R'

is non-fluorinated, partially fluorinated or perfluorinated C₁- to C₁₈-alkyl, saturated C₃- to C₇-cycloalkyl, non-substituted or substituted phenyl.

Without restricting generality, examples of substituents R, R² to R¹³ and R^{1'}

5 to R^{4'} modified in this way are:

-OCH₃, -OCH(CH₃)₂, -CH₂OCH₃, -CH₂-CH₂-O-CH₃, -C₂H₄OCH(CH₃)₂,
-C₂H₄SC₂H₅, -C₂H₄SCH(CH₃)₂, -S(O)CH₃, -SO₂CH₃, -SO₂C₆H₅, -SO₂C₃H₇,
-SO₂CH(CH₃)₂, -SO₂CH₂CF₃, -CH₂SO₂CH₃, -O-C₄H₈-O-C₄H₉, -CF₃, -C₂F₅,
-C₃F₇, -C₄F₉, -C(CF₃)₃, -CF₂SO₂CF₃, -C₂F₄N(C₂F₅)C₂F₅, -CHF₂, -CH₂CF₃,
10 -C₂F₂H₃, -C₃FH₆, -CH₂C₃F₇, -C(CFH₂)₃, -CH₂C(O)OH, -CH₂C₆H₅, -C(O)C₆H₅
or P(O)(C₂H₅)₂.

In R' or in R^{1'}, C₃- to C₇-cycloalkyl is, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl or cycloheptyl.

15

In R' or in R^{1'}, substituted phenyl denotes phenyl which is substituted by straight-chain or branched C₁- to C₆-alkyl, straight-chain or branched C₁- to C₆-alkenyl, -CN, -NO₂, F, Cl, Br, I, -OH, straight-chain or branched-C₁-C₆-alkoxy, N(R'')₂, -COOH, -C(O)OR'', -C(O)R'', -SO₂X', -SR'', -S(O)R'', -

20

SO₂R'', SO₂N(R'')₂ or SO₃H, where X' denotes F, Cl or Br and R'' denotes a non-fluorinated, partially fluorinated or perfluorinated straight-chain or branched C₁- to C₆-alkyl or C₃- to C₇-cycloalkyl as defined for R', for example o-, m- or p-methylphenyl, o-, m- or p-ethylphenyl, o-, m- or p-propylphenyl, o-, m- or p-isopropylphenyl, o-, m- or p-tert-butylphenyl, o-,

25

m- or p-nitrophenyl, o-, m- or p-hydroxyphenyl, o-, m- or p-methoxyphenyl, o-, m- or p-ethoxyphenyl, o-, m-, p-(trifluoromethyl)phenyl, o-, m-, p-(trifluoromethoxy)phenyl, o-, m-, p-(trifluoromethylsulfonyl)phenyl, o-, m- or p-fluorophenyl, o-, m- or p-chlorophenyl, o-, m- or p-bromophenyl, o-, m- or p-iodophenyl, further preferably 2,3-, 2,4-, 2,5-, 2,6-, 3,4- or 3,5-dimethyl-

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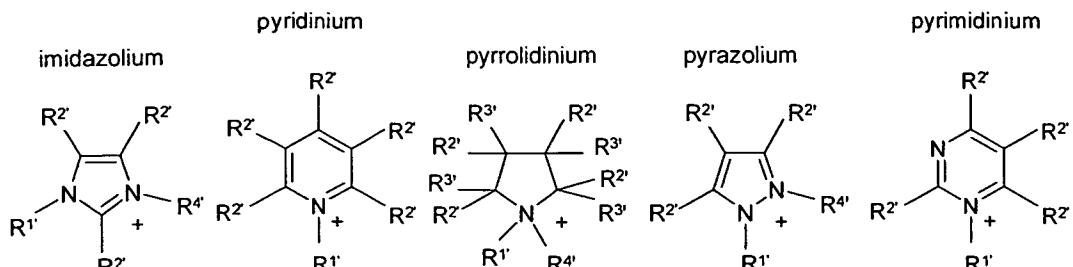
phenyl, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- or 3,5-dihydroxyphenyl, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- or 3,5-difluorophenyl, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- or 3,5-dichlorophenyl, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- or 3,5-dibromophenyl, 2,3-, 2,4-, 2,5-, 2,6-,

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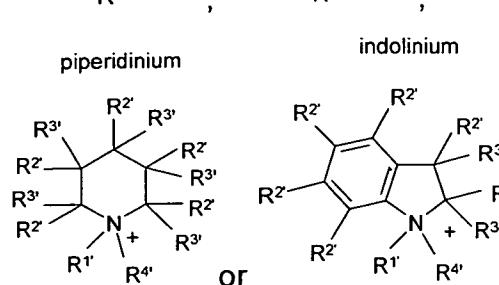
3,4- or 3,5-dimethoxyphenyl, 5-fluoro-2-methylphenyl, 3,4,5-trimethoxy-phenyl or 2,4,5-trimethylphenyl.

HetN^{z+} is preferably

5



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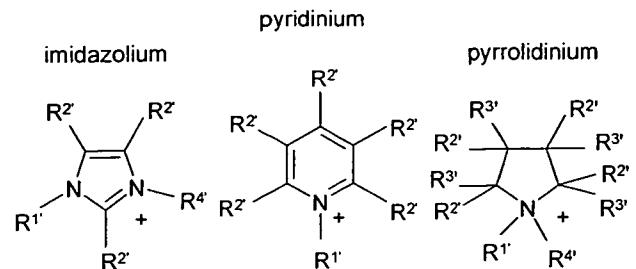


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where the substituents R^1 to R^4 each, independently of one another, have a meaning described above.

HetN^{z+} is particularly preferably

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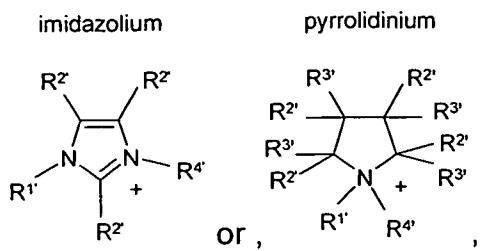


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where the substituents R^1 to R^4 each, independently of one another, have a meaning described above.

HetN^{z+} is very particularly preferably

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where the substituents R¹ to R⁴ each, independently of one another, have a meaning described above. Preferred meanings of R¹ to R⁴ within imidazolium or pyrrolidinium cations are defined in the following terms:

Preferred 1,1-dialkylpyrrolidinium cations are, for example, 1,1-dimethylpyrrolidinium, 1-methyl-1-ethylpyrrolidinium, 1-methyl-1-propylpyrrolidinium, 1-methyl-1-butylpyrrolidinium, 1-methyl-1-pentylpyrrolidinium, 1-methyl-1-hexylpyrrolidinium, 1-methyl-1-heptylpyrrolidinium, 1-methyl-1-octylpyrrolidinium, 1-methyl-1-nonylpyrrolidinium, 1-methyl-1-decylpyrrolidinium, 1,1-diethylpyrrolidinium, 1-ethyl-1-propylpyrrolidinium, 1-ethyl-1-butylpyrrolidinium, 1-ethyl-1-pentylpyrrolidinium, 1-ethyl-1-hexylpyrrolidinium, 1-ethyl-1-heptylpyrrolidinium, 1-ethyl-1-octylpyrrolidinium, 1-ethyl-1-nonylpyrrolidinium, 1-ethyl-1-decylpyrrolidinium, 1,1-dipropylpyrrolidinium, 1-propyl-1-methylpyrrolidinium, 1-propyl-1-butylpyrrolidinium, 1-propyl-1-pentylpyrrolidinium, 1-propyl-1-hexylpyrrolidinium, 1-propyl-1-heptylpyrrolidinium, 1-propyl-1-octylpyrrolidinium, 1-propyl-1-nonylpyrrolidinium, 1-propyl-1-decylpyrrolidinium, 1,1-dibutylpyrrolidinium, 1-butyl-1-methylpyrrolidinium, 1-butyl-1-pentylpyrrolidinium, 1-butyl-1-hexylpyrrolidinium, 1-butyl-1-heptylpyrrolidinium, 1-butyl-1-octylpyrrolidinium, 1-butyl-1-nonylpyrrolidinium, 1-butyl-1-decylpyrrolidinium, 1,1-dipentylpyrrolidinium, 1-pentyl-1-hexylpyrrolidinium, 1-pentyl-1-heptylpyrrolidinium, 1-pentyl-1-octylpyrrolidinium, 1-pentyl-1-nonylpyrrolidinium, 1-pentyl-1-decylpyrrolidinium, 1,1-dihexylpyrrolidinium, 1-hexyl-1-heptylpyrrolidinium, 1-hexyl-1-octylpyrrolidinium, 1-hexyl-1-nonylpyrrolidinium, 1-hexyl-1-decylpyrrolidinium, 1,1-dihexylpyrrolidinium, 1-hexyl-1-heptylpyrrolidinium, 1-hexyl-1-octylpyrrolidinium, 1-hexyl-1-nonylpyrrolidinium, 1-hexyl-1-decylpyrrolidinium, 1,1-diheptylpyrrolidinium, 1-heptyl-1-octylpyrrolidinium, 1-heptyl-1-nonylpyrrolidinium,

1-heptyl-1-decylpyrrolidinium, 1,1-dioctylpyrrolidinium, 1-octyl-1-nonylpyrrolidinium, 1-octyl-1-decylpyrrolidinium, 1,1-dinonylpyrrolidinium, 1-nonyl-1-decylpyrrolidinium or 1,1-didecylpyrrolidinium. Very particular preference is given to 1-butyl-1-methylpyrrolidinium or 1-propyl-1-methylpyrrolidinium.

5

Preferred 1-alkyl-1-alkoxyalkylpyrrolidinium cations are, for example, 1-methoxymethyl-1-methylpyrrolidinium, 1-methoxymethyl-1-ethylpyrrolidinium, 1-(2-methoxyethyl)-1-methylpyrrolidinium, 1-(2-methoxyethyl)-1-ethylpyrrolidinium, 1-(2-methoxyethyl)-1-propylpyrrolidinium, 1-(2-methoxyethyl)-1-butylypyrrolidinium, 1-(2-ethoxyethyl)-1-methylpyrrolidinium, 1-ethoxymethyl-1-methylpyrrolidinium, 1-ethoxymethyl-1-ethylpyrrolidinium. Very particular preference is given to 1-(2-methoxyethyl)-1-methylpyrrolidinium.

10

Preferred 1,3-dialkylimidazolium cations are, for example, 1-ethyl-3-methylimidazolium, 1-methyl-3-propylimidazolium, 1,2,3-trimethylimidazolium, 1-ethyl-2,3-dimethylimidazolium, 1-propyl-2,3-dimethylimidazolium, 1-butyl-2,3-dimethylimidazolium, 1-butyl-3-methylimidazolium, 1-methyl-3-

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pentylimidazolium, 1-ethyl-3-propylimidazolium, 1-butyl-3-ethylimidazolium, 1-ethyl-3-pentylimidazolium, 1-butyl-3-propylimidazolium, 1,3-dimethylimidazolium, 1,3-diethylimidazolium, 1,3-dipropylimidazolium, 1,3-dibutylimidazolium, 1,3-dipentylimidazolium, 1,3-dihexylimidazolium, 1,3-dihexylimidazolium, 1,3-dioctylimidazolium, 1,3-dinonylimidazolium, 1,3-

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didecylimidazolium, 1-hexyl-3-methylimidazolium, 1-heptyl-3-methylimidazolium, 1-methyl-3-octylimidazolium, 1-methyl-3-nonylimidazolium, 1-decyl-3-methylimidazolium, 1-ethyl-3-hexylimidazolium, 1-ethyl-3-heptylimidazolium, 1-ethyl-3-octylimidazolium, 1-ethyl-3-nonylimidazolium or 1-decyl-3-ethylimidazolium. Particularly preferred cations are 1-ethyl-3-methylimidazolium, 1-butyl-3-methylimidazolium or 1-methyl-3-propylimidazolium.

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Preferred 1-alkoxyalkyl-3-alkylimidazolium cations are, for example 1-methoxymethyl-3-methylimidazolium, 1-methoxymethyl-3-ethylimidazolium, 1-methoxymethyl-3-butylimidazolium, 1-(2-methoxyethyl)-3-methylimidazolium, 1-(2-methoxyethyl)-3-ethylimidazolium, 1-(2-methoxyethyl)-3-propylimidazolium, 1-(2-methoxyethyl)-3-butylimidazolium, 1-(2-ethoxyethyl)-3-methylimidazolium, 1-ethoxymethyl-3-methylimidazolium.

Preferred 1-alkenyl-3-alkylimidazolium cations are, for example 1-allyl-3-methyl-imidazolium or 1-allyl-2,3-dimethylimidazolium.

10

The organic cations of the compounds of formula I or compounds of formulae IA to IE according to the invention are preferably sulfonium, ammonium, phosphonium cations of formula (2), (3) and (4) or heterocyclic cations of formula (8), particularly preferably sulfonium cations of formula (2) or heterocyclic cations of formula (8) as described above.

15

The organic cations of the compounds of formula I according to the invention are very particularly preferably heterocyclic cations of formula (8) in which HetN^{z+} is as defined above, where the substituents R^1 to R^4 each, independently of one another, have a meaning described above, for the application as electrolyte component. The organic cation of the compound of formula I is very particularly preferably imidazolium, where the substituents R^1 to R^4 each, independently of one another, have a meaning described above or has one of the particularly preferred meanings of 1,3-dialkylimidazolium, 1-alkenyl-3-alkylimidazolium or 1-alkoxyalkyl-3-alkylimidazolium as described above.

20

25

Particularly suitable organic cations of the formula I are for this application 1-butyl-1-methylpyrrolidinium, 1-ethyl-3-methylimidazolium, 1-ethyl-2,3-dimethylimidazolium, 1-(2-methoxyethyl)-3-methylimidazolium, 1-butyl-3-methylimidazolium, tributyl-methylammonium, tetra-*n*-butylammonium, tributyl-methylphosphonium, tetra-phenylphosphonium, diethyl-

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methylsulfonium, S-ethyl-N,N,N',N'-tetramethylisothiouronium, 1-allyl-3-methylimidazolium, 1-allyl-2,3-dimethylimidazolium, 1-cyanomethyl-3-methylimidazolium, 1-methyl-3-propynylimidazolium, 1,1-dimethylpyrrolidinium or trimethylsulfonium.

5

It goes without saying to the person skilled in the art that substituents, such as, for example, C, H, N, O, Cl, F, in the compounds according to the invention may be replaced by the corresponding isotopes.

10

Compounds of formula I in which $[Kt]^{z+}$ is Li^+ can be preferably used as conductive salts in primary batteries, secondary batteries, capacitors, supercapacitors or electrochemical cells, optionally also in combination with further conductive salts and/or additives, as constituent of a polymer electrolyte or phase-transfer medium.

15

Compounds of formula I or formulae IA to IE, in which $[Kt]^{z+}$ is Na^+ or K^+ can be preferably used as starting materials for compounds of formula I or formulae IA to IE in which $[Kt]^{z+}$ is an organic cation or another inorganic cation than sodium or potassium.

20

Compounds of formula I in which $[Kt]^{z+}$ corresponds to formula (2), (5), (6), (9), tritylium, pyrylium, 1-benzopyrylium or 2-benzopyrylium as described above or preferably described above are preferably used as cationic polymerization initiator, photo-polymerization initiator or photo-acid generator.

25

Particularly preferred organic cations to be used for this technical application corresponds to triarylsulfonium- or diaryliodonium cations in which aryl is defined as described above for the cations of formula (9).

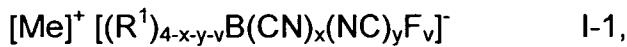
Very particularly preferred organic cations to be used for this technical

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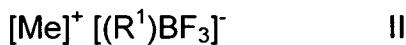
application as cationic polymerization initiator, photo-polymerization initiator or photo-acid generator are triphenylsulfonium, tritolylsulfonium, *p*-(*tert*-butyl)phenyl-diphenylsulfonium, *p*-methoxyphenyl-diphenylsulfonium, *p*-

$C_6H_{13}S$ -phenyl-diphenylsulfonium, *m*- or (p - C_6H_5S -phenyl)-diphenylsulfonium, tri[4-(4-acetyl-phenylsulfanyl)phenyl]sulfonium, tri(4-*tert*-butylphenyl)sulfonium, diphenyliodonium, ditolyliodonium, phenyltolyliodonium, di(*p*-*tert*-butylphenyl)iodonium, *m*- or (p - C_6H_5S -phenyl)-phenyliodonium or tolyl-(4-*sec*.-butylphenyl)iodonium.

In addition, the invention relates to a process for the preparation of a compound of formula I as described before in which $[Kt]^{z+}$ is an alkali metal cation, z denotes 1 and the sum of $x+y+v$ denotes 3, which denotes a compound of formula I-1,



in which $[Me]^+$ denotes an alkali metal cation and R^1 , x , y and v have a meaning as described or preferably described, comprising the reaction of a compound of formula II



in which $[Me]^+$ denotes an alkali metal cation and R^1 has a meaning as described or preferably described above with trialkylsilylcyanide, in which the alkyl groups are each independently of one another straight-chain or branched alkyl having 1 to 8 C atoms.

Compounds of formula II are in most cases commercially available or can be synthesized by known processes.

Trialkylsilylcyanide in which the alkyl groups independently denotes straight-chain or branched alkyl groups having 1 to 8 C atoms are in some cases commercially available or can be synthesised by known processes. For example, it is possible to generate trialkylsilylcyanide by the reaction of alkali metal cyanide with trialkylsilylchloride in the presence of alkali metal iodide and optionally elemental iodine (M.T. Reetz, I. Chatziosifidis, Synthesis, 1982, p. 330; J.K. Rasmussen, S. M. Heilmann and L.R. Krebski, The Chemistry of Cyanotrimethylsilane in G.L. Larson

(Ed.) „Advances in Silicon Chemistry“, Vol. 1, p. 65-187, JAI Press Inc., 1991; WO 2008/102661 A1).

5 The use of sodium cyanide and sodium iodide or potassium cyanide or potassiumiodide is particular preferred. Preferably, the alkalinetaliodide will be used in 0.1 mol/l related to 1 mol/l alkalicyanide and trialkylsilylchloride. The reaction has to be carried out in a dry atmosphere, for example under dry air, nitrogen or argon.

10 The alkyl groups of trialkylsilylcyanide may be the same or different. Preferably, they are the same. Examples of trialkylsilylcyanides are such as trimethylsilylcyanide, triethylsilylcyanide, dimethylethylsilylcyanide, triisopropylsilylcyanide, tripropylsilylcyanide or tributylsilylcyanide. Particularly preferred is the use of trimethylsilylcyanide.

15 This process can be carried out in air, preferably in a dry atmosphere, for example under dry air, nitrogen or argon.

20 Trialkylsilylchloride can be used as additive in the above described process in excess of 0.1 mol % to 50 mol % to the other described reagents. Addition of catalytic quantitities (0.1 mol % to 50 mol %) or excess of trialkylsilylchloride when trialkylsilylcyanide is generated *in situ* accelerate the reaction of the compound of formula II as described above with trialkylsilylcyanide. Without being bound by said theory it is believed that 25 trialkylsilylchloride acts in this reaction as catalyst.

30 The reaction for the synthesis of compounds of formula IA as described above in which $[Kt]^{z+}$ is an alkali metal cation is carried out without a solvent or with a solvent using at least 2 equivalents of the trialkylsilylcyanide which is described above.

Preferred organic solvents are acetonitrile, propionitrile, benzonitrile, monoglyme, diglyme, tetrahydrofuran or dioxane, preferably acetonitrile.

The reaction for the synthesis of compounds of formula IA as described above in which $[Kt]^{z+}$ is an alkali metal cation without a solvent is carried out at temperatures between 30°C and 70°C, preferably at 50°C and the reaction time is in the range of minutes to hours, preferably 30 minutes. If the reaction is carried out in an organic solvent, the reaction temperature is between 70°C and 120°C, preferably at 100°C and the reaction time is in the range of hours, preferably 4 hours. It is possible that this reaction is carried out in the presence of ethoxytrimethylsilane while the reaction temperature is in this case room temperature and the reaction time is in the range of hours, preferably 12 hours. The reaction time can be reduced by addition of catalytic amount of trialkylsilylchloride as additive as described before.

The reaction for the synthesis of compounds of formula IB or IC as described above in which $[Kt]^{z+}$ is an alkali metal cation is carried out without a solvent or with a solvent using at least 3 equivalents of the trialkylsilylcyanide which is described above.

In this type of reaction, the reaction is preferably carried out without a solvent.

The reaction for the synthesis of compounds of formula IB as described above in which $[Kt]^{z+}$ is an alkali metal cation without a solvent is carried out at temperatures between 70°C and 120°C, preferably at 110°C and the reaction time is in the range of days, preferably 3 days, followed by an oxidative purification with aqueous H_2O_2 (5-30 weight.%)

In addition, it is possible to isomerise a compound of formula IC as described above, in which $[Kt]^{z+}$ is an alkali metal cation through heating at temperatures between 70°C and 120°C resulting in the corresponding compound of formula IB having the same alkali metal cation as the starting

material. The reaction conditions, especially the reaction temperatures and reaction times strongly depend on the kind of the substituent R¹. Slight modifications belong to the general knowledge of the artisan in the field of preparative chemistry.

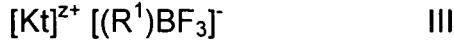
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The reaction for the synthesis of compounds of formula IC as described above in which [Kt]^{z+} is an alkali metal cation without a solvent is carried out at temperatures between 30°C and 100°C, preferably at 50°C to 80°C and the reaction time is in the range of days, preferably 3 days.

10

Additionally, the invention is directed to a process for the preparation of a compound of formula I as described before in which [Kt]^{z+} is an organic cation and the sum of x+y+v denotes 3, comprising the reaction of a compound of formula III

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in which [Kt]^{z+} denotes the organic cation and R¹ has a meaning as described above with trialkylsilylcyanide, in which the alkyl groups are each independently of one another straight-chain or branched alkyl having 1 to 8 C atoms. The reaction time can be reduced by addition of catalytic amount of trialkylsilylchloride as additive as described before.

25

The reaction for the synthesis of compounds of formula ID in which [Kt]^{z+} is an organic cation via the above described reaction of a compound of formula III as described before is carried out with a solvent using 1 equivalent of the trialkylsilylcyanide as described before. This reaction is carried out at room temperature within a reaction time of days, preferably 3 days. The reaction time can be reduced by addition of catalytic amount of trialkylsilylchloride as additive as described before.

30

The reaction for the synthesis of compounds of formula IC in which [Kt]^{z+} is an organic cation via the above described reaction of a compound of formula III as described before is carried out with a solvent using 3

equivalents of the trialkylsilylcyanide as described above. This reaction is carried out at room temperature and heated up to 90°C within a reaction time of days, preferably 3 days. The reaction time can be reduced by addition of catalytic amount of trialkylsilylchloride as additive as described before.

5

In addition, the invention relates to a process for the preparation of a compound of formula I as described before in which $[Kt]^{z+}$ is an alkali metal cation, z denotes 1 and the sum of $x+y+v$ denotes 2, comprising the reaction of a compound of formula IV



in which R^1 has a meaning as described above with trialkylsilylcyanide in the presence of an alkali metal fluoride, wherein the alkyl groups within the trialkylsilylcyanide are each independently of one another straight-chain or branched alkyl having 1 to 8 C atoms.

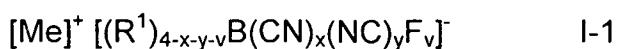
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This process describes especially the synthesis of compounds of formula I-E.

A compound of formula IV which is commercially available, is reacted with at least 2 equivalents of trialkylsilylcyanide in the presence of an alkali metal fluoride followed by an oxidative purification with aqueous H_2O_2 (5-30 weight %). This reaction is carried out in an organic solvent, preferably acetonitrile and the reaction temperature is room temperature and the reaction time is hours, preferably 12 hours.

25

In addition, the invention relates to a process for the preparation of a compound of formula I as described above in which $[Kt]^{z+}$ is another cation than the used alkali metal cation in the starting material in a salt-exchange reaction, characterized in that an alkali metal salt of formula I-1



30

in which $[Me]^+$ is an alkali metal cation and R^1 , x , y , v and the sum of $x+y+v$ have a meaning as described or preferably described before 1 is reacted with a compound of formula V

KtA V,

in which

Kt has a meaning of an organic cation or an inorganic cation other than the alkali metal cation of the compound of formula I-1 and

5 A denotes F^- , Cl^- , Br^- , I^- , OH^- , $[\text{HF}_2]^-$, $[\text{CN}]^-$, $[\text{SCN}]^-$, $[\text{R}_1\text{COO}]^-$,
 $[\text{R}_1\text{OC(O)O}]^-$, $[\text{R}_1\text{SO}_3]^-$, $[\text{R}_2\text{COO}]^-$, $[\text{R}_2\text{SO}_3]^-$, $[\text{R}_1\text{OSO}_3]^-$, $[\text{BF}_4]^-$, $[\text{PF}_6]^-$,
 $[\text{HSO}_4]^{1-}$, $[\text{NO}_3]^-$, $[(\text{R}_2)_2\text{P(O)O}]^-$, $[\text{R}_2\text{P(O)O}_2]^{2-}$, $[(\text{R}_1\text{O})_2\text{P(O)O}]^-$,
 $[(\text{R}_1\text{O})\text{P(O)O}_2]^{2-}$, $[(\text{R}_1\text{O})\text{R}_1\text{P(O)O}]^-$, tosylate, malonate which may be
substituted by straight-chain or branched alkyl groups having 1 to 4 C
10 atoms, $[\text{HOCO}_2]^-$ or $[\text{CO}_3]^{2-}$ (merely for the synthesis of other compounds
of formula I-1 having an other alkali metal cation than the starting material),
in which R_1 is each independently of another a straight-chain or branched
alkyl group having 1 to 12 C atoms and
R₂ is each independently of one another a straight-chain or branched
15 perfluorinated alkyl group having 1 to 12 C atoms and where
electroneutrality should be taken into consideration in the formula of the salt
KtA.

20 R₂ is particularly preferred trifluoromethyl, pentafluoroethyl or
nonafluorobutyl, very particularly preferred trifluoromethyl or
pentafluoroethyl.

R₁ is particularly preferred methyl, ethyl, n-butyl, n-hexyl or n-octyl, very
particularly preferred methyl or ethyl.

25 Compounds of formula I-1, as described above, are preferably used in the
metathesis reaction as described above.

Substituted malonates are for example methyl malonate or ethyl malonate.

30 The compounds of formula V are in most cases commercially available or
can be synthesised by known processes. Known processes for the

preparation of of compounds of formula V are described, for example, in P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Second Edition, WILEY-VCH, Weinheim, 2008.

5 The anion in the formula V is preferably OH^- , Cl^- , Br^- , I^- , $[\text{HF}_2]^-$, $[\text{CN}]^-$, $[\text{SCN}]^-$, $[\text{CH}_3\text{OC(O)O}]^-$, $[\text{CH}_3\text{C(O)O}]^-$, $[\text{CH}_3\text{SO}_3]^-$, $[\text{CF}_3\text{C(O)O}]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{CH}_3\text{OSO}_3]^-$, $[\text{SiF}_6]^{2-}$, $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{HSO}_4]^-$, $[\text{NO}_3]^-$, $[\text{C}_2\text{H}_5\text{OSO}_3]^-$, $[(\text{C}_2\text{F}_5)_2\text{P(O)O}]^-$, $[\text{C}_2\text{F}_5\text{P(O)O}_2]^{2-}$, tosylates, malonates or $[\text{SO}_4]^{2-}$ and $[\text{CO}_3]^{2-}$ with the proviso that $[\text{SO}_4]^{2-}$ and $[\text{CO}_3]^{2-}$ are used merely for the synthesis of compounds of formula I having another metal cation than the alkali metal cation of the compound of formula I-1, particularly preferably OH^- , Cl^- , Br^- , I^- , $[\text{CH}_3\text{SO}_3]^-$, $[\text{CH}_3\text{OSO}_3]^-$, $[\text{CF}_3\text{COO}]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[(\text{C}_2\text{F}_5)_2\text{P(O)O}]^-$ or $[\text{CO}_3]^{2-}$.

10 The anion in the formula V is very particularly preferably OH^- , Cl^- , Br^- , $[\text{CH}_3\text{OSO}_3]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{CH}_3\text{SO}_3]^-$ for the synthesis of compounds of formula I having an inorganic cation and the anion in the formula V is very particularly preferably OH^- , Cl^- , Br^- , $[\text{PF}_6]^-$, $[\text{CH}_3\text{OSO}_3]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{CH}_3\text{SO}_3]^-$ or $[(\text{C}_2\text{F}_5)_2\text{P(O)O}]^-$ for the synthesis of compounds of formula I having an organic cation or alternatively very particularly preferably OH^- , Cl^- , Br^- , $[\text{CH}_3\text{OSO}_3]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{CH}_3\text{SO}_3]^-$ or $[(\text{C}_2\text{F}_5)_2\text{P(O)O}]^-$ for the synthesis of compounds of formula I having an organic cation.

15 Suitable organic salts for the preparation of the compounds of the formula I in which $[\text{Kt}]^{z+}$ is an organic cation are salts with cations of formula (1) to (9) or tritylium or their preferred embodiments together with anions as defined as A described above or its preferred embodiments which means salts of cations of formula (1) to (9) or their preferred embodiments and OH^- , Cl^- , Br^- , $[\text{PF}_6]^-$, $[\text{CH}_3\text{OSO}_3]^-$, $[\text{CF}_3\text{SO}_3]^-$, $[\text{CH}_3\text{SO}_3]^-$ or $[(\text{C}_2\text{F}_5)_2\text{P(O)O}]^-$ anions.

20

25 Suitable substance for the preparation of the compound of the formula I in which $[\text{Kt}]^{z+}$ is H^+ are aqueous $\text{H}[\text{BF}_4]$ and $\text{H}[\text{PF}_6]$ or $\text{H}[\text{BF}_4]$ and $\text{H}[\text{PF}_6]$ in

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organic solvents, preferably in diethylether. Reaction of $K[R^1B(CN)_3]$ or $Na[R^1B(CN)_3]$ with $H[BF_4]$ or $H[PF_6]$ results in the formation of $H[R^1B(CN)_3]$ in solvated form in which R^1 has a meaning as described or preferably described above and poorly soluble potassium or sodium

5 hexafluorophosphate or tetrafluoroborate.

Suitable inorganic salts for the preparation of the compounds of the formula I in which $[Kt]^{z+}$ is a metal cation e.g. from the group silver, magnesium, copper, zinc and calcium are, for example,

10 Ag_2O , Ag_2CO_3 , $MgCO_3$, CuO , ZnO , $Zn[HCO_3]_2$, $CaCO_3$ or $Ca(OC(O)CH_3)_2$. Useful salts for metathesis reaction to another alkali metal salt of formula I than potassium are e.g. $LiBF_4$ or $LiPF_6$.

15 The reaction is advantageously carried out in water in the case of the compounds of formula I-1 or in organic solvent, where temperatures of 10°-100°C, preferably 15°-60°C, particularly preferably room temperature, are suitable.

20 However, the reaction can alternatively also be carried out for the compounds of formula I in organic solvents at temperatures between 10° and 100°C. Suitable solvents here are acetonitrile, dialkylethers, tetrahydrofurane, dioxane, dichloromethane, dimethoxyethane or an alcohol, for example methanol, ethanol or iso-propanol.

25 The present invention furthermore relates to the use of the compounds of formula I as described above as media for chemical reactions, as catalyst and/or as media in catalytical processes, as conducting salts, as components of electrolytes for the application in electrochemical cells, as components of supporting electrolytes for electrochemical processes, as 30 surfactants, as phase-transfer catalysts, as entrainer, as extractant; as antistatic additive, as plasticiser; as heat-transfer-medium, as modifier for membranes and textile materials; as lubricant, as additive to lubricant

compositions or to other engineering fluids; as hydraulic fluid or as additive to hydraulic fluids.

Preferably, compounds of formula I having inorganic cations as described

5 above are useful as catalyst, as conducting salts, as components of electrolytes for the application in electrochemical cells, as components of supporting electrolytes for electrochemical processes, as surfactants, as phase-transfer catalysts or as antistatic additive.

10 Preferably, compounds of formula I having organic cations as described above or H^+ are useful as media for chemical reactions, as catalyst and/or as media in catalytical processes, as conducting salts, as components of electrolytes for the application in electrochemical cells, as components of supporting electrolytes for electrochemical processes, as surfactants, as

15 phase-transfer catalysts, as entrainer, as extractant; as antistatic additive, as plasticiser; as heat-transfer-medium, as modifier for membranes and textile materials; as lubricant, as additive to lubricant compositions or to other engineering fluids; as hydraulic fluid or as additive to hydraulic fluids.

20 In the case of the use of the said organic salts of formula I as media in catalytical processes or as solvents, these are suitable in any type of reaction known to the person skilled in the art, for example for transition-metal- or enzyme-catalysed reactions, such as, for example, hydroformylation reactions, oligomerisation reactions, esterifications or

25 isomerisations, where the said list is not exhaustive.

On use as extractant, the organic salts of formula I can be employed to separate off reaction products, but also to separate off impurities, depending on the solubility of the respective component in the ionic liquid.

30 In addition, the ionic liquids may also serve as separation media in the separation of a plurality of components, for example in the distillative separation of a plurality of components of a mixture.

Further possible applications are use as plasticiser in polymer materials and as conductive salt or additive in various electrochemical cells and applications, for example in galvanic cells, in capacitors or in fuel cells.

5

Further fields of applications of the organic salts of formula I, according to this invention are solvents for carbohydrate containing solids in particular biopolymers and derivatives or degradation products thereof. In addition, these new compounds can be applied as lubricants, working fluids for machines, such as compressors, pumps or hydraulic devices. A further field of application is the field of particle or nanomaterial synthesis where these 10 ionic liquids can act as medium or additive.

15 The compounds of formula I in which $[Kt]^{z+}$ corresponds to formula (2), (5), (6), (9), tritylium, pyrylium, 1-benzopyrylium or 2-benzopyrylium as described above or preferably described above are preferably used as cationic polymerization initiator, photo-polymerization initiator or photo-acid generator.

20 A cationic polymerization initiator is able to start the polymerization of at least one monomer, for example the polymerization of cationic polymerizable compounds such as *iso*-butylene, styrene, vinylethers, lactones, lactames, cyclic ethers or epoxy-containing compounds.

25 The process of polymerization is started via radiation in case a photo-polymerization initiator is used which means that the mixture of photo-initiator and at least one monomer is irradiated through energetic rays such as light, electrons or gamma rays. This kind of photo-polymerization normally leads especially to quickly crosslinked end products. The 30 compounds of formula I with cations of formula (2), (5), (6), (9), tritylium, pyrylium, 1-benzopyrylium or 2-benzopyrylium as described above are

cationic photo-polymerization initiators. Particularly, compounds of formula I with cations of formula (2) and (9) are preferred.

5 Photo-polymerization initiators are often components of formulations of lacquers or resins which often need a curing in fractional amounts of seconds. The curing may be initiated through light, laser, electrons or gamma rays, especially through UV-light.

10 Photo-polymerization is often used in various technical applications for example for curing a coating film, forming a planographic printing plate, a resin letterpress printing plate and a printed circuit board, preparing a photoresist and a photomask, and making a black-and-white or color transfer sheet and a coloring sheet.

15 In case the compounds of formula I with cations of formula (2), (5), (6), (9), tritylium, pyrylium, 1-benzopyrylium or 2-benzopyrylium are irradiated with light, laser, electrons or gamma rays, they are able to build the corresponding Brønsted acid or Lewis acid on spot which means in a catalytic amount and are therefore able to start the polymerization through 20 this acid. Such compounds which show such a property are commonly known as photo-acid generator (PAG). PAG's are highly active and have been shown to catalyze the deprotection of acid-sensitive organic functional groups with good photospeeds. PAG's are very often used in resists.

25 Another object of the invention is therefore a curable composition comprising at least one compound of formula I with cations of formula (2), (5), (6), (9), tritylium, pyrylium, 1-benzopyrylium or 2-benzopyrylium as described before and at least one polymerizable compound.

30 Another object of the invention is therefore a curable composition comprising at least one compound of formula I with cations of formula (2)

and (9) as described or preferably described before and at least one polymerizable compound.

5 The compounds of formula I with organic cations, e.g. ionic liquids according to this invention may be preferably used in electrochemical and/or optoelectronic devices, especially in electrolyte formulations.

10 The present invention therefore relates furthermore to an electrolyte formulation comprising at least one compound of formula I as described above or preferably described.

15 Electrolyte formulations comprising compounds of formula I in which $[Kt]^{z+}$ is Li^+ or an organic cation can be preferably used in primary batteries, secondary batteries, capacitors, supercapacitors or electrochemical cells, optionally also in combination with further conductive salts and/or additives, as constituent of a polymer electrolyte or phase-transfer medium. Preferred batteries are lithium batteries or lithium-ion batteries. A preferred capacitor is a lithium-ion capacitor.

20 Electrolyte formulations comprising compounds of formula I as described or preferably described before can be preferably used in electrochemical and/or optoelectronic devices such as a photovoltaic cell, a light emitting device, an electrochromic or photo-electrochromic device, an electrochemical sensor and/or biosensor, particularly preferred in a dye 25 sensitized solar cell.

Such electrolyte formulations form a crucial part of the disclosed devices and the performance of the device largely depends on the physical and chemical properties of the various components of these electrolytes.

30 Factors which are still impeding the technical application of many electrochemical and/or optoelectronic devices and in particular of dye or

quantum dot sensitized solar cells, are reliability problems caused by the volatility of organic solvents based electrolytes. It is very difficult to maintain a tight sealing of the electrolyte in e.g. a DSC panel, which has to withstand the temperature differences of daily day-night cycles and the concomitant thermal expansion of the electrolyte. The abbreviation DSC means dye sensitized solar cell. This problem can be solved in principle by the use of 5 ionic liquid-based electrolytes. For review "Ionic liquid electrolytes for dye-sensitized solar cells" see: William R Pitner *et al.*, "Application of Ionic Liquids in Electrolyte System" *Green Chemistry*. vol.6, (2010).

10 Ionic liquids or liquid salts are typically ionic species which consist of an organic cation and a generally inorganic anion usually having melting points below 373 K. Various binary ionic liquid electrolytes have recently been applied to dye-sensitized solar cells. WO 2007/093961 and WO 2009/083901 describe so far the best power conversion efficiencies in ionic 15 liquid-based electrolytes for DSC containing a significant quantity of organic salts with tetracyanoborate (TCB) anions.

20 Electrolyte formulations according to the invention are alternatives to already known electrolyte formulations. They show especially in the field of electrolyte formulations of dye sensitized solar cells an good performance particularly under high temperature. The advantage of the use of compounds of formula I having an organic cation and an alkyl-cyano-borate or alkyl-cyanofluoroborate anion is their low viscosity and good thermal 25 stability.

25 In chemistry, an electrolyte is any substance containing free ions that make the substance electrically conductive. The most typical electrolyte is an ionic solution, but molten electrolytes and solid electrolytes are also possible.

30 An electrolyte formulation according to the invention is therefore an electrically conductive medium, basically due to the presence of at least one substance that is present in a dissolved and or in molten state and

undergo dissociation into ionic species, i.e. supporting an electric conductivity via motion of ionic species. However, the said electric conductivity may not be of the major relevance to the role of the electrolyte of a dye-sensitised solar cell. Therefore, the scope of this invention is not limited to highly conductive electrolyte media.

The term electrolyte may be used for the term electrolyte formulation as well comprising all ingredients as disclosed for the electrolyte formulation.

10 Typical molar concentrations of the borate anion as disclosed in formula I as described above or in formulae IA to ID as described above in the electrolyte formulations range from 0.1 to 5.5 M, preferably from 0.8 to 3.5 M. This molar concentration in the electrolyte may be achieved with one or more compounds of formula I in which Kt^{2+} has a meaning as described or 15 preferably described above.

Preferably, the molar concentration is achieved with at least one compound of formula I as described or preferably described above.

20 For the purpose of the present invention, the molar concentration refer to the concentration at 25°C.

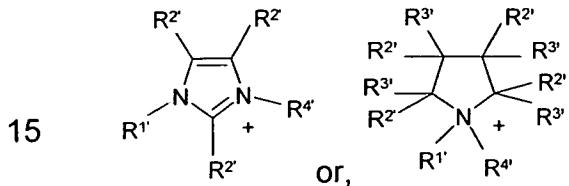
The present invention relates furthermore to an electrolyte formulation comprising at least one compound of formula I as described above or 25 preferably described together with redox active species such as iodide/tri-iodide, Ferrocene derivatives or Co(II)/Co(III) complex couples such as Co(II)/Co(III)(dbbip)₂ in which dbbip means 2,6-bis(1'-butylbenzimidazol-2'-yl)pyridine, Co(II)/Co(III)(bpy)₃ where bpy denotes bipyridine or alkylated bipyridine derivates thereof, the counter anion being either perchlorate, fluoroperfluoroalkylphosphate such as perfluoroethylpentafluorophosphate, 30 or (fluoro)cyanoborate, particularly tetracyanoborate, preferably a redox couple of iodine and at least one iodide salt.

The electrolyte formulation of the invention preferably comprises iodine (I_2). Preferably, it comprises from 0.0005 to 7 mol/dm³, more preferably 0.01 to 5 mol/dm³ and most preferably from 0.05 to 1 mol/dm³ of I_2 .

5 The iodide salt consists of an inorganic or organic cation and I^- as anion. There exists no limitation to the kind of cation. However, to limit the amount of different cations in the electrolyte formulations, especially for DSC, organic cations preferably be used as already described for the compounds of formula I. Particularly preferably, the electrolyte formulation comprises at 10 least one iodide salt in which the organic cation is independently selected from the group of

imidazolium

pyrrolidinium



in which the substituents

R^2 and R^3 each, independently of one another, denote H or straight-chain or branched alkyl having 1 to 20 C atoms,

20 R^1 and R^4 each, independently of one another, denote straight-chain or branched alkyl having 1-20 C atoms, which optionally may be partially fluorinated or perfluorinated, straight-chain or branched alkenyl having 2-20 C atoms and one or more double bonds, which optionally may be partially fluorinated, straight-chain or branched alkynyl having 2-20 C atoms and one or more triple bonds, which optionally may be partially fluorinated.

25

Particularly preferred examples of the at least one iodide salt are 1-ethyl-3-methylimidazolium iodide (emim I), 1-propyl-3-methylimidazolium iodide (pmim I), 1-butyl-3-methyl-imidazolium iodide (bmim I), 1-hexyl-3-methylimidazolium iodide (hmim I), 1,3-dimethyl-imidazolium iodide (mmim

I), 1-allyl-3-methylimidazolium iodide (amim I), N-butyl-N-methylpyrrolidinium iodide (bmpl I) or N,N-dimethyl-pyrrolidinium iodide (mmpl I).

Other components of the electrolyte formulation are one or several further
5 salts, solvents, and others, as indicated further below.

If the electrolyte formulation is a binary system, it comprises two salts, one further salt or iodide salt and a compound of formula I as described above.

If the electrolyte formulation is a ternary system, it comprises two further
10 salts and/or iodide salts and a compound of formula I as described above.

The binary system comprises 90-10 weight %, preferably 70-30 weight %, more preferably 55-40 weight % of the further salt or iodide salt and 10-90 weight %, preferably 30-70 weight % or more preferably 45-60 weight % of the compound of formula I as described above. The percentages in this

15 paragraph are expressed with respect to the total of salts (= 100 weight %) present in the electrolyte formulation according to the invention. Amounts of further, generally optional components (additives) indicated below, such as N-containing compounds having unshared electron pairs, iodine, solvents, polymers, and nanoparticles, for example, are not considered therein. The
20 same percentages apply to ternary or quaternary systems which means the total of the further salts has to be used in the given ranges, e.g. two further ionic liquids are comprised in e.g. 90-10 weight.% in the electrolyte formulation according to the invention.

25 According to another embodiment of the present invention, the electrolyte formulation comprises at least one further salt with organic cations comprising a quaternary nitrogen and an anion selected from a F⁻, Cl⁻, a polyhalide ion, a fluoroalkanesulfonate, a fluoroalkanecarboxylate, a tris(fluoroalkylsulfonyl)methide, a bis(fluoroalkylsulfonyl)imide,

30 bis(fluorsulfonyl)imide, a nitrate, a hexafluorophosphate, a tris-, bis- and mono-(fluoroalkyl)fluorophosphate, a tetrafluoroborate, a dicyanamide, a tricyanomethide, a tetracyanoborate, a thiocyanate, an alkylsulfonate or an

alkylsulfate, with fluoroalkane-chain having 1 to 20 C atoms, preferably perfluorinated, fluoroalkyl having 1 to 20 C atoms and alkyl having 1 to 20 C atoms. Fluoroalkane-chain or fluoroalkyl is preferably perfluorinated.

5 Preferably, the further salts are selected from salts comprising anions such as thiocyanate or tetracyanoborate, particularly preferred further salts are tetracyanoborates.

10 The cation of the at least one further salt or of a preferred further salt may be selected amongst organic cations as defined above for the compounds of formula I including also the preferred meanings.

15 In another embodiment of the invention, guanidinium thiocyanate may be added to the electrolyte formulation according to the invention.

20 In a preferred embodiment, the electrolyte formulation of the present invention further comprises at least one compound containing a nitrogen atom having non-shared electron pairs. Examples of such compounds are found in EP 0 986 079 A2, starting on page 2, lines 40-55, and again from page 3, lines 14 extending to page 7, line 54, which are expressly incorporated herein by reference. Preferred examples of compounds having non-shared electron pairs include imidazole and its derivatives, particularly benzimidazole and its derivatives.

25 The electrolyte formulation of the present invention comprises less than 50 vol.% of an organic solvent. Preferably, the electrolyte formulation comprises less than 40%, more preferably less than 30%, still more preferably less than 20% and even less than 10 %. Most preferably, the electrolyte formulation comprises less than 5% of an organic solvent. For example, it is substantially free of an organic solvent. Percentages are indicated on the basis of weight %.

Organic solvents, if present in such amounts as indicated above, may be selected from those disclosed in the literature. Preferably, the solvent, if present, has a boiling point higher than 160 degrees centigrade, more preferably higher than 190 degrees such as propylene carbonate, ethylene carbonate, butylene carbonate, gamma-butyrolactone, gamma-valerolactone, glutaronitrile, adiponitrile, N-methyloxazolidinone, N-methylpyrrolidinone, N,N'-dimethylimidazolidinone, N,N-dimethylacetamide, cyclic ureas preferably 1,3-dimethyl-2-imidazolidinone or 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone, glymes preferably tetraglyme, sulfolane, sulfones which are preferably asymmetrically substituted such as 2-ethanesulfonyl-propane, 1-ethanesulfonyl-2-methyl-propane or 2-(propane-2-sulfonyl)-butane, 3-methylsulfolane, dimethylsulfoxide, trimethylphosphate and methoxy-substituted nitriles. Other useful solvents are acetonitrile, benzonitrile and or valeronitrile.

15

If a solvent is present in the electrolyte formulation, there may further be comprised a polymer as gelling agent, wherein the polymer is polyvinylidenefluoride, polyvinylidene-hexafluoropropylene, polyvinylidene-hexafluoropropylene-chlorotrifluoroethylene copolymers, nafion, polyethylene oxide, polymethylmethacrylate, polyacrylonitrile, polypropylene, polystyrene, polybutadiene, polyethyleneglycol, polyvinylpyrrolidone, polyaniline, polypyrrole, polythiophene. The purpose of adding these polymers to electrolyte formulations is to make liquid electrolytes into quasi-solid or solid electrolytes, thus improving solvent retention, especially during aging.

The electrolyte formulation of the invention may further comprise metal oxide nanoparticles like SiO_2 , TiO_2 , Al_2O_3 , MgO or ZnO , for example, which are also capable of increasing solidity and thus solvent retention.

30

The electrolyte formulation of the invention has many applications. For example, it may be used in an optoelectronic and/or electrochemical device

such as a photovoltaic cell, a light emitting device, an electrochromic or photo-electrochromic device, an electrochemical sensor and/or biosensor.

5 The present invention therefore relates further to the use of the electrolyte formulation as described in detail above in an electrochemical and/or optoelectronic device which is a photovoltaic cell, a light emitting device, an electrochromic or photo-electrochromic device, an electrochemical sensor and/or biosensor. Preferably, the electrolyte formulation may be used in dye sensitized solar cells.

10

The present invention therefore relates furthermore to an electrochemical and/or optoelectronic device which is a photovoltaic cell, a light emitting device, an electrochromic or photo-electrochromic device, an electrochemical sensor and/or biosensor comprising an electrolyte formulation comprising at least one compound of formula I as described or

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preferably described above.

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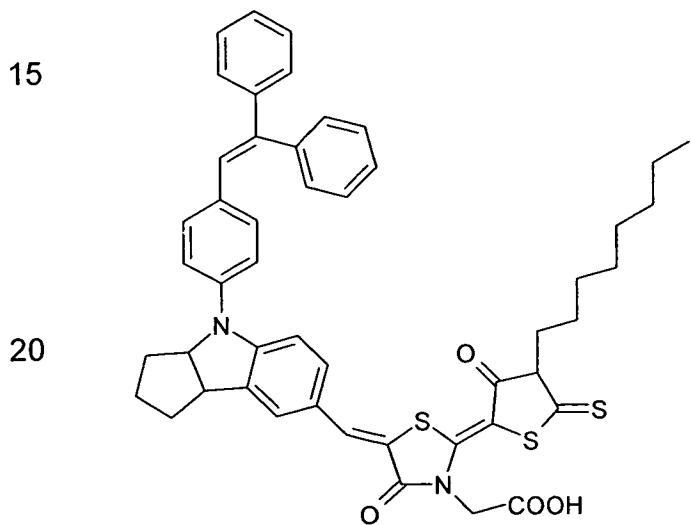
Preferably, the compound of formula I is a compound of formula I in which $[Kt]^{z+}$ is an organic cation as described above including all preferred meanings for application in dye-sensitized solar cells.

According to a preferred embodiment, the device of the present invention is a dye or quantum dot sensitized solar cell, particularly preferably a dye sensitized solar cell.

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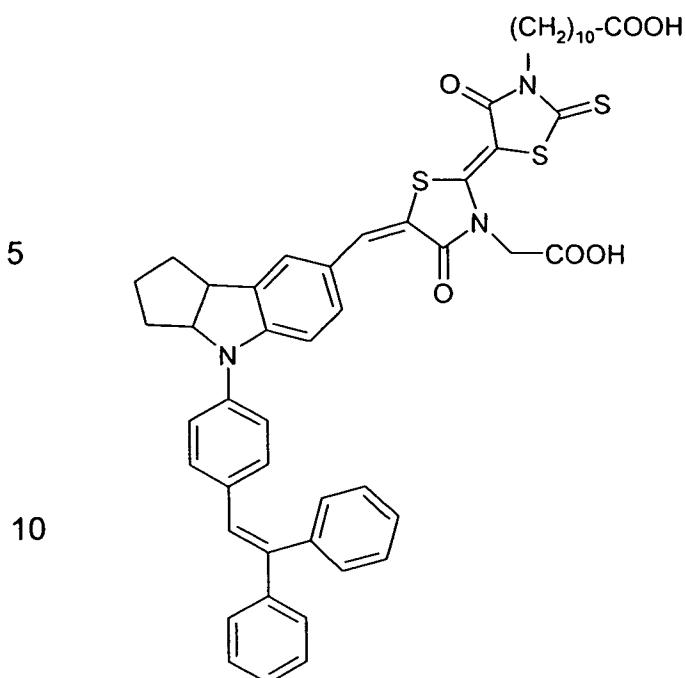
Quantum dot sensitized solar cells are disclosed in US 6,861,722, for example. In dye -sensitized solar cells, a dye is used to absorb the sunlight to convert into the electrical energy. There are no restrictions per se with respect to the choice of the dye as long as the LUMO energy state is marginally above the conduction bandedge of the photoelectrode to be sensitized. Examples of dyes are disclosed in EP 0 986 079 A2, EP 1 180 774 A2 or EP 1 507 307 A1.

Preferred dyes are organic dyes such as MK-1, MK-2 or MK-3 (its structures are described in figure 1 of N. Koumura et al, J.Am.Chem.Soc. Vol 128, no.44, 2006, 14256-14257), D102 (CAS no. 652145-28-3), D-149 (CAS no. 786643-20-7), D205 (CAS no. 936336-21-9), D358 (CAS no. 1207638-53-6), YD-2 as described in T. Bessho et al, Angew. Chem. Int. Ed. Vol 49, 37, 6646-6649, 2010, Y123 (CAS no. 1312465-92-1), bipyridin-Ruthenium dyes such as N3 (CAS no. 141460-19-7), N719 (CAS no. 207347-46-4), Z907 (CAS no. 502693-09-6), C101 (CAS no. 1048964-93-7), C106 (CAS no. 1152310-69-4), K19 (CAS no. 847665-45-6), HRS-1 (CAS no. 906061-30-1 as disclosed in K.J. Jiang et al, Chem. Comm. 2460, 2006) or terpyridine-Ruthenium dyes such as N749 (CAS no. 359415-47-7). The structure of D205 is



25 The structure of D358 is

30



15 Particularly preferred dyes are Z907 or Z907Na which are both an amphiphilic ruthenium sensitizer, C106, D358 or HRS-1. The dye Z907Na means $\text{NaRu}(2,2'\text{-bipyridine-4-carboxylic acid-4'-carboxylate})(4,4'\text{-dinonyl-2,2'\text{-bipyridine}})(\text{NCS})_2$.

20 Very particularly preferred dyes are Z907 or Z907Na and/or D358. Very very particularly preferred dyes are Z907 or Z907Na.

25 In a preferred embodiment, the dye is coadsorbed with a phosphinic acid. A preferred example of a phosphinic acid is bis(3,3-dimethyl-butyl)-phosphinic acid (DINHOP) as disclosed in M. Wang et al, Dalton Trans., 2009, 10015-10020.

The dye Z907Na means $\text{NaRu}(2,2'\text{-bipyridine-4-carboxylic acid-4'-carboxylate})(4,4'\text{-dinonyl-2,2'\text{-bipyridine}})(\text{NCS})_2$.

30 For example, a dye-sensitized solar cell comprises a photo-electrode, a counter electrode and, between the photo-electrode and the counter electrode, an electrolyte formulation or a charge transporting material, and

wherein a sensitizing dye is absorbed on the surface of the photo-electrode, on the side facing the counter electrode.

According to a preferred embodiment of the device according to the
5 invention, it comprises a semiconductor, the electrolyte formulation as described above and a counter electrode.

According to a preferred embodiment of the invention, the semiconductor is based on material selected from the group of Si, TiO₂, SnO₂, Fe₂O₃, WO₃, ZnO, Nb₂O₅, CdS, ZnS, PbS, Bi₂S₃, CdSe, GaP, InP, GaAs, CdTe, CuInS₂,
10 and/or CuInSe₂. Preferably, the semiconductor comprises a mesoporous surface, thus increasing the surface optionally covered by a dye and being in contact with the electrolyte. Preferably, the semiconductor is present on a glass support or plastic or metal foil. Preferably, the support is conductive.

15 The device of the present invention preferably comprises a counter electrode. For example, fluorine doped tin oxide or tin doped indium oxide on glass (FTO- or ITO-glass, respectively) coated with Pt, carbon of preferably conductive allotropes, polyaniline or poly (3,4-ethylenedioxythiophene) (PEDOT). Metal substrates such as stainless steel
20 or titanium sheet may be possible substrates beside glass.

The device of the present invention may be manufactured as the corresponding device of the prior art by simply replacing the electrolyte by the electrolyte formulation of the present invention. For example, in the
25 case of dye-sensitized solar cells, device assembly is disclosed in numerous patent literature, for example WO 91/16719 (examples 34 and 35), but also scientific literature, for example in Barbé, C.J., Arendse, F., Comte, P., Jirousek, M., Lenzmann, F., Shklover, V., Grätzel, M. J. Am. Ceram. Soc. 1997, 80, 3157; and Wang, P., Zakeeruddin, S. M., Comte, P.,
30 Charvet, R., Humphry-Baker, R., Grätzel, M. J. Phys. Chem. B 2003, 107, 14336.

Preferably, the sensitized semi-conducting material serves as a photo-anode. Preferably, the counter electrode is a cathode.

The present invention provides a method for preparing a photoelectric cell
5 comprising the step of bringing the electrolyte formulation of the invention in contact with a surface of a semiconductor, said surface optionally being coated with a sensitizer. Preferably, the semiconductor is selected from the materials given above, and the sensitizer is preferably selected from quantum dots and/or a dye as disclosed above, particularly preferably
10 selected from a dye.

Preferably, the electrolyte formulation may simply be poured on the semiconductor. Preferably, it is applied to the otherwise completed device already comprising a counter electrode by creating a vacuum in the internal
15 lumen of the cell through a hole in the counter electrode and adding the electrolyte formulation as disclosed in the reference of Wang et al., J. Phys. Chem. B 2003, 107, 14336.

The present invention will now be illustrated, without limiting its scope, by
20 way of the following examples. Even without further comments, it is assumed that a person skilled in the art will be able to utilise the above description in the broadest scope. The preferred embodiments and examples should therefore merely be regarded as descriptive disclosure which is absolutely not limiting in any way.

25

Examples:

NMR samples were measured in 5 mm precision glass NMR tubes at 25 °C on a Bruker Avance III spectrometer equipped with a 9.3980 T cryomagnet. The ¹H and ¹⁹F NMR spectra were acquired using a 5 mm combination
30 ¹H/¹⁹F probe operating at 400.17 and 376.54 MHz, respectively. The ³¹P NMR spectra were obtained using a 5 mm broad-band inverse probe operating at 161.99 MHz. The ¹H NMR chemical shifts were referenced

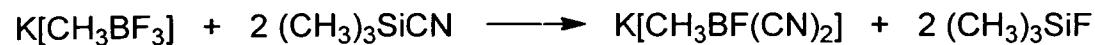
with respect to tetramethylsilane (TMS) using the chemical shifts 2.05 ppm for the solvent Aceton-D₆. The ¹³C-NMR chemical shifts were referenced to the chemical shifts 29.9 ppm for the solvent Aceton-D₆. The ¹⁹F NMR spectra were referenced with respect to CFCl₃ using the internal standard C₆H₅CF₃ (−63.9 ppm). The ³¹P NMR spectra were referenced with respect to aqueous H₃PO₄ (85 %).

The aceton-D₆ was used as a solvent and Deuterium lock if it is not given separately.

The disclosed viscosities are measured by means of Anton Paar Stabinger Viskosimeter SV 3000.

Example 1: Potassium methyldicyanofluoroborate – K[CH₃BF(CN)₂]

A)



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Potassium methyltrifluoroborate, K[CH₃BF₃] (100 mg, 0.82 mmol), is suspended in trimethylsilyl cyanide (20 ml, 149.9 mmol) and stirred at 50°C for 30 minutes. All volatile constituents are removed in vacuo, giving a colorless solid. The unreacted trimethylsilyl cyanide is recovered as a mixture with trimethylfluorosilane and can be employed for further reactions.

20

The yield of potassium methyldicyanofluoroborate, K[CH₃BF(CN)₂], is 110 mg (0.81 mmol). The purity is about 90%, and about 10% of K[CH₃B(CN)₂(NC)] are present as by-product.

25 ¹¹B{¹H}-NMR: δ , ppm = -8.9 (d, ¹J_{F,B} = 56.4 Hz).

¹⁹F-NMR: δ , ppm = -202.8 (qq, ¹J_{F,B} = 55.7 Hz, ³J_{F,H} = 13.8 Hz, BF, 1F).

¹H{¹¹B}-NMR: δ , ppm = -0.11 (d, ³J_{F,H} = 14.4 Hz, CH₃, 3H).

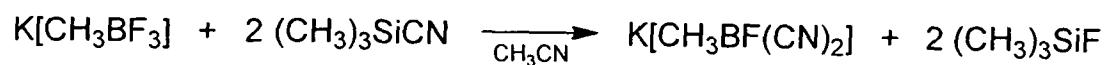
30 ¹H-NMR: δ , ppm = -0.11 (dq, ³J_{F,H} = 14.4 Hz, ²J_{B,H} ≈ 4.3 Hz, CH₃, 3H).

Raman spectrum: $\tilde{\nu}$ (CN) = 2211 cm⁻¹.

The by-product $K[MeB(CN)_2(NC)]$ is detected by NMR spectroscopy, and the data are identical to those indicated in Example 3.

B)

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10

Potassium methyltrifluoroborate (93.6 mg, 0.768 mmol) is taken up in acetonitrile (5 ml), trimethylsilyl cyanide (1.0 ml, 7.499 mmol) is added, and the mixture is stirred at 100°C for 4 hours. All volatile constituents are subsequently removed in vacuo, and the residue is dissolved in acetone (1 ml). Potassium methyldicyanofluoroborate is precipitated by addition of chloroform (10 ml).

15

The yield of potassium methyldicyanofluoroborate is 94 mg (0.691 mmol).

The spectroscopic data correspond to those from Example 1A.

15

C)

20

Potassium methyltrifluoroborate, $K[CH_3BF_3]$ (500 mg, 4.10 mmol), is taken up in acetonitrile (5 ml). Trimethylsilyl cyanide (10 ml, 74.99 mmol) and ethoxytrimethylsilane (1.0 ml, 6.40 mmol) are added to the suspension, and the mixture is stirred at room temperature for 12 hours. All volatile constituents are subsequently removed. The residue is dissolved in acetone (5 ml), and $K[CH_3BF(CN)_2]$ is precipitated by addition of CH_2Cl_2 (20 ml) and filtered off.

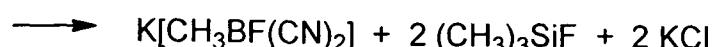
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The yield of potassium methyldicyanofluoroborate is 492 mg (3.62 mmol).

The spectroscopic data correspond to those from Example 1A.

D)

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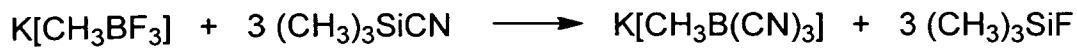


KCN (400 mg, 6.15 mmol) and $K[CH_3BF_3]$ (100 mg, 0.819 mmol) are suspended in acetonitrile (2 mL) and a solution of trimethylchlorsilane (0.3

mL, 2.38 mmol) in acetonitrile (5 mL) is added slowly. The suspension is stirred for 20 minutes at room temperature. The reaction mixture is filtered to remove all solid materials (excess of KCN as well as the side-product KCl). The solid material is washed with acetonitrile (2 mL) and the organic phases are combined. All volatile materials are removed under reduced pressure at 50 °C.

5 The yield of potassium methyldicyanofluoroborate is 85 mg (0.63 mmol).
10 The spectroscopic data of the product correspond to those from Example 1A.

Example 2: Potassium methyltricyanoborate – K[CH₃B(CN)₃]



A) Potassium methyltrifluoroborate, K[CH₃BF₃] (7.00 g, 57.42 mmol), is suspended in trimethylsilyl cyanide (45.0 ml, 337.45 mmol) and warmed at 15 80°C for one hour and subsequently stirred at 110°C for 3 days. All volatile constituents were removed in vacuo, and the residue is dissolved in acetone (10 ml) and precipitated by addition of CHCl₃ (50 ml). The crude product is taken up in 20% aqueous hydrogen peroxide solution (50 ml) and stirred 20 overnight. Potassium disulfite K₂S₂O₅ is added until peroxides were no longer detectable (Merckoquant® peroxide test). The product is then extracted with THF (3 × 25 ml), and the combined organic phases are dried using K₂CO₃, filtered and evaporated in vacuo to a volume of about 5 ml. CH₂Cl₂ (100 ml) is added with vigorous stirring, and the white precipitate 25 formed is filtered off and dried in vacuo.

The yield of potassium methyltricyanoborate, K[CH₃B(CN)₃], is 5.1 g (35.67 mmol).

The NMR spectra of K[CH₃B(CN)₃] were measured in CD₃CN.

30 ¹¹B{¹H}-NMR: δ, ppm = -32.6 s.

¹H{¹¹B}-NMR: δ, ppm = 0.03 (s, CH₃, 3H).

¹H-NMR: δ , ppm = 0.03 (q, $^2J_{B,H}$ = ~3 Hz, CH₃, 3H).

¹³C{¹H}-NMR: δ , ppm = 130.8 (q, $^1J_{C,B}$ = 64 Hz, CN), 3.3 (q, $^1J_{C,B}$ = 44 Hz, CH₃).

B) Potassium methyltrifluoroborate (7.9 g, 64.81 mmol) is suspended in a mixture (100 mL) of recycled trimethylsilylcyanide (90 mol%), fluorotrimethylsilane (4 mol%), chlorotrimethylsilane (2 mol%), acetonitril (4 mol%) and trimethylsilylcyanide (CH₃)₃SiCN (10.0 mL, 74.99 mmol) and (CH₃)₃SiCl (as catalyst, 10.0 mL, 79.16 mmol) is added. The mixture is heated to 75°C and stirred for 9 hours. All volatile compounds are removed in vacuo and the residue is dissolved in water and stirred with aqueous H₂O₂ (30 %, 15 mL) and K₂CO₃ (~5 g) for 2 hours resulting in a solution. Peroxide is reduced through K₂S₂O₅. The pH of the mixture remains basic through addition of potassium carbonate. The mixture is then extracted with tetrahydrofuran (5 × 75 mL) and the organic phases are dried with potassium carbonate, filtrated and the organic solvent is removed in vacuum. The resulting concentrated solution is added to CHCl₃ and the potassium salt K[CH₃B(CN)₃] precipitates and is filtrated and dried in vacuum.

The yield of potassium methyltricyanoborate is 7.8 g (54.54 mmol).

20

Elemental analysis:

Calculated C 33.60; H 2.11; N 29.39

found: C 33.29; H 2.59; N 27.16

25 The spectroscopic data of the product correspond to those from Example 2A.

Example 3: Potassium methyldicyanoisocyanoborate –
K[CH₃B(CN)₂(NC)]

30



Potassium methyltrifluoroborate, $K[CH_3BF_3]$ (500 mg, 4.10 mmol), is suspended in trimethylsilyl cyanide (20 ml, 149.9 mmol). The reaction mixture is stirred at 50°C for 2 days and subsequently at 80°C for 24 hours. Excess trimethylsilyl cyanide and trimethylfluorosilane formed are distilled off and can be employed for further reactions. A slightly reddish solid is obtained.

The yield of potassium methyldicyanoisocyanoborate, $K[CH_3B(CN)_2(NC)]$, is 583 mg (4.08 mmol). The product contains about 10% of potassium methyltricyanoborate.

The NMR spectra of $K[CH_3B(CN)_2(NC)]$:

$^{11}B\{^1H\}$ -NMR: δ , ppm = -23.9 s.

$^1H\{^{11}B\}$ -NMR: δ , ppm = -0.02 (s, CH_3).

1H -NMR: δ , ppm = -0.02 (broadened, CH_3).

MALDI-MS m/e $[C_4H_3BN_3]^-$:

calculated: 104.0 (100.0%), 103.0 (24.8%), 105.0 (4.4%).

found: 103.7 (100.0%), 102.7 (24.4%), 104.7 (4.3%).

20

Raman spectrum: $\tilde{\nu}$ (CN) = 2221 cm^{-1}

Raman spectrum: $\tilde{\nu}$ (NC) = 2166 cm^{-1}

The by-product $K[MeB(CN)_3]$ is detected by NMR spectroscopy, and the data are identical to the values indicated in Example 2.

25

The product, $K[CH_3B(CN)_2(NC)]$, isomerizes in potassium methyltricyanoborate, $K[CH_3B(CN)_3]$, on heating in the solid state or in an organic solvent at about 100°C.

30 **Example 4: Potassium *n*-butyldicyanoisocyanoborate – $K[n-C_4H_9B(CN)_2(NC)]$**



Potassium *n*-butyltrifluoroborate, $\text{K}[n\text{-C}_4\text{H}_9\text{BF}_3]$ (20 mg, 0.122 mmol), is weighed out in an NMR tube with a valve with Teflon spindle (Young, London) and taken up in trimethylsilyl cyanide (1.0 ml, 7.49 mmol). The suspension is stored at room temperature for two days and subsequently at 80°C for 7 hours. The solution obtained is evaporated to dryness in vacuo. Yield of potassium *n*-butyldicyanoisocyanoborate, $\text{K}[n\text{-C}_4\text{H}_9\text{B}(\text{CN})_2(\text{NC})]$, is 22 mg (0.12 mmol). The product contains about 7% of potassium *n*-butyltricyanoborate, $\text{K}[n\text{-C}_4\text{H}_9\text{B}(\text{CN})_3]$.

10

The ^{11}B -NMR spectrum of $\text{K}[n\text{-C}_4\text{H}_9\text{B}(\text{CN})_2(\text{NC})]$:

$^{11}\text{B}\{\text{H}\}$ -NMR: δ , ppm = -22.2 s.

15

$\text{K}[n\text{-C}_4\text{H}_9\text{B}(\text{CN})_3]$:

$^{11}\text{B}\{\text{H}\}$ -NMR: δ , ppm = -30.6 s.

MALDI-MS m/e $[\text{C}_7\text{H}_9\text{BN}_3]^-$:

calculated: 146.1 (100.0%), 145.1 (24.8%), 147.1 (7.8%).

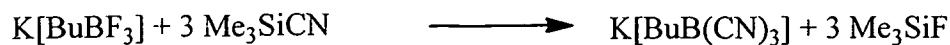
found: 145.8 (100.0%), 144.8 (14.7%), 146.8 (14.1%).

20

The product, $\text{K}[n\text{-C}_4\text{H}_9\text{B}(\text{CN})_2(\text{NC})]$, isomerizes in potassium *n*-butyltricyanoborate, $\text{K}[n\text{-C}_4\text{H}_9\text{B}(\text{CN})_3]$, on heating in the solid state or in an organic solvent at about 100°C.

25

Example 5: Potassium *n*-butyltricyanoborate - $\text{K}[n\text{-C}_4\text{H}_9\text{B}(\text{CN})_3]$



Potassium *n*-butyltrifluoroborate (5.2 g, 31.7 mmol) is suspended in a mixture (150 mL) of recycled trimethylsilyl cyanide (86 mol%), fluorotrimethylsilane (4 mol%), chlorotrimethylsilane (3 mol%), acetonitril (4 mol%). The mixture is heated to 60°C and stirred for 12 hours. All volatile

compounds are removed in vacuo and the residue is dissolved in water (30 mL) and stirred with aqueous H₂O₂ (30 %, 30 mL) and K₂CO₃ (~5 g) for 4 hours resulting in a solution. Peroxide is reduced through K₂S₂O₅. The pH of the mixture remains basic through addition of potassium carbonate. The mixture is then extracted with tetrahydrofuran (5 × 75 mL) and the organic phases are dried with potassium carbonate, filtrated and the organic solvent is removed in vacuum. The resulting concentrated solution is added to hexane and the potassium salt K[n-C₄H₉B(CN)₃] precipitates and is filtrated and dried in vacuum.

10 The yield of potassium *n*-butyltricyanoborate is 4.8 g (25.94 mmol).

¹¹B{¹H}-NMR: δ , ppm = -31.5 (s).

¹¹B-NMR: δ , ppm = -31.5 (broad s).

¹H{¹¹B}-NMR: δ , ppm = 1.30 (m, 4H, CH₂), 0.86 (m, 3H, CH₃), 0.43 (m, 2H, BCH₂).

15 ¹H-NMR: δ , ppm = 1.30 (m, 4H), 0.86 (m, 3H), 0.43 (broad m, ³J_{H,H} = 7.3 Hz, 2H).

¹³C{¹H}-NMR: δ , ppm = 138.4 (q, ¹J_{C,B} ≈ 70 Hz, CN, 3C), 30.6 (s, 1C), 26.3 (s, 1C), 20.5 (q, ¹J_{C,B} ≈ 50 Hz, 1C), 14.3 (s, 1C).

20 Elemental analysis:

calculated: C 45.43; H 4.90; N 22.70

found: C 44.10; H 4.95; N 22.14

Example 6: 1-Ethyl-3-methylimidazolium *n*-butyltricyanoborate –

25 **EMIM[n-C₄H₉B(CN)₃]**



30 1-Ethyl-3-methylimidazolium chloride, (EMIMCl) (3.57 g, 24.36 mmol) and K[n-C₄H₉B(CN)₃] (4.1 g, 22.15 mmol) are dissolved in deionized water (50 mL) and the mixture is diluted with CH₂Cl₂ (50 mL). The aqueous phase is

removed and the organic phase is washed with water (VE, 5 × 1 mL) and dried with magnesium sulfate. After filtration and distillation of methylene chloride, the ionic liquid is dried for three days at 50 °C in vacuum.

5 The yield of 1-ethyl-3-methylimidazolium *n*-butyltricyanoborate is 5.1 g (19.83 mmol).

$^{11}\text{B}\{^1\text{H}\}$ -NMR: δ , ppm = -33.5 (s).

^{11}B -NMR: δ , ppm = -33.5 (broad s).

10 $^1\text{H}\{^{11}\text{B}\}$ -NMR: δ , ppm = 8.99 (broad dd, $^4J_{\text{H,H}} \approx 1.6$ Hz, CH, 1H), 7.74 (dd, $^3J_{\text{H,H}} \approx ^4J_{\text{H,H}} \approx 1.8$ Hz, CH, 1H), 7.67 (dd, $^3J_{\text{H,H}} \approx ^4J_{\text{H,H}} \approx 1.8$ Hz, CH, 1H), 4.39 (q, $^3J_{\text{H,H}} = 7.4$ Hz, CH₂, 2H), 4.02 (s, CH₃, 3H), 1.57 (t, $^3J_{\text{H,H}} = 7.3$ Hz, CH₃, 3H), 1.31 (m, 4H, CH₂), 0.86 (m, 3H, CH₃), 0.43 (m, 2H, CH₂).

15 ^1H -NMR: δ , ppm = 8.99 (broad dd, $^4J_{\text{H,H}} \approx 1.6$ Hz, CH, 1H), 7.74 (dd, $^3J_{\text{H,H}} \approx ^4J_{\text{H,H}} \approx 1.8$ Hz, CH, 1H), 7.67 (dd, $^3J_{\text{H,H}} \approx ^4J_{\text{H,H}} \approx 1.8$ Hz, CH, 1H), 4.39 (q, $^3J_{\text{H,H}} = 7.4$ Hz, CH₂, 2H), 4.02 (s, CH₃, 3H), 1.57 (t, $^3J_{\text{H,H}} = 7.3$ Hz, CH₃, 3H), 1.31 (m, 4H, CH₂), 0.86 (m, 3H, CH₃), 0.43 (broad m, 2H, CH₂).

$^{13}\text{C}\{^1\text{H}\}$ -NMR: δ , ppm = 137.0 (s, 1C), 130.9 (q, $^1J_{\text{C,B}} = 62$ Hz, CN, 3C), 124.7 (s, 1C), 123.0 (s, 1C), 45.7 (s, 1C), 36.6 (s, 1C), 30.6 (s, 1C), 26.3 (s, 1C), 20.9 (q, $^1J_{\text{C,B}} \approx 44$ Hz, 1C), 15.6 (s, 1C), 14.3 (s, 1C).

20 Elemental analysis:

calculated: C 60.72; H 7.84; N 27.24

found: C 60.03; H 8.12; N 27.63

Dynamic viscosity:

25	°C	mPa·s
20		49.8
40		21.3
60		11.4
80		7.0

30

Decomposition's temperature: 290° C.

Example 7: Potassium allyltricyanoborate – K[CH₂=CHCH₂B(CN)₃]

K[CH₂=CHCH₂BF₃] + 3 (CH₃)₃SiCN → K[CH₂=CHCH₂B(CN)₃] + 3 (CH₃)₃SiF

5 Potassium allyltrifluoroborate, K[CH₂=CHCH₂BF₃] (20 mg, 0.135 mmol), is initially introduced in an NMR tube with a valve with Teflon spindle (Young, London) and taken up in trimethylsilyl cyanide (1.0 ml, 7.49 mmol). The suspension is kept at room temperature for two days and subsequently at 10 80°C for 7 hours, at 100°C for 8 hours and then at 120°C for 12 hours. All volatile constituents are removed in vacuo.

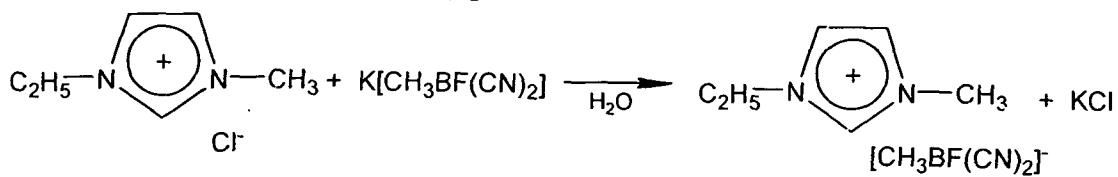
15 The yield of potassium allyltricyanoborate, K[CH₂=CHCH₂B(CN)₃], is 21 mg (0.124 mmol). The product contains about 2% impurities.

The ¹¹B-NMR spectrum of K[CH₂=CHCH₂B(CN)₃]:

¹¹B{¹H}-NMR: δ, ppm = -30.8 s.

15 MALDI-MS m/e [C₆H₅BN₃]⁻:
calculated: 130.0 (100.0%), 129.0 (24.8%), 131.0 (6.7%).
found: 129.7 (100.0%), 128.7 (31.7%), 130.7 (5.2%).

20 **Example 8: 1-Ethyl-3-methylimidazolium methyldicyanofluoroborate – EMIM [CH₃BF(CN)₂]**



25 Potassium methyldicyanofluoroborate (50 mg, 0.367 mmol) and 1-ethyl-3-methylimidazolium chloride, EMIM Cl (100 mg, 0.684 mmol), are combined in deionized water (1 ml) and mixed. The reaction solution is extracted with CH₂Cl₂ (2 × 1 ml), and the CH₂Cl₂ is subsequently removed in vacuo. The liquid remaining is dried in vacuo for 12 hours.

30 The yield of EMIM [CH₃BF(CN)₂] is 54 mg (0.259 mmol).

The NMR spectra of EMIM [CH₃BF(CN)₂]:

¹¹B{¹H}-NMR: δ , ppm = -8.9 d ($^1J_{F,B} = 56.5$ Hz).

¹¹B-NMR: δ , ppm = -8.9 d,q ($^1J_{F,B} = 56.5$ Hz, $^2J_{B,H} \approx 4.3$ Hz).

¹⁹F-NMR: δ , ppm = -202.8 q,q ($^1J_{F,B} = 56.2$ Hz, $^3J_{F,H} = 14.2$ Hz, BF).

5

¹H{¹¹B}-NMR: δ , ppm = 9.03 br. s (CH, 1H), 7.75 t ($^3J_{H,H} \approx 4J_{H,H} \approx 1.8$ Hz, CH, 1H), 7.68 t ($^3J_{H,H} \approx 4J_{H,H} \approx 1.7$ Hz, CH, 1H), 4.40 q ($^3J_{H,H} = 7.3$ Hz, CH₂, 2H), 4.05 s (CH₃, 3H), 1.57 t ($^3J_{H,H} = 7.3$ Hz, CH₃, 3H), -0.12 d ($^3J_{F,H} = 14.4$ Hz, BCH₃, 3H).

10

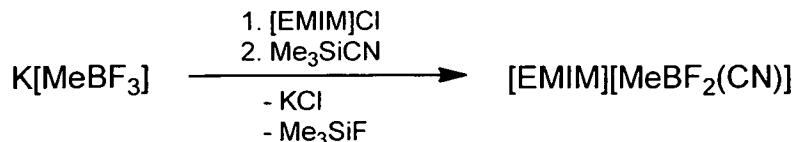
¹H-NMR: δ , ppm = 9.03 br. s (CH, 1H), 7.75 t ($^3J_{H,H} \approx 4J_{H,H} \approx 1.8$ Hz, CH, 1H), 7.68 t ($^3J_{H,H} \approx 4J_{H,H} \approx 1.7$ Hz, CH, 1H), 4.40 q ($^3J_{H,H} = 7.3$ Hz, CH₂, 2H), 4.05 s (CH₃, 3H), 1.57 t ($^3J_{H,H} = 7.3$ Hz, CH₃, 3H), -0.12 d,q ($^3J_{F,H} = 14.4$ Hz, $^2J_{B,H} \approx 4.3$ Hz, BCH₃, 3H).

15

¹³C{¹H}-NMR: δ , ppm = 136.4 s (EMIM, 1C), 134.0 q,q ($^1J_{C,B} = 62$ Hz, $^2J_{F,C} = 39$ Hz, 2CN, 2C), 124.0 s (EMIM, 1C), 122.3 s (EMIM, 1C), 45.0 s (EMIM, 1C), 35.9 s (EMIM, 1C), 14.8 s (EMIM, 1C), 8.1 m (BCH₃, 1C).

20

Example 9: 1-Ethyl-3-methylimidazolium methylcyanodifluoroborate - EMIM [CH₃BF₂(CN)]



25

A suspension of potassium methyltrifluoroborate (5.22 g, 42.81 mmol) in H₂O (10 ml) is added to an aqueous solution of [EMIM]Cl (6.5 g, 44.34 mmol) and mixed, and the solution is evaporated to dryness. The residue is taken up in dichloromethane (20 ml), undissolved precipitate is separated off, and the CH₂Cl₂ is removed in vacuo. The ionic liquid [EMIM]-[CH₃BF₃] obtained (7.93 g, 40.87 mmol) is dissolved in acetonitrile (15 ml), and trimethylsilyl cyanide (5.45 ml, 40.87 mmol) is added. The reaction

30

mixture is stirred at room temperature for 3 days. All volatile constituents are subsequently removed in vacuo.

The yield of [EMIM][CH₃BF₂(CN)] is 8.2 g (40.79 mmol).

(The purity is about 70%; the product contains about 22% of [EMIM]

5 [MeBF₃]⁻ and 8% of further impurities.)

NMR data of the [CH₃BF₂(CN)]⁻ anion (70%):

¹¹B{¹H}-NMR: δ , ppm = 2.5 t (¹J_{F,B} = 62.3 Hz).

¹¹B-NMR: δ , ppm = 2.5 t,q (¹J_{F,B} = 62.3 Hz, ²J_{B,H} = 2.6 Hz).

10 ¹⁹F-NMR: δ , ppm = -147.7 t,q (³J_{F,H} = 10.4 Hz, 3H).

¹H{¹¹B}-NMR: δ , ppm = -0.32 t (³J_{F,H} = 11.8 Hz, CH₃, 3H).

¹H-NMR: δ , ppm = -0.32 br. t (³J_{F,H} = 11.8 Hz, CH₃, 3H).

NMR data of the [CH₃BF₃]⁻ anion (22%):

15

¹¹B{¹H}-NMR: δ , ppm = 5.3 q (¹J_{F,B} = 62.1 Hz).

¹¹B-NMR: δ , ppm = 5.3 q,q (¹J_{F,B} = 62.1 Hz, ²J_{B,H} = ~3 Hz).

¹⁹F-NMR: δ , ppm = -132.9 q,q (¹J_{F,B} = 61.4 Hz, ³J_{F,H} = 5.1 Hz, 3F).

¹H{¹¹B}-NMR: δ , ppm = -0.44 q (³J_{F,H} = 8.2 Hz, CH₃, 3H).

20

¹H-NMR: δ , ppm = -0.44 br. q (³J_{F,H} = 8.2 Hz, CH₃, 3H).

NMR data of the [EMIM]⁺ cation:

25

¹H{¹¹B}-NMR: δ , ppm = 9.25 s (CH, 1H), 7.78 m (CH, 1H), 7.70 m (CH, 1H), 4.38 q (³J_{H,H} = 7.4 Hz, CH₂, 2H), 4.03 s (CH₃, 3H), 1.54 t (³J_{H,H} = 7.3 Hz, CH₃, 3H).

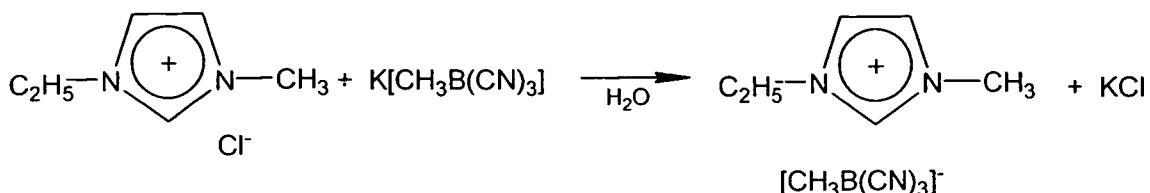
30

¹H-NMR: δ , ppm = 9.25 s (CH, 1H), 7.78 m (CH, 1H), 7.70 m (CH, 1H), 4.38 q (³J_{H,H} = 7.4 Hz, CH₂, 2H), 4.03 s (CH₃, 3H), 1.54 t (³J_{H,H} = 7.3 Hz, CH₃, 3H).

Raman spectrum [EMIM][MeBF₂(CN)]: $\tilde{\nu}$ (CN) = 2189 cm⁻¹

Example 10: 1-Ethyl-3-methylimidazolium tricyanomethylborate –
[EMIM][CH₃B(CN)₃]

5



10

A solution of ethylmethylimidazolium chloride, [EMIM]Cl, (4.50 g, 30.69 mmol), in bidistilled water (10 ml) and a solution of potassium methyltricyanoborate (4.33 g, 30.28 mmol) in bidistilled water (5 ml) are combined and mixed. The reaction solution is extracted with CH₂Cl₂ (4 × 50 ml). The combined dichloromethane phases are dried using MgSO₄, and the solvent is removed using a rotary evaporator. The ionic liquid obtained is dried in vacuo.

15

The yield of 1-ethyl-3-methylimidazolium tricyanomethylborate is 6.35 g (29.53 mmol).

20

The NMR spectra of EMIM [CH₃B(CN)₃]:

¹¹B{¹H}-NMR: δ , ppm = -32.5 s.

¹¹B-NMR: δ , ppm = -32.5 q (²J_{B,H} = 4.2 Hz).

25

¹H{¹¹B}-NMR: δ , ppm = 8.91 br. s (CH, 1H), 7.68 t (³J_{H,H} ≈ ⁴J_{H,H} ≈ 1.7 Hz, CH, 1H), 7.62 t (³J_{H,H} ≈ ⁴J_{H,H} ≈ 1.7 Hz, CH, 1H), 4.36 q (³J_{H,H} = 7.3 Hz, CH₂, 2H), 4.02 s (CH₃, 3H), 1.57 t (³J_{H,H} = 7.3 Hz, CH₃, 3H), -0.03 s (BCH₃, 3H).

30

¹H-NMR: δ , ppm = 8.91 br. s (CH, 1H), 7.68 t (³J_{H,H} ≈ ⁴J_{H,H} ≈ 1.7 Hz, CH, 1H), 7.62 t (³J_{H,H} ≈ ⁴J_{H,H} ≈ 1.7 Hz, CH, 1H), 4.36 q (³J_{H,H} = 7.3 Hz, CH₂,

2H), 4.02 s (CH₃, 3H), 1.57 t (³J_{H,H} = 7.3 Hz, CH₃, 3H), -0.03 q (²J_{B,H} = 4.4 Hz, BCH₃, 3H).

¹³C{¹H}-NMR: δ , ppm = 131.5 q (¹J_{C,B} = 63.9 Hz, BCN, 3C), 136.7 s (1C), 124.5 s (1C), 122.9 s (1C), 45.6 s (1C), 36.5 s (1C), 15.4 s (1C), 4.7 q (¹J_{C,B} = 45 Hz, BCH_3 , 1C).

Analysis:

Water content (Karl-Fischer titration): 37 ppm.

10 Halogen impurities (ion chromatography): $\text{Cl}^- = 97 \text{ ppm}$.

Dynamic viscosity:

°C	mPa·s
20	21.1
30	14.9
40	11.0
50	8.5
60	6.8
70	5.5
80	4.6

Example 11: 1-Butyl-3-methylimidazolium methyltricyanoborate –

BMIM[CH₃B(CN)₃]

25



A suspension of potassium methyltricyanoborate (5.0 g, 34.96 mmol) and 1-butyl-3-methylimidazolium chloride (6.72 g; 38.45 mmol) in deionised H₂O (10 ml) is prepared and CH₂Cl₂ (50 mL) is added. The aqueous phase is removed and the organic phase is washed with deionised H₂O (5 × 1 mL)

and dried with magnesium sulfate. After filtration, the organic solvent CH_2Cl_2 is removed under reduced pressure. The resulting liquid is dried in vacuum at 50°C for three days.

5 The Yield of 1-butyl-3-methylimidazolium methyltricyanoborate is 6.9 g (28.38 mmol).

$^{11}\text{B}\{\text{H}\}$ -NMR: δ , ppm = -33.5 (s).

^{11}B -NMR: δ , ppm = -33.5 (broad s).

10 $^1\text{H}\{\text{H}\}$ -NMR: δ , ppm = 8.98 (dd, $^4J_{\text{H,H}} \approx 1.5$ Hz, CH, 1H), 7.73 (dd, $^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.6$ Hz, CH, 1H), 7.68 (dd, $^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.5$ Hz CH, 1H), 4.35 (t, $^3J_{\text{H,H}} = 7.28$ Hz, CH_2 , 2H), 4.05 (s, CH_3 , 3H), 1.93 (m, CH_2 , 2 H), 1.39 (m, CH_2 , 2H), 0.95 (t, $^3J_{\text{H,H}} = 7.40$ Hz, CH_3 , 3H), -0.05 (s, BCH_3 , 3H).

15 ^1H -NMR: δ , ppm = 8.98 (dd, $^4J_{\text{H,H}} \approx 1.5$ Hz, CH, 1H), 7.73 (dd, $^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.6$ Hz, CH, 1H), 7.68 (dd, $^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.5$ Hz CH, 1H), 4.35 (t, $^3J_{\text{H,H}} = 7.28$ Hz, CH_2 , 2H), 4.05 (s, CH_3 , 3H), 1.93 (m, CH_2 , 2 H), 1.39 (m, CH_2 , 2H), 0.95 (t, $^3J_{\text{H,H}} = 7.40$ Hz, CH_3 , 3H), -0.05 (deformed q, $^2J_{\text{B,H}} \approx 4$ Hz, BCH_3 , 3H).

20 $^{13}\text{C}\{\text{H}\}$ -NMR: δ , ppm = 137.3 (s, CH, 1C), 131.4 (q, $^1J_{\text{C,B}} = 63.3$ Hz, CN, 3C), 124.7 (s, CH, 1C), 123.4 (s, CH, 1C), 50.2 (s, CH_2 , 1C), 36.7 (s, CH_3 , 1C), 32.6 (s, CH_2 , 1C), 19.9 (s, CH_2 , 1C), 13.6 (s, CH_3 , 1C), 4.6 (q, $^1J_{\text{C,B}} = 44.3$ Hz, BCH_3 , 1C).

Elemental analysis:

Calc.: C 59.04; H 7.84; N 28.69

25 Found: C 58.53; H 7.64; N 29.40

Dynamic viscosity:

°C	mPa·s
20	39.2
40	17.4
60	9.6

80	6.1
----	-----

Decomposition's temperature: 240° C.

5 **Example 12: Triethylsulfonium methyltricyanoborate** –

$[(C_2H_5)_3S][CH_3B(CN)_3]$

$[(C_2H_5)_3S]I + AgCl \longrightarrow [(C_2H_5)_3S]Cl + AgI$

$[(C_2H_5)_3S]Cl + K[CH_3B(CN)_3] \longrightarrow [(C_2H_5)_3S][CH_3B(CN)_3] + KCl$

10 A mixture of triethylsulfonium iodide, $[(C_2H_5)_3S]I$ (8.6 g, 34.96 mmol), and AgCl (10.0 g, 69.78 mmol) in deionised water (50 mL) is stirred in the dark for four hours. The suspension is then filtered and the filtrate is treated with $K[CH_3B(CN)_3]$ (5.0 g, 34.96 mmol) thus forming two phases. The mixture is extracted with dichloromethane (3×25 mL) and the combined organic phases are washed with deionised water (5×25 mL) and dried over magnesium sulfate. After filtration, the organic solvent CH_2Cl_2 is removed under reduced pressure. The resulting liquid is dried in vacuum at 50°C for three days.

15 The yield of triethylsulfonium methyltricyanoborate is 5.8 g (25.99 mmol).

20 $^{11}B\{^1H\}$ -NMR: δ , ppm = -33.5 (s).

^{11}B -NMR: δ , ppm = -33.5 (s, broad).

$^1H\{^{11}B\}$ -NMR: δ , ppm = 3.61 (q, $^3J_{H,H} = 7.4$ Hz, SCH_2 , 6H), 1.65 (t, $^3J_{H,H} = 7.4$ Hz, CH_3 , 3H), 0.09 (s, BCH_3 , 3H).

25 1H -NMR: δ , ppm = 3.61 (q, $^3J_{H,H} = 7.4$ Hz, SCH_2 , 6H), 1.65 (t, $^3J_{H,H} = 7.4$ Hz, CH_3 , 3H), 0.09 (m, BCH_3 , 3H).

$^{13}C\{^1H\}$ -NMR: δ , ppm = 131.4 (q, $^1J_{C,B} = 63.3$ Hz, CN, 3C), 33.3 (s, 3C), 9.0 (s, 3C), 4.4 (q, $^1J_{C,B} = 44.9$ Hz, BCH_3 , 1C).

30 Elemental analysis:
calculated: C 53.82; H 8.13; N 18.83; S 14.37

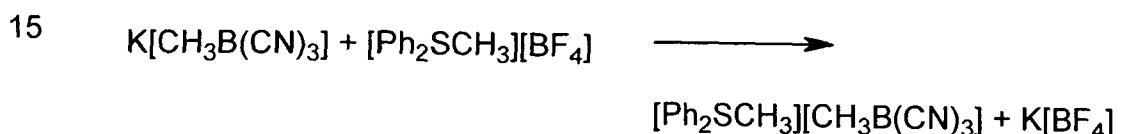
found: C 53.13; H 8.20, N 18.9, S 14.07

Dynamic viscosity:

5	°C	mPa·s
20		22.8
40		12.0
60		7.3
80		4.9

10 Decomposition's temperature: 160° C.

Example 13: Methyl diphenylsulfonium methyltricyanoborate –
 $[(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{S}][\text{CH}_3\text{B}(\text{CN})_3]$



A solution of methyl diphenylsulfonium tetrafluoroborate, $[(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{S}][\text{BF}_4]$, (4.50 g, 30.69 mmol), 100 mg, 0.347 mmol in acetonitrile (2 ml) and a solution of potassium methyltricyanoborate (50 mg, 0.347 mmol in acetonitrile (2 ml) are combined and mixed. The salt potassium tetrafluoroborate is filtered at 0°C and all volatile components are removed under reduced pressure resulting in the compound methyl diphenylsulfonium methyltricyanoborate.

20 25 The yield of methyl diphenylsulfonium methyltricyanoborate is 101 mg (0.33 mmol). The product contains 2% tetrafluoroborate.

$^{11}\text{B}\{\text{H}\}$ -NMR: δ , ppm = -33.5 (s).

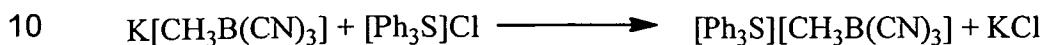
^{11}B -NMR: δ , ppm = -33.5 (s, broad).

30 $^1\text{H}\{^{11}\text{B}\}$ -NMR: δ , ppm = 8.10 (m, $\text{C}_{\text{arom}}\text{H}$, 4H), 7.84 (m, $\text{C}_{\text{arom}}\text{H}$, 2H), 7.78 (m, $\text{C}_{\text{arom}}\text{H}$, 4H), 3.97 (s, CH_3 , 3H), -0.02 (s, BCH_3 , 3H).

¹H-NMR: δ , ppm = 8.10 (m, C_{arom}H, 4H), 7.84 (m, C_{arom}H, 2H), 7.78 (m, C_{arom}H, 4H), 3.97 (s, CH₃, 3H), -0.02 (verzerrtes q, ²J_{B,H} ~ 5 Hz, BCH₃, 3H).

¹³C{¹H}-NMR: δ , ppm = 134.7 (s, C_{arom}, 2C), 131.6 (s, C_{arom}, 4C), 131.1 (q, ¹J_{C,B} = 63 Hz, CN, 3C), 130.4 (s, C_{arom}, 4C), 127.4 (s, C_{arom}, 2C), 27.6 (s, CH₃, 1C), 4.3 (q, ¹J_{C,B} = 44 Hz, BCH₃, 1C).

Example 14: Triphenylsulfonium methyltricyanoborate –
[(C₆H₅)₃S][CH₃B(CN)₃]



K[CH₃B(CN)₃] (70 mg, 0.489 mmol) is added to a solution of triphenylsulfonium chloride, [(C₆H₅)₃S]Cl, (50 mg, 0.167 mmol) in 2 mL CH₂Cl₂. The suspension is vigorously stirred for 2 hours and filtered. The 15 volatile components are removed under reduced pressure and the crystalline product triphenylsulfonium methyltricyanoborate is received. The yield of triphenylsulfonium methyltricyanoborate is 57 mg (0.155 mmol).

20 ¹¹B{¹H}-NMR: δ , ppm = -33.5 (s).

¹¹B-NMR: δ , ppm = -33.5 (q, ²J_{B,H} = 4.4 Hz).

¹H{¹¹B}-NMR: δ , ppm = 7.9 (m, C_{arom}H, 15H), -0.03 (s, BCH₃, 3H).

¹H-NMR: δ , ppm = 7.9 (m, C_{arom}H, 15H), -0.03 (deformed q, ²J_{B,H} ≈ 5 Hz, BCH₃, 3H).

25 ¹³C{¹H}-NMR: δ , ppm = 135.7 (s, C_{arom}, 3C), 132.6 (s, C_{arom}, 6C), 132.2 (s, C_{arom}, 6C), 131.5 (q, ¹J_{C,B} = 64 Hz, CN, 3C), 125.9 (s, C_{arom}, 3C), 4.8 (q, ¹J_{C,B} = 45.0 Hz, BCH₃, 1C).

Example 15: Diphenyliodonium methyltricyanoborate –
[(C₆H₅)₂I][CH₃B(CN)₃]

- 70 -



K[CH₃B(CN)₃] (50 mg, 0.157 mmol) is added to a suspension of diphenyliodonium chloride, [(C₆H₅)₂I]Cl, (50 mg, 0.157 mmol) in 2 mL

5 CH₂Cl₂. The suspension is vigorously stirred for 2 hours and filtered. The volatile components are removed under reduced pressure and the crystalline product diphenyliodonium methyltricyanoborate is received.

The yield of diphenyliodonium methyltricyanoborate is 58 mg (0.150 mmol).

10 ¹¹B{¹H}-NMR: δ , ppm = -33.5 (s).

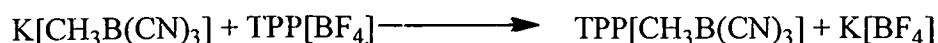
¹¹B-NMR: δ , ppm = -33.5 (s, broad).

¹H{¹¹B}-NMR: δ , ppm = 8.32 (m, C_{arom}H, 4H), 7.76 (m, C_{arom}H, 2H), 7.61 (m, C_{arom}H, 4H), -0.02 (s, BCH₃, 3H).

15 ¹H-NMR: δ , ppm = 8.32 (m, C_{arom}H, 4H), 7.76 (m, C_{arom}H, 2H), 7.61 (m, C_{arom}H, 4H), -0.02 (verzertertes q, ²J_{B,H} ~ 5 Hz, BCH₃, 3H).

¹³C{¹H}-NMR: δ , ppm = 136.3 (s, C_{arom}, 4C), 133.6 (s, C_{arom}, 2C), 133.2 (s, C_{arom}, 4C), 131.5 (q, ¹J_{C,B} = 64 Hz, CN, 3C), 115.7 (s, C_{arom}, 2C), 4.7 (q, ¹J_{C,B} = 45 Hz, BCH₃, 1C).

20 **Example 16: 2,4,6-Triphenylpyrylium methyltricyanoborate –**
TPP[CH₃B(CN)₃]



25 A solution of triphenylpyrylium tetrafluoroborate, [TPP][BF₄], (100 mg, 0.252 mmol), in acetonitrile (2 ml) and a solution of potassium methyltricyanoborate (36 mg, 0.252 mmol) in acetonitrile (2 ml) are combined and mixed. The salt potassium tetrafluoroborate is filtered at 0°C and all volatile components are removed under reduced pressure resulting in 30 the solid compound 2,4,6-triphenylpyrylium methyltricyanoborate.

The yield of 2,4,6-triphenylpyrylium methyltricyanoborate is 95 mg (0.2298 mmol) containing 1 % $[\text{BF}_4]^-$.

$^{11}\text{B}\{^1\text{H}\}$ -NMR (CD₃CN): δ , ppm = -33.5 (s).

5 ^{11}B -NMR (CD₃CN): δ , ppm = -33.5 (s).

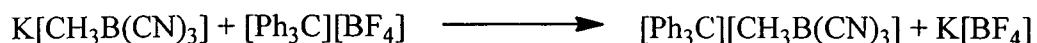
$^1\text{H}\{^{11}\text{B}\}$ -NMR: δ , ppm = 8.69 (s, C_{arom}, 2H), 8.41 (m, C_{arom}, 4H), 8.29 (m, C_{arom}, 2H), 7.85 (m, C_{arom}, 3H), 7.76 (m, C_{arom}, 6H), -0.03 (s, BCH_3 , 3H).

^1H -NMR: δ , ppm = 8.69 (s, C_{arom}, 2H), 8.41 (m, C_{arom}, 4H), 8.29 (m, C_{arom}, 2H), 7.85 (m, C_{arom}, 3H), 7.76 (m, C_{arom}, 6H), -0.03 (verzerrtes q, $^2J_{\text{B},\text{H}} \approx 5$ Hz, BCH_3 , 3H).

10 $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ , ppm = 171.8 (s, C_{arom}), 167.4 (s, C_{arom}), 136.4 (s, C_{arom}), 136.3 (s, C_{arom}), 133.8 (s, C_{arom}), 131.7 (q, $^1J_{\text{C},\text{B}} = 64$ Hz, CN, 3C), 131.04 (s, C_{arom}), 131.02 (s, C_{arom}), 130.6 (s, C_{arom}), 129.9 (s, C_{arom}), 129.7 (s, C_{arom}), 116.7 (s, C_{arom}), 4.3 (q, $^1J_{\text{C},\text{B}} = 45$ Hz, BCH_3 , 1C).

15

Example 17: Triphenylcarbenium methyltricyanoborate –
[Ph₃C][CH₃B(CN)₃]



20

A solution of triphenylcarbenium (tritylium) tetrafluoroborate, [Ph₃C][BF₄], (100 mg, 0.303 mmol), in acetonitrile (2 ml) and a solution of potassium methyltricyanoborate (43 mg, 0.301 mmol) in acetonitril (2 ml) are combined and mixed. The salt potassium tetrafluoroborate is filtered at 0°C and all volatile components are removed under reduced pressure resulting in the compound tritylium methyltricyanoborate.

The yield of triphenylcarbenium methyltricyanoborate is 102 mg (0.29 mmol) containing 1 % $[\text{BF}_4]^-$ and 19 % unknown boron species.

30

$^{11}\text{B}\{^1\text{H}\}$ -NMR (CD₃CN): δ , ppm = -33.5 (s).

^{11}B -NMR (CD₃CN): δ , ppm = -33.5 (s).

$^1\text{H}\{^{11}\text{B}\}$ -NMR: δ , ppm = 8.25 (m, C_{arom}, 3H), 7.86 (m, C_{arom}, 6H), 7.69 (m, C_{arom}, 6H), 0.00 (s, BCH_3 , 3H).

^1H -NMR: δ , ppm = 8.25 (m, C_{arom}, 3H), 7.86 (m, C_{arom}, 6H), 7.69 (m, C_{arom}, 6H), 0.00 (m, BCH_3 , 3H).

5

Example 18: 1-Ethyl-3-methylimidazolium Vinyltricyanoborate –

EMIM[H₂C=HCB(CN)₃]



10



15

A mixture of trimethylsilylcyanide (86 mol%), fluorotrimethylsilane (4 mol%), chlorotrimethylsilane (3 mol%) and acetonitril (4 mol%) is added to 1-Ethyl-3-methylimidazolium vinyltrifluoroborate, EMIM[H₂C=HCBF₃], (1.48 g, 7.18 mmol) and stirred for 12 hours at room temperature. All volatile components are removed under reduced pressure.

The yield of EMIM[H₂C=HCB(CN)₃] is 1.55 g (6.82 mmol) containing 2 % [H₂C=HCBF₂(CN)]⁻ and 2.5 % [H₂C=HCB(NC)(CN)₂]⁻.

$^{11}\text{B}\{^1\text{H}\}$ -NMR: δ , ppm = -31.4 (s).

20

^{11}B -NMR: δ , ppm = -31.4 (s, verbreitert).

$^1\text{H}\{^{11}\text{B}\}$ -NMR: δ , ppm = 8.89 (verbreitertes s, CH, 1H), 7.67 (dd, $^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.8$ Hz, CH, 1H), 7.62 (dd, $^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.8$ Hz, CH, 1H), 5.75 (dd, $J_{\text{H,H}} = 19.0$ Hz, $J_{\text{H,H}} = 12.4$ Hz, 1H), 5.40 (m, 2H), 4.35 (q, $J_{\text{H,H}} = 7.3$ Hz, CH₂, 2H), 4.00 (s, CH₃, 3H), 1.55 (t, $^3J_{\text{H,H}} = 7.3$ Hz, CH₃, 3H).

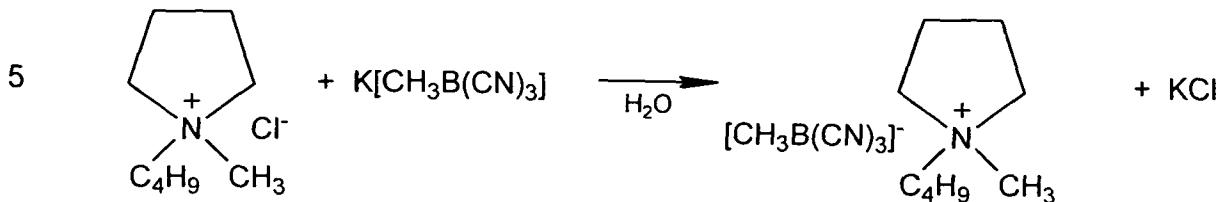
25

^1H -NMR: δ , ppm = 8.89 (breites s, CH, 1H), 7.67 (dd, $^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.8$ Hz, CH, 1H), 7.62 (dd, $^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.8$ Hz, CH, 1H), 5.75 (dd, verbreitert, $J_{\text{H,H}} = 19.0$ Hz, $J_{\text{H,H}} = 12.4$ Hz, 1H), 5.40 (m, 2H), 4.35 (q, $^3J_{\text{H,H}} = 7.3$ Hz, CH₂, 2H), 4.00 (s, CH₃, 3H), 1.55 (t, $^3J_{\text{H,H}} = 7.3$ Hz, CH₃, 3H).

30

$^{13}\text{C}\{^1\text{H}\}$ -NMR: δ , ppm = 139.29 (q, $^1J_{\text{C,B}} = 55.3$ Hz, BCH , 1C), 136.69 (s, 1C), 129.04 (q, $^1J_{\text{C,B}} = 63.7$ Hz, BCN , 3C), 124.5 (s, 1C), 123.7 (s, 1C), 122.8 (s, 1C), 45.5 (s, 1C), 36.5 (s, 1C), 15.4 (s, 1C).

Example 19. Butylmethylpyrrolidinium tricyanomethylborate –
[BMPL][CH₃B(CN)₃]



10 Butylmethylpyrrolidinium chloride, [BMPL]Cl, (190 mg, 1.07 mmol), and potassium methyltricyanoborate (168 mg, 1.18 mmol) are suspended in chloroform (5 ml) and stirred for one hour. The potassium chloride formed and excess potassium methyltricyanoborate are subsequently filtered off. The filtrate is evaporated in vacuo, giving an ionic liquid.

15 Yield: 243 mg (0.987 mmol).

The NMR spectra of BMPL [CH₃B(CN)₃]:

¹¹B{¹H}-NMR: δ , ppm = -32.5 s.

¹¹B-NMR: δ , ppm = -32.5 q ($^2J_{\text{B},\text{H}} = 4.2$ Hz).

20 ¹H{¹¹B}-NMR: δ , ppm = 3.75-3.67 m (CH₂, 4H), 3.56-3.52 m (CH₂, 2H), 3.25 s (CH₃, 3H), 2.37-2.29 m (CH₂, 4H), 1.95-1.87 m (CH₂, 2H), 1.49-1.40 m (CH₂, 2H), 0.99 t ($^3J_{\text{H},\text{H}} = 7.4$ Hz, CH₃, 3H), -0.03 s (BCH₃, 3H).

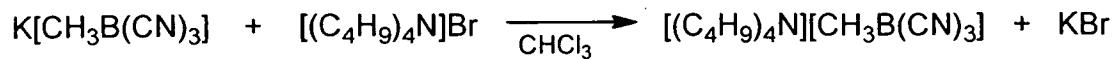
25 ¹H-NMR: δ , ppm = 3.75-3.67 m (CH₂, 4H), 3.56-3.52 m (CH₂, 2H), 3.25 s (CH₃, 3H), 2.37-2.29 m (CH₂, 4H), 1.95-1.87 m (CH₂, 2H), 1.49-1.40 m (CH₂, 2H), 0.99 t ($^3J_{\text{H},\text{H}} = 7.4$ Hz, CH₃, 3H), -0.03 q ($^2J_{\text{B},\text{H}} = 4.4$ Hz, BCH₃, 3H).

30 ¹³C{¹H}-NMR: δ , ppm = 131.5 q ($^1J_{\text{C},\text{B}} = 63.9$ Hz, BCN, 3C), 65.3 t ($^1J_{\text{N},\text{C}} = 3.2$ Hz, NCH₂, 2C), 65.1 t ($^1J_{\text{N},\text{C}} = 2.9$ Hz, NCH₂, 1C), 49.1 t ($^1J_{\text{N},\text{C}} = 4.0$ Hz,

NCH₃, 1C), 26.3 s (CH₂, 1C), 22.4 s (1C), 20.4 t (²J_{N,C} = 1.4 Hz, NCH₂CH₂, 1C), 13.8 s (CH₃, 1C), 4.7 q (¹J_{C,B} = 45 Hz, BCH₃, 1C).

Example 20. Tetrabutylammonium tricyanomethylborate –

5 [TBA][CH₃B(CN)₃]



Tetrabutylammonium bromide, [TBA]Br, (200 mg, 0.620 mmol), and potassium methyltricyanoborate (98 mg, 0.685 mmol) are suspended in 10 chloroform (5 ml) and stirred for one hour. The potassium chloride formed and excess potassium methyltricyanoborate are subsequently filtered off, and the filtrate is evaporated in vacuo. A slightly yellow solid is obtained.

15 The yield of tetrabutylammonium tricyanomethylborate is 211 mg (0.609 mmol), corresponding to 98%, based on the [TBA]Br employed.

The NMR spectra of TBA [CH₃B(CN)₃]:

¹¹B{¹H}-NMR: δ , ppm = -32.5 s.

¹¹B-NMR: δ , ppm = -32.5 q (²J_{B,H} = 4.2 Hz, 1B).

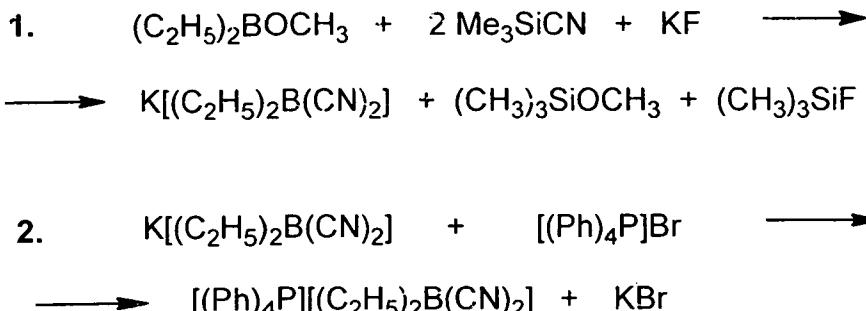
20 ¹H{¹¹B}-NMR: δ , ppm = 3.43-3.38 m (CH₂, 8H), 1.85-1.77 m (CH₂, 8H), 1.48-1.39 m (CH₂, 8H), 0.98 t (³J_{H,H} = 7.4 Hz, CH₃, 12H), -0.02 s (BCH₃, 3H).

25 ¹H-NMR: δ , ppm = 3.43-3.38 m (CH₂, 8H), 1.85-1.77 m (CH₂, 8H), 1.48-1.39 m (CH₂, 8H), 0.98 t (³J_{H,H} = 7.4 Hz, CH₃, 12H), -0.02 q (²J_{B,H} = 4.4 Hz, BCH₃, 3H).

30 ¹³C{¹H}-NMR: δ , ppm = 131.5 q (¹J_{C,B} = 63.3 Hz, BCN, 3C), 59.4 s (4C), 24.4 s (CH₂, 4C), 20.4 s (CH₂, 4C), 13.9 s (CH₃, 4C), 4.8 q (¹J_{C,B} = 45 Hz, BCH₃, 1C).

Example 21. Tetraphenylphosphonium diethyldicyanoborate –

- 75 -

[PPh₄][(C₂H₅)₂B(CN)₂]

Potassium fluoride, KF (1.0 g, 17.24 mmol), is suspended in acetonitrile (4 ml). (C₂H₅)₂BOCH₃ (2.26 ml, 1.72 g, 17.24 mmol) and trimethylsilyl cyanide (5.0 ml, 37.49 mmol) are added at 0°C. The reaction mixture is stirred overnight at room temperature, and the yellow suspension obtained is then taken up in aqueous H₂O₂ (20%, 15 ml). Tetraphenylphosphonium bromide, [PPh₄]Br (7.5 g, 17.88 mmol), is added to the solution under stirring, and the reaction mixture is extracted with CH₂Cl₂ (2 × 20 ml) after 30 min stirring. The combined dichloromethane phases are dried using MgSO₄ and evaporated to dryness. The residue obtained is dissolved in acetone (5 ml) and precipitated by addition of Et₂O (15 ml) and subsequently filtered.

20 The yield of solid tetraphenylphosphonium diethyldicyanoborate is 3.52 g (7.64 mmol).

The NMR spectra of [PPh₄][(C₂H₅)₂B(CN)₂]:

25 ¹¹B-NMR: δ, ppm = -22.1 s.

¹H{¹¹B}-NMR: δ, ppm = 8.05-7.98 m (p-H, 4Ph, 4H), 7.90-7.83 m (o- and m-H, 4Ph, 16H), 0.85 t (³J_{H,H} = 7.7 Hz, 2CH₂, 4H), 0.23 q (³J_{H,H} = 7.6 Hz, 2CH₃, 6H).

30 ¹H-NMR: δ, ppm = 8.05-7.98 m (p-H, 4Ph, 4H), 7.90-7.83 m (o- and m-H, 4Ph, 16H), 0.85 br. t (³J_{H,H} = 7.7 Hz, 2CH₂, 4H), 0.23 br. q (³J_{H,H} = 7.6 Hz, 2CH₃, 6H).

5 $^{13}\text{C}\{\text{H}\}$ -NMR: δ , ppm = 138.4 q ($^1J_{\text{C},\text{B}} = 53.1$ Hz, 2CN, 2C), 136.4 d ($^4J_{\text{P},\text{C}} = 3.1$ Hz, 4C), 135.7 d ($^2J_{\text{P},\text{C}} = 10.3$ Hz, 8C), 131.4 d ($^3J_{\text{P},\text{C}} = 12.8$ Hz, 8C), 119.0 d ($^1J_{\text{P},\text{C}} = 89.6$ Hz, 4C), 15.0 q ($^1J_{\text{C},\text{B}} = 46.8$ Hz, 2CH₂, 2C), 12.3 s (2CH₃, 2C).

10 ^{13}C -NMR (only [(C₂H₅)₂B(CN)₂] anion): δ , ppm = 138.4 q ($^1J_{\text{C},\text{B}} = 53.1$ Hz, 2CN, 2C), 15.0 t,q ($^1J_{\text{H},\text{C}} = 113.7$ Hz, $^1J_{\text{C},\text{B}} = 46.8$ Hz, 2CH₂, 2C), 12.3 q,t ($^1J_{\text{H},\text{C}} = 122.9$ Hz, $^2J_{\text{H},\text{C}} = 4.2$ Hz, 2CH₃, 2C).

15 MALDI-MS m/e [C₆H₁₀BN₂]⁻:

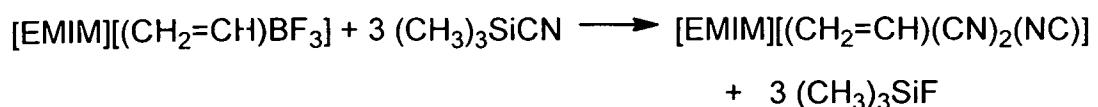
calculated: 120 (24%), 121 (100%), 122 (7%).
found: 120 (26%), 121 (100%), 122 (10%).

20 Raman spectrum: $\tilde{\nu}$ (CN) = 2185 cm⁻¹

Melting point (DSC, onset): 116°C

Decomposition (DSC, onset): 336°C

25 **Example 22. 1-Ethyl-3-methylimidazolium vinylidicyanoisocyanoborate**
– [EMIM][(CH₂=CH)B(CN)₂(NC)]



25 Trimethylsilyl cyanide (15 ml, 112.48 mmol) is condensed at -196°C into a reaction vessel filled with 1-ethyl-3-methylimidazolium vinyltrifluoroborate, [EMIM][(CH₂=CH)BF₃] (0.5 g, 2.42 mmol), and the mixture is warmed to room temperature. The solution obtained is stirred overnight, then warmed at 65°C for three hours, at 80°C for two hours and finally at 90°C for four hours. The excess trimethylsilyl cyanide is subsequently distilled off (recovered) as a mixture with trimethylfluorosilane formed and employed for further reactions. A colorless ionic liquid is isolated.

The yield of ethylmethyliimidazolium vinylidicyanoisocyanoborate, [EMIM]
[(CH₂=CH)B(CN)₂(NC)], (93% purity), is 0.52 g (2.41 mmol). The liquid
contains about 3% of [EMIM][(CH₂=CH)B(CN)₃], 3% of
5 [EMIM][(CH₂=CH)B(CN)₂F] and about 1% of [EMIM][B(CN)₂F₂].

NMR data of the [(CH₂=CH)B(CN)₂(NC)]⁻ anion:

¹¹B{¹H}-NMR: δ , ppm = -23.0 s.

¹¹B-NMR: δ , ppm = -23.0 s.

10 ¹H{¹¹B}-NMR: δ , ppm = 5.89-5.71 m (CH₂=CH, 1H), 5.45-5.28 m (CH₂=CH,
2H).

¹H-NMR: δ , ppm = 5.89-5.71 br. m (CH₂=CH, 1H), 5.45-5.28 br. m
(CH₂=CH, 2H).

15 ¹³C{¹H}-NMR: δ , ppm = 170.0 s (BNC, 1C), 141.3 q (¹J_{C,B} = 59.0 Hz,
BCH=CH₂, 1C), 129.8 q (¹J_{C,B} = 67.8 Hz, BCN, 2C), 122.6 s (BCH=CH₂,
1C).

NMR data of the [(CH₂=CH)B(CN)₃]⁻ anion:

¹¹B{¹H}-NMR: δ , ppm = -30.4 s.

20 ¹¹B-NMR: δ , ppm = -30.4 s.

NMR data of the [(CH₂=CH)B(CN)₂F]⁻ anion:

¹¹B{¹H}-NMR: δ , ppm = -9.2 d (¹J_{F,B} = 54.6 Hz).

¹¹B-NMR: δ , ppm = -9.2 d (¹J_{F,B} = 54.6 Hz).

25 ¹⁹F-NMR: δ , ppm = -132.9 q (¹J_{F,B} = 51.9 Hz).

NMR data of the [BF₂(CN)₂]⁻ anion:

¹¹B{¹H}-NMR: δ , ppm = -7.3 t (¹J_{F,B} = 41.2 Hz).

¹¹B-NMR: δ , ppm = -7.3 t (¹J_{F,B} = 41.2 Hz).

30

NMR data of the [EMIM]⁺ cation:

$^1\text{H}\{^{11}\text{B}\}$ -NMR: δ , ppm = 8.91 br. s (CH, 1H), 7.68 t ($^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.7$ Hz, CH, 1H), 7.62 t ($^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.7$ Hz, CH, 1H), 4.36 q ($^3J_{\text{H,H}} = 7.3$ Hz, CH₂, 2H), 4.02 s (CH₃, 3H), 1.57 t ($^3J_{\text{H,H}} = 7.3$ Hz, CH₃, 3H).

5 ^1H -NMR: δ , ppm = 8.91 br. s (CH, 1H), 7.68 t ($^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.7$ Hz, CH, 1H), 7.62 t ($^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.7$ Hz, CH, 1H), 4.36 q ($^3J_{\text{H,H}} = 7.3$ Hz, CH₂, 2H), 4.02 s (CH₃, 3H), 1.57 t ($^3J_{\text{H,H}} = 7.3$ Hz, CH₃, 3H).

10 $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ , ppm = 136.7 s (1C), 124.5 s (1C), 122.9 s (1C), 45.6 s (1C), 36.5 s (1C), 15.4 s (1C).

Example 23. Potassium methylidicyanofluoroborate - K [CH₃BF(CN)₂]

A)



15

Potassium methyltrifluoroborate (3.00 g, 24.6 mmol) is suspended in trimethylsilyl cyanide (40.0 ml, 300.0 mmol) and stirred for 3 days at room temperature. After 3 days, the reaction mixture is stirred for 1 hour at 60°C and 2 hours at 70°C until the reaction mixture is clear. All volatile constituents are removed in vacuo. The unreacted trimethylsilyl cyanide and trimethylfluorosilane can be employed for further reactions. The residue is dissolved in acetone (30 ml) and filtered. CHCl₃ (100ml) is added to the organic phase and K[CH₃BF(CN)₂] precipitates (batch I). Said precipitate is dried in vacuo. The organic solvent of the filtrate is distilled in vacuo until 5 ml are received and 50 ml CHCl₃ are added. K[CH₃BF(CN)₂] precipitates (batch II).

Batch I: 2.3 g (16.9 mmol) without by-product as described in Example 1A. The spectroscopic data correspond to those from Example 1A.

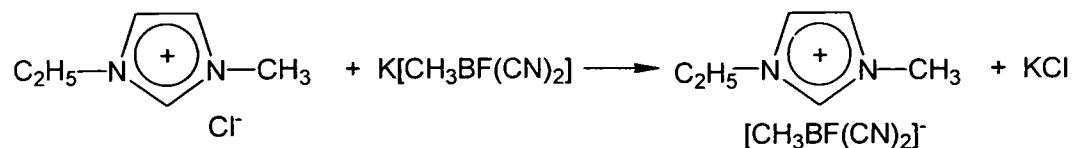
30 Batch II: 0.53 g of a mixture of K[CH₃BF(CN)₂] (82%) and K[CH₃B(NC)(CN)₂] (17%) and other impurities (1%).

B)

Potassium methyltrifluoroborate (8.00 g, 65.6 mmol) is suspended in trimethylsilyl cyanide (120.0 ml, 900.0 mmol, 30 ml trimethylsilyl cyanide recovered from Example 22 and stirred 2 hours at 70°C until the solution is nearly clear. All volatile constituents are removed in vacuo. The residue is dissolved in acetone (40 ml) and filtered. The filtrate is stirred and 400 ml CHCl₃ is added within 45 minutes. The precipitate of K[CH₃BF(CN)₂] is filtered and dried in vacuo (6.71 g (49.3 mmol)). The spectroscopic data correspond to those from Example 1A.

10

Example 24. 1-Ethyl-3-methylimidazolium methyldicyanofluoroborate - EMIM [CH₃BF(CN)₂]



K[CH₃BF(CN)₂] (6.0 g, 44.1 mmol) and 1-ethyl-3-methylimidazolium chloride, [EMIM]Cl, (6.45 g, 44.0 mmol) are suspended in CH₂Cl₂ (50 mL) and stirred for 5 hours at room temperature. Magnesium sulfate is added (1g) and the reaction mixture is stirred for 30 min and filtered. The precipitate is washed with 15 ml of CH₂Cl₂ and the organic phases are combined. All volatile compounds are removed in vacuo and the resulted ionic liquid is dried in vacuo for 2 days.

25 8.8 g (42.31 mmol) of EMIM [CH₃BF(CN)₂]

The spectroscopic data correspond to Example 8.

Dynamic viscosity:

30

°C	mPa·s
20	16.2
40	9.3
60	6.0

80	4.2
----	-----

Example 25. 1-Butyl-1-methylpyrrolidinium methyldicyanofluoroborate - [BMPL] [CH₃BF(CN)₂]

5



10

15

K[CH₃BF(CN)₂] (2.8 g, 20.6 mmol) and 1-butyl-1-methylpyrrolidinium Chloride, [BMPL]Cl (3.6 g, 20.5 mmol) are suspended in CH₂Cl₂ (25 mL) and stirred for 5 hours at room temperature. Magnesium sulfate is added (1g) and the reaction mixture is stirred for 30 min and filtered. The precipitate is washed with 10 ml of CH₂Cl₂ and the organic phases are combined. All volatile compounds are removed in vacuo and the resulted ionic liquid is dried in vacuo for 2 days.

The yield of [BMPL] [CH₃BF(CN)₂] is 4.3 g (18.0 mmol)

20

The NMR spectra of [BMPL][CH₃BF(CN)₂]:

¹¹B{¹H}-NMR: δ , ppm = -8.9 d (¹J_{F,B} = 56.6 Hz).

¹¹B-NMR: δ , ppm = -8.9 br. d (¹J_{F,B} = 56.5 Hz).

¹⁹F-NMR: δ , ppm = -202.7 q,q (¹J_{F,B} = 56.2 Hz, ³J_{F,H} = 14.1 Hz, BF).

25

¹H{¹¹B}-NMR: δ , ppm = 3.78-3.72 m (2CH₂, 4H), 3.75-3.60 m (CH₂, 2H), 3.27 s (CH₃, 3H), 2.35-2.30 m (2CH₂, 4H), 1.95-1.88 m (CH₂, 2H), 1.49-1.42 m (CH₂, 2H), 0.99 t (³J_{H,H} = 7.4 Hz, CH₃, 3H), -0.10 d (³J_{F,H} = 14.3 Hz, BC_H₃, 3H).

30

¹H-NMR: δ , ppm = 3.78-3.72 m (2CH₂, 4H), 3.75-3.60 m (CH₂, 2H), 3.27 s (CH₃, 3H), 2.35-2.30 m (2CH₂, 4H), 1.95-1.88 m (CH₂, 2H), 1.49-1.42 m

(CH₂, 2H), 0.99 t (³J_{H,H} = 7.4 Hz, CH₃, 3H), -0.10 d (³J_{F,H} = 14.3 Hz, ²J_{B,H} ≈ 4.6 Hz, BCH₃, 3H).

Dynamic viscosity:

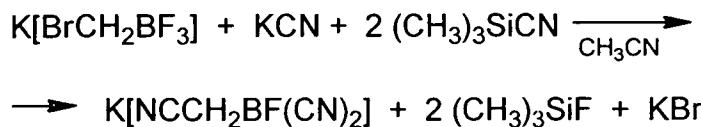
5	°C	mPa·s
20		46.0
40		22.8
60		13.1
80		8.4

10

Example 26. Potassium cyanomethyldicyanofluoroborate -
K[NCCH₂BF(CN)₂]

A)

15



20

K[BrCH₂BF₃] (86 mg, 0.428 mmol) and KCN (200 mg, 3.07 mmol) are suspended in trimethylsilylcyanide (2.0 mL, 14.99 mmol). The reaction mixture is warmed to 60 °C over night, to 70 °C for 5 days, and to 80 °C for further 2 days. All volatile materials were removed under reduced pressure and the remaining solid material is extracted with acetone (5 mL). Extract is evaporated in vacuum yielding a light-brown solid.

25

The yield of potassium cyanomethyldicyanofluoroborate is 55 mg (0.34 mmol).

The spectroscopic data of K[NCCH₂BF(CN)₂]:

¹¹B{¹H}-NMR: δ, ppm = -10.5 d (¹J_{F,B} = 54.2 Hz).

¹¹B-NMR: δ, ppm = -10.5 dt, (¹J_{F,B} = 54.2 Hz, ²J_{H,B} = 5.6 Hz).

¹⁹F-NMR: δ, ppm = -205.6 qt (¹J_{F,B} = 54.2 Hz, ³J_{F,H} = 10.9 Hz, BF).

¹H{¹¹B}-NMR: δ, ppm = 1.38 d (³J_{F,H} = 10.9 Hz, CH₂).

¹H-NMR: δ, ppm = 1.38 dq (³J_{F,H} = 10.9 Hz, ²J_{B,H} = ≈6 Hz, CH₂).

30

¹³C{¹H}-NMR: δ , ppm = 130.45 qd ($^1J_{C,B} = 69.7$ Hz, $^2J_{F,C} = 38.2$ Hz, B-CN, 2C), 121.18 s (CH₂-CN, 1C), 10.37 qd ($^1J_{C,B} = 45.9$ Hz, $^2J_{F,C} = 28.8$ Hz, CH₂, 1C).

5

¹³C-NMR: δ , ppm = 130.45 dq ($^1J_{C,B} = 69.7$ Hz, $^2J_{F,C} = 38.2$ Hz, B-CN, 2C), 121.18 broad t ($^3J_{C,H} \approx 7$ Hz, CH₂-CN, 1C), 10.37 qd ($^1J_{C,B} = 45.9$ Hz, $^2J_{F,C} = 28.8$ Hz, CH₂, 1C).

10 10 MALDI-MS m/z [C₄H₂BFN₃]⁺:

calculated: 122 (100%), 121 (25%), 123 (5%)

found: 122 (100%), 121 (26%), 123 (4%)

B)

A mixture (50 mL) of trimethylsilylcyanide (86 mol%), fluorotrimethylsilane (4 mol%), chlorotrimethylsilane (3 mol%) and acetonitril (4 mol%) and 15 ml trimethylsilylcyanide (112.5 mmol) are added to potassium cyanomethyltrifluoroborate (5.7 g, 38.77 mmol) and the suspension is stirred for 2 hours at room temperature. All volatile components are removed under reduced pressure. These volatile components can be stored and be used for further syntheses. If the remaining product still contains [NCCH₂BF₃]⁻ and [NCCH₂BF₂(CN)]⁻, the mixture will be added to a mixture of [(CH₃)₃SiCN, (CH₃)₃SiF, (CH₃)₃SiCl, CH₃CN] and pure (CH₃)₃SiCN (15 mL, 112.5 mmol) and said suspension should be stirred for another two days. All volatile compounds are removed under reduced pressure again. The remainder is solved in acetone (10 mL) and 120 mL dichloromethane are added. The resulting precipitate of potassium cyanomethyldicyanofluoroborate is filtered and dried under reduced pressure.

The yield of potassium cyanomethyldicyanofluoroborate is 4.5 g (27.95 mmol).

Elemental analysis:

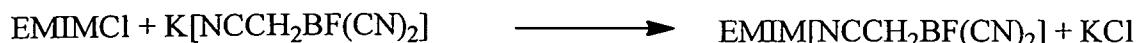
5 Calculated: C 29.84; H 1.25; N 26.10

Found: C 30.08; H 1.16; N 26.06

The spectroscopic data of the product correspond to those from Example 26A.

10 **Example 27: 1-Ethyl-3-methylimidazolium**

cyanomethyldicyanofluoroborate - EMIM[NCCH₂BF(CN)₂]



15 Dichloromethane (60 mL) is added to a mixture of potassium cyanomethyldicyanofluoroborate, K[NCCH₂BF(CN)₂], (4.3 g, 26.71 mmol) and 1-ethyl-3-methylimidazolium chloride (EMIMCl) (4.3 g, 29.32 mmol) in H₂O (deionised, 30 mL). The aqueous phase is removed and the organic phase is washed with deionised water (5 × 1 mL) and dried over 20 magnesium sulfate. The sulfate is filtered and dichloromethane is removed under reduced pressure. The product is dried for three days at 50°C in vacuum.

The yield of 1-ethyl-3-methylimidazolium cyanomethyldicyanofluoroborate is 4.9 g (21.03 mmol).

25

¹¹B{¹H}-NMR: δ , ppm = -11.4 (d, $^1J_{\text{B},\text{F}} = 54.3$ Hz).

¹¹B-NMR: δ , ppm = -11.4 (dt, $^1J_{\text{B},\text{F}} = 54.3$ Hz, $^2J_{\text{B},\text{H}} = 5.7$ Hz).

¹⁹F-NMR: δ , ppm = -205.5 qt ($^1J_{\text{F},\text{B}} = 54.3$ Hz, $^3J_{\text{F},\text{H}} = 11.0$ Hz, BF).

¹H{¹¹B}-NMR: δ , ppm = 8.90 (broad dd, $^4J_{\text{H},\text{H}} \approx 1.6$ Hz, CH, 1H), 7.69 (dd,

30 $^3J_{\text{H},\text{H}} \approx 4J_{\text{H},\text{H}} \approx 1.8$ Hz, CH, 1H), 7.62 (dd, $^3J_{\text{H},\text{H}} \approx 4J_{\text{H},\text{H}} \approx 1.8$ Hz, CH, 1H), 4.36 (q, $^3J_{\text{H},\text{H}} = 7.4$ Hz, CH₂, 2H), 4.02 (s, CH₃, 3H), 1.55 (t, $^3J_{\text{H},\text{H}} = 7.3$ Hz, CH₃, 3H), 1.40 (d, $^3J_{\text{F},\text{H}} = 10.9$ Hz, 2H, CH₂).

- 84 -

¹H-NMR: δ , ppm = 8.90 (broad dd, $^4J_{H,H} \approx 1.6$ Hz, CH, 1H), 7.69 (dd, $^3J_{H,H} \approx 4J_{H,H} \approx 1.8$ Hz, CH, 1H), 7.62 (dd, $^3J_{H,H} \approx 4J_{H,H} \approx 1.8$ Hz, CH, 1H), 4.36 (q, $^3J_{H,H} = 7.4$ Hz, CH₂, 2H), 4.02 (s, CH₃, 3H), 1.55 (t, $^3J_{H,H} = 7.3$ Hz, CH₃, 3H), 1.40 (m, 2H, CH₂).

5 ¹³C{¹H}-NMR: δ , ppm = 136.8 (s, 1C), 131.2 (qd, $^1J_{C,B} = 69$ Hz, $^2J_{F,C} = 37$ Hz, CN, 2C), 124.6 (s, 1C), 122.9 (s, 1C), 122.1 (broad, s, 1C, CH₂CN), 45.6 (s, 1C), 36.6 (s, 1C), 15.5 (s, 1C), 10.9 (qd, $^1J_{C,B} = 47$ Hz, $^2J_{F,C} \approx 28$ Hz, 1C).

10 Elemental analysis:

calculated: C 51.54; H 5.62; Z 30.05

found: C 50.86; H 5.79, N, 30.35.

Dynamic viscosity:

15	°C	mPa·s
20		27.0
40		13.5
60		8.0
80		5.3

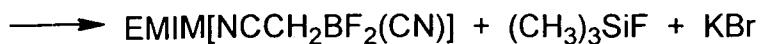
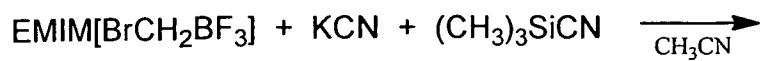
20

Decomposition's temperature: 180° C.

Example 28. 1-Ethyl-3-methylimidazolium

Cyanomethylcyanodifluoroborate - [EMIM][NCCH₂BF₂(CN)]

25



30

1-Ethyl-3-methylimidazolium cyanomethyltrifluoroborate, EMIM[BrCH₂BF₃], (120 mg, 0.439 mmol) and KCN (500 mg, 7.678 mmol) are added to stirred solution of trimethylsilyl cyanide in acetonitrile (2.5 mol/L, 2 mL, 5.0 mmol).

The reaction mixture is stirred at 75 °C (temperature in the oil-bath) for 24 hours and 4 days at 100 °C. All volatiles are removed in vacuum and residue is dissolved in 2 mL of acetone. The non-soluble solids (presumably excess of KCN and KBr) are filtered off and the solution is 5 evaporated in vacuum. The residue (oily material) is dissolved in acetone-D6 and analysed by means of mass- and NMR-spectroscopy. The NMR spectra confirm the formation of the [EMIM][NCCH₂BF₂(CN)] in 90% yield. The product contains of about 7 % [EMIM][NCCH₂BF(CN)₂].

10 The spectroscopic data of the anion [NCCH₂BF₂(CN)]:

¹¹B{¹H}-NMR: δ , ppm = 0.0 t (¹J_{F,B} = 55.8 Hz).

¹¹B-NMR: δ , ppm = 0.0 tt (¹J_{F,B} = 55.8 Hz, ²J_{H,B} = 6.1 Hz).

¹⁹F-NMR: δ , ppm = -152.7 qt (¹J_{F,B} = 55.8 Hz, ³J_{F,H} = 8.0 Hz, BF).

¹H{¹¹B}-NMR: δ , ppm = 1.13 t (³J_{F,H} = 8.2 Hz, CH₂).

15 ¹H-NMR: δ , ppm = 1.13 tq (³J_{F,H} ≈ 9 Hz, ²J_{B,H} ≈ 6 Hz, CH₂).

NMR spectroscopic data of the cation [EMIM]⁺:

¹H-NMR: δ , ppm = 9.00 s (CH, 1H), 7.72 broad s (CH, 1H), 7.65 broad s (CH, 1H), 4.37 q (³J_{H,H} = 7.3 Hz, CH₂, 2H), 4.03 (s, Me, 3H), 1.55 (t, ³J_{H,H} = 7.3 Hz, Me, 3H).

MALDI-MS m/z [C₃H₂BF₂N₂]⁻:

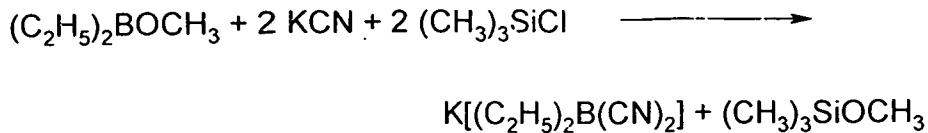
calculated: 115 (100%), 114 (25%), 116 (4%)

found: 115 (100%), 114 (23%), 116 (2%)

25

The NMR spectroscopic data of the anion [NCCH₂BF(CN)₂]⁻, that is formed in approximately 7% yield are consistent with those of the anion as found for K[NCCH₂BF(CN)₂] in Example 26.

30 **Example 29: Potassium diethyldicyanoborate – K[(C₂H₅)₂B(CN)₂]**



5 A suspension of potassium cyanide (35.0 g, 537.46 mmol) in acetonitrile (100 mL) is prepared and $(C_2H_5)_2BOCH_3$ (25.0 mL, 192.31 mmol) is added (moderate exothermic reaction) and to said mixture, chlorotrimethylsilane (30.0 mL, 237.48 mmol) is added (exothermic reaction). The suspension is stirred for two days at 65°C and filtered. The filtrate is washed with 100 mL acetonitrile. The content of acetonitrile is reduced within the combined organic phases through distillation under reduced pressure. After addition of pentane, the product potassium diethyldicyanoborate precipitates and is filtered and dried in vaccum.

10 The yield of potassium diethyldicyanoborate is 29.1 g (181.85 mmol).

15

^{11}B -NMR (CD_3CN): δ , ppm = - 23.1 (s, broad).

$^{11}B\{^1H\}$ -NMR (CD_3CN): δ , ppm = - 23.1 (s).

$^1H\{^{11}B\}$ -NMR (CD_3CN): δ , ppm = 0.83 (t, broad, $^3J_{H,H}$ = 7.6 Hz, CH_3 , 6H), 0.19 (q, $^3J_{H,H}$ = 7.6 Hz, CH_2 , 4H).

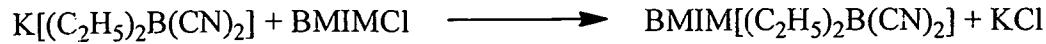
20

1H -NMR (CD_3CN): δ , ppm = 0.83 (t, $^3J_{H,H}$ = 7.5 Hz, CH_3 , 6H), 0.19 (q, broad, $^3J_{H,H}$ = 7.6 Hz, CH_2 , 4H).

$^{13}C\{^1H\}$ -NMR (CD_3CN): δ , ppm = 139.3 (m, broad, CN, 2C), 14.6 (q, broad, $^1J_{C,B}$ = 48 Hz, CH_2 , 2C), 12.0 (s, CH_3 , 2C).

25

Example 30. 1-Butyl-3-methylimidazolium diethyldicyanoborate -
BMIM[$(C_2H_5)_2B(CN)_2$]



30

Dichloromethane (50 mL) is added to a mixture of potassium diethyldicyanoborate (6.0 g, 37.48 mmol) and 1-butyl-3-methylimidazolium chloride (BMIMCl) (6.5 g, 37.21 mmol) in H_2O (deionised, 20 mL). The

aqueous phase is removed and the organic phase is washed with deionised water (5×1 mL) and dried over magnesium sulfate. The sulfate is filtered and dichloromethane is removed under reduced pressure. The product is dried for three days at 50°C in vacuum.

5 The yield of 1-butyl-3-methylimidazolium diethyldicyanoborate is 8.9 g (34.21 mmol).

$^{11}\text{B}\{\text{H}\}$ -NMR: δ , ppm = -23.1 (s).

^{11}B -NMR: δ , ppm = -23.1 (s, broad).

10 $^1\text{H}\{\text{H}\}$ -NMR: δ , ppm = 8.90 (dd, $^4J_{\text{H,H}} \approx 1.7$ Hz, CH, 1H), 7.63 (dd, $^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.7$ Hz, CH, 1H), 7.57 (dd, $^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.7$ Hz, CH, 1H), 4.22 (t, $^3J_{\text{H,H}} = 7.28$ Hz, CH₂, 2H), 3.92 (s, CH₃, 3H), 1.80 (m, CH₂, 2 H), 1.26 (m, CH₂, 2H), 0.82 (t, $^3J_{\text{H,H}} = 7.40$ Hz, CH₃, 3H), 0.83 (t, $^3J_{\text{H,H}} = 7.7$ Hz, CH₃, 6H), 0.20 (q, $^3J_{\text{H,H}} = 7.7$ Hz, CH₂, 4H).

15 ^1H -NMR: δ , ppm = 8.90 (dd, $^4J_{\text{H,H}} \approx 1.7$ Hz, CH, 1H), 7.63 (dd, $^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.7$ Hz, CH, 1H), 7.57 (dd, $^3J_{\text{H,H}} \approx 4J_{\text{H,H}} \approx 1.7$ Hz, CH, 1H), 4.22 (t, $^3J_{\text{H,H}} = 7.28$ Hz, CH₂, 2H), 3.92 (s, CH₃, 3H), 1.80 (m, CH₂, 2 H), 1.26 (m, CH₂, 2H), 0.82 (t, $^3J_{\text{H,H}} = 7.40$ Hz, CH₃, 3H), 0.83 (t, verbreitert, $^3J_{\text{H,H}} = 7.7$ Hz, CH₃, 6H), 0.20 (q, broad, $^3J_{\text{H,H}} = 7.7$ Hz, CH₂, 4H).

20 $^{13}\text{C}\{\text{H}\}$ -NMR: δ , ppm = 138.7 (q, $^1J_{\text{C,B}} = 53$ Hz, CN, 2C), 137.2 (s, CH, 1C), 124.6 (s, CH, 1C), 123.3 (s, CH, 1C), 50.1 (s, CH₂, 1C), 36.6 (s, CH₃, 1C), 32.6 (s, CH₂, 1C), 19.8 (s, CH₂, 1C), 14.6 (q, $^1J_{\text{C,B}} = 44$ Hz, BCH_2 , 2C), 13.6 (s, CH₃, 1C), 12.1 (s, CH₃, 2C).

25 Elemental analysis:

calculated: C 64.63; H 9.68; N 21.53

found: C 63.38; H 9.82; N 21.41

Dynamic viscosity:

	$^{\circ}\text{C}$	mPa·s
30	20	63.1

40	26.7
60	13.9
80	8.3

5 Decomposition's temperature: 190° C.

**Example 31. *N*-Butyl-*N*-methylpyrrolidinium diethyldicyanoborate -
BMPL[(C₂H₅)₂B(CN)₂]**



Dichloromethane (50 mL) is added to a mixture of potassium diethyldicyanoborate (5.0 g, 31.23 mmol) and 1-butyl-1-methylpyrrolidinium chloride (BMPLCl) (5.5 g, 31.23 mmol) in H₂O (deionised, 50 mL). The aqueous phase is removed and the organic phase is washed with deionised water (5 × 1 mL) and dried over magnesium sulfate. The sulfate is filtered and dichloromethane is removed under reduced pressure. The product is dried for three days at 50°C in vacuum.

15 The yield of *N*-butyl-*N*-methylpyrrolidinium diethyldicyanoborate is 7.5 g (28.49 mmol).

20 Elemental analysis:

calculated: C 68.44; H 11.49; N 15.96

25 found: C 67.91; H 11.57; N 15.99

11B{¹H}-NMR: δ , ppm = -23.1(s).

11B-NMR: δ , ppm = -23.1 (s, broad).

1H{¹¹B}-NMR : \square , ppm = 3.7 (m, CH₂, 4H), 3.52 (m, CH₂, 2H), 3.22 (s, CH₃,

3H), 2.30 (m, 2CH₂, 4H), 1.87 (m, CH₂, 2H), 1.44 (m, CH₂, 2H), 0.84 (t,

30 $^3J_{H,H}$ = 7.4 Hz, CH₃, 3H), 0.83 (t, $^3J_{H,H}$ = 7.5 Hz, CH₃, 6H), 0.22 (q, $^3J_{H,H}$ = 7.6 Hz, CH₂, 4H).

¹H-NMR: δ , ppm = 3.7 (m, CH₂, 4H), 3.52 (m, CH₂, 2H), 3.22 (s, CH₃, 3H), 2.30 (m, CH₂, 4H), 1.87 (m, CH₂, 2H), 1.44 (m, CH₂, 2H), 0.84 (t, broad, ³J_{H,H} = 7.4 Hz, CH₃, 3H), 0.83 (t, ³J_{H,H} = 7.5 Hz, CH₃, 6H), 0.22 (q, broad, ³J_{H,H} = 7.6 Hz, CH₂, 4H).

5 ¹³C{¹H}-NMR: δ , ppm = 138.7 (q, ¹J_{C,B} = 53 Hz, 2C, CN), 65.0 (s, CH₂, 2C), 64.8 (s, CH₂, 1C), 48.9 (s, CH₃, 1C), 26.2 (s, CH₂, 1C), 22.3 (s, CH₂, 2C), 20.3 (s, CH₂, 1C), 14.7 (q, ¹J_{C,B} = 45 Hz, CH₂, 2C), 13.8 (s, CH₃, 1C), 12.2 (s, CH₃, 2C).

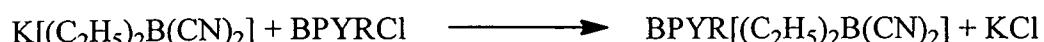
10 Dynamic viscosity:

	°C	mPa·s
	20	83.0
	40	35.1
	60	18.1
15	80	10.7

Decomposition's temperature: 190° C.

20 **Example 32. N-Butylpyridinium diethyldicyanoborate -**

BPYR[(C₂H₅)₂B(CN)₂]



25 Dichloromethane (50 mL) is added to a mixture of potassium diethyldicyanoborate (6.0 g, 37.48 mmol) and N-butylpyridinium chloride (BPYRCl) (6.5g, 37.86 mmol) in H₂O (deionised, 30 mL). The aqueous phase is removed and the organic phase is washed with deionised water (5 \times 1 mL) and dried over magnesium sulfate. The sulfate is filtered and dichloromethane is removed under reduced pressure. The product is dried 30 for three days at 50°C in vacuum.

The yield of N-butylpyridinium diethyldicyanoborate is 9.2 g (35.77 mmol).

$^{11}\text{B}\{^1\text{H}\}$ -NMR: δ , ppm = -23.1 (s).

^{11}B -NMR: δ , ppm = -23.1 (s, broad).

5 $^1\text{H}\{^{11}\text{B}\}$ -NMR: δ , ppm = 9.17 (m, $\text{C}_{\text{arom}}\text{H}$, 2H), 8.73 (m, $\text{C}_{\text{arom}}\text{H}$, 1H), 8.27 (m, $\text{C}_{\text{arom}}\text{H}$, 2H), 4.83 (t, $^3J_{\text{H,H}} = 7.5$ Hz, CH_2 , 2H), 2.10 (m, CH_2 , 2H), 1.45 (m, CH_2 , 2 H), 0.83 (t, $^3J_{\text{H,H}} = 7.30$ Hz, CH_3 , 3H), 0.83 (t, $^3J_{\text{H,H}} = 7.6$ Hz, CH_3 , 6H), 0.20 (q, $^3J_{\text{H,H}} = 7.6$ Hz, CH_2 , 4H).

10 ^1H -NMR: δ , ppm = 9.17 (m, $\text{C}_{\text{arom}}\text{H}$, 2H), 8.73 (m, $\text{C}_{\text{arom}}\text{H}$, 1H), 8.27 (m, $\text{C}_{\text{arom}}\text{H}$, 2H), 4.83 (t, $^3J_{\text{H,H}} = 7.5$ Hz, CH_2 , 2H), 2.10 (m, CH_2 , 2H), 1.45 (m, CH_2 , 2 H), 0.83 (t, $^3J_{\text{H,H}} = 7.30$ Hz, CH_3 , 3H), 0.83 (t, broad, $^3J_{\text{H,H}} = 7.7$ Hz, CH_3 , 6H), 0.20 (q, broad, $^3J_{\text{H,H}} = 7.7$ Hz, CH_2 , 4H).

15 $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ , ppm = 146.6 (s, C_{arom} , 1C), 145.6 (t, $^1J_{\text{N,C}} = 8.0$ Hz, NC_{arom} , 2C), 138.8 (q, $^1J_{\text{C,B}} = 54$ Hz, CN , 2C), 129.3 (s, C_{arom} , 2C), 62.4 (s, CH_2 , 1C), 33.9 (s, CH_2 , 1C), 19.8 (s, CH_2 , 1C), 14.6 (q, $^1J_{\text{C,B}} = 44$ Hz, BCH_2 , 2C), 13.6 (s, CH_3 , 1C), 12.1 (s, CH_3 , 2C).

Elemental analysis:

calculated: C 70.05; H 9.41; N 16.34

found: C 69.22; H 9.46; N 16.50

20

Dynamic viscosity:

$^{\circ}\text{C}$	$\text{mPa}\cdot\text{s}$
20	78.5
40	31.4
60	15.7
80	9.3

25 Decomposition's temperature: 160° C.

30

Example A:

The following electrolyte formulations are synthesized to demonstrate the application of electrolyte formulations according to the invention relative to electrolyte formulations of the prior art containing emim TCB in dye sensitized solar cells.

5

The electrolyte formulations are prepared through mixing of one or more of 1,3-dimethylimidazolium iodide (mmimI), 1-propyl-3-methylimidazolium iodide (pmimI), iodine, N-butylbenzimidazole (NBB) and guanidinium thiocyanate (guaSCN) and the corresponding ionic liquid as indicated such as emim TCB and EMIM $[(CH_3)_3BF(CN)_2]$ (N-ethyl-3-methylimidazolium methylfluorodicyano-borate or bmpl TCB and and BMPL $[(CH_3)_3BF(CN)_2]$ (N-butyl-N-methylpyrrolidinium methylfluorodicyanoborate in weight% as listed below.

15	Electrolyte 1	weight %
	I ₂	1,6
	mmim I	35
	guaSCN	0,7
	NBB	2,7
20	emim TCB	60
	total	100

25	Electrolyte 2	weight %
	I ₂	1,6
	mmim I	35
	guaSCN	0,7
	NBB	2,7
	emim $[(CH_3)_3BF(CN)_2]$	60
	total	100

30

	Electrolyte 3	weight %
	I ₂	1,6
	mmim I	35
	guaSCN	0,7
5	NBB	2,7
	bmpl TCB	60
	total	100

	Electrolyte 4	weight %
10	I ₂	1,6
	mmim I	35
	guaSCN	0,7
	NBB	2,7
	bmpl [(CH) ₃ BF(CN) ₂]	60
15	total	100

	Electrolyte 5	weight %
	I ₂	1,6
	mmim I	35
20	guaSCN	0,7
	NBB	2,7
	emim [(CH ₃)B(CN) ₃]	60
	total	100

25 The Electrolytes 1 to 5 are measured using two different dyes (Z907 and D205) at 10°C and 25°C.

The above cited compounds are commercially available or are synthesized according to known literature methods.

30 The dye sensitized solar cells are fabricated as disclosed in US 5,728,487 or WO 2007/093961:

A double-layer, mesoporous TiO_2 electrode was prepared as disclosed in Wang P et al., J. Phys. Chem. B 2003, 107, 14336, in particular page 14337, in order to obtain a photoanode consisting of a double layer structure. To prepare a transparent nanoporous TiO_2 electrode, a screen printing paste containing terpineol solvent and nanoparticulate TiO_2 of anatase phase with 20 nm diameter was deposited on a transparent conductive substrate to 5 mm x 5 mm squared shape by using a hand printer. The paste was dried for 10 minutes at 120 degrees Celsius.

Another screen printing paste containing TiO_2 with 400 nm diameter was then deposited on top of the nanoporous layer to prepare an opaque layer. The double layer film was then sintered at 500 degrees Celsius for an hour with the result of an underlying transparent layer (7 microns thick) and a top opaque layer (4 microns thick). After sintering, the electrode was immersed in 40 mM aqueous solution of TiCl_4 (Merck) for 30 minutes at 70 degrees Celsius and then rinsed with pure water sufficiently. Thus TiCl_4 -treated electrode was dried at 500 degrees Celsius for 30 minutes just before dye sensitization. The electrode was dipped into a 0.3 mM Z907 dye solution of acetonitrile (Merck HPLC grade) and tert-butyl alcohol (Merck), v:v = 1:1 for 60 hours at 19 degrees Celsius. The counter electrode was prepared with thermal pyrolysis method as disclosed in the reference above. A droplet of 5 mM solution of platinic acid (Merck) was casted at 8 $\mu\text{l}/\text{cm}^2$ and dried on a conductive substrate. The dye sensitized solar cell was assembled by using 30 micron thick Bynel (DuPont, USA) hot-melt film to seal up by heating. The internal space was filled with each of the electrolyte formulations as described above to produce the corresponding devices.

The dye Z907 is an amphiphilic ruthenium sensitizer $\text{Ru}(2,2'\text{-bipyridine } 4,4'\text{-dicarboxylic acid}) (4,4'\text{-dinonyl-2,2'-bipyridine})(\text{NCS})_2$ or synonymously $[\text{Ru}(\text{H}_2\text{dcbpy})(\text{dnbpy})(\text{NCS})_2]$.

The indolin dye D205 is described before.

In order to obtain accurate light intensity level, Air Mass 1.5 Global (AM 1.5G) simulated sunlight is calibrated spectrally according to Seigo Ito et al, "Calibration of solar simulator for evaluation of dye-sensitized solar cells", Solar Energy Materials & Solar Cells, 82, 2004, 421.

5

The measurements of photocurrent-voltage curves are carried out under Air Mass 1.5 simulated sunlight (AM 1.5) with temperature control for devices fabricated as described above containing electrolytes 1 to 4 placed on a black plate chilled down to 25°C under 1 Sun illumination. A photomask of 4 mm x 4 mm is placed on top of the devices to define the light projection area. The cell gap is around 20 micron.

10

Energy conversion efficiency is generally the ratio between the useful output of an energy conversion machine and the input of light radiation, in energy terms, determined by using adjustable resistant load to optimize the electric power output.

15

Table 1 summarises the results of the measurements of the above cited electrolyte formulations at 10 °C:

20

Dye	electrolyte	1*	3*	5	2	4
Z907	J_{sc} (mA/cm ²)	8.26	5.57	9.90	10.45	8.51
	V_{oc} (V)	0.74	0.73	0.72	0.69	0.72
	FF	0.65	0.59	0.57	0.66	0.40
	η (%)	3.94	2.38	4.04	4.70	2.48
D205	J_{sc} (mA/cm ²)	10.94	10.36	11.87	11.85	11.40
	V_{oc} (V)	0.73	0.75	0.74	0.74	0.72
	FF	0.67	0.67	0.70	0.73	0.61
	η (%)	5.21	5.19	6.10	6.12	5.05

25

Table 2 summarises the results of the measurements of the above cited electrolyte formulations at 25°C:

30

Dye	electrolyte	1*	3*	5	2	4
Z907	J_{sc} (mA/cm ²)	10.45	7.57	10.27	10.47	9.14

5	V_{oc} (V)	0.69	0.68	0.70	0.66	0.70
	FF	0.70	0.62	0.59	0.68	0.47
	η (%)	4.98	3.20	4.18	4.72	2.99
	D205	J_{sc} (mA/cm ²)	11.73	10.17	11.63	12.17
		V_{oc} (V)	0.70	0.73	0.71	0.70
		FF	0.70	0.65	0.69	0.70
		η (%)	5.74	4.83	5.62	5.95

* not according to the invention

J_{sc} = short circuit current

10 V_{oc} = open circuit voltage

FF = fill factor

η = power conversion efficiency

Table 1 and 2 document that electrolytes comprising

15 methylfluorodicyanoborate as anion perform better or equal than electrolytes comprising TCB as anion if the same cation is used particularly at lower temperature like 10 degrees Celsius due to aforementioned lower negative temperature coefficient of viscosity.

20 Example B:

The following electrolyte formulations are synthesized to demonstrate the application of electrolyte formulations according to the invention relative to electrolyte formulations of the prior art containing 1-butyl-1-methylpyrrolidinium TCB and N-butyl-pyridinium TCB in dye sensitized solar cells.

25 The electrolyte formulations are prepared through mixing of one or more of 1,3-dimethylimidazolium iodide (mmimI), iodine, N-butylbenzimidazole (NBB) and guanidinium thiocyanate (guaSCN) and the corresponding ionic liquid in weight % as listed below.

30 Electrolyte 6

weight %

			weight %
	I ₂	1.3	
	mmim I	35	
	guaSCN	0,7	
	NBB	3.0	
5	Triethylsulfonium methyltricyanoborate	60	
	total	100	
	Electrolyte 7		weight %
	I ₂	1.3	
10	mmim I	35	
	guaSCN	0.7	
	NBB	3.0	
	bmpl diethyldicyanoborate	60	
	total	100	
15			
	Electrolyte 8*		weight %
	I ₂	1.3	
	mmim I	35	
	guaSCN	0.7	
20	NBB	3.0	
	bmpl TCB	60	
	total	100	
	Electrolyte 9		weight %
25	I ₂	1.3	
	mmim I	35	
	guaSCN	0.7	
	NBB	3.0	
	emim <i>n</i> -butyltricyanoborate	60	
30	total	100	
	Electrolyte 10		weight %

	I ₂	1.3
	mmim I	35
	guaSCN	0.7
	NBB	3.0
5	bmim diethyldicyanoborate	60
	total	100
	Electrolyte 11	weight %
	I ₂	1.3
10	mmim I	35
	guaSCN	0.7
	NBB	3.0
	BPYR diethyldicyanoborate	60
	total	100
15	Electrolyte 12*	weight %
	I ₂	1.3
	mmim I	35
	guaSCN	0.7
20	NBB	3.0
	BPYR TCB	60
	total	100

The electrolytes marked with * are not according to the invention.

25 The Electrolytes 6 to 12 are measured using 0.3 mM Z907 solution at 25°C.

The above cited compounds are commercially available or are synthesized according to known literature methods.

30 The dye sensitized solar cells are fabricated as disclosed in Example A and the measurements are done as disclosed in Example A.

Table 3 summarises the results of the measurements of the above cited electrolyte formulations at 25°C:

electrolyte	6	7	8*	9	10
J_{SC} (mA/cm ²)	12.27	11.85	12.24	6.58	11.24
V_{OC} (V)	0.67	0.72	0.72	0.70	0.77
FF	0.68	0.69	0.68	0.69	0.72
η (%)	5.60	5.92	5.98	3.21	6.15
electrolyte	11	12*			
J_{SC} (mA/cm ²)	11.06	10.21			
V_{OC} (V)	0.76	0.74			
FF	0.73	0.69			
η (%)	6.12	5.20			

* not according to the invention

15 J_{SC} = short circuit current

V_{OC} = open circuit voltage

FF = fill factor

η = power conversion efficiency

20 Table 3 documents that electrolytes comprising diethyldicyanoborate as anion perform better or equal than electrolytes comprising TCB as anion if the same cation or similar heterocyclic cations are used.

25

30

Patent Claims**1. Compounds of formula I**

5

in which

R¹ each independently denotes

a straight-chain or branched alkyl group having 1 to 20 C atoms, which optionally may contain at least one Cl, Br or I atom, at least one CN group and/or one or more oxygen or sulphur atoms,

10

a straight-chain or branched alkenyl group having 2 to 20 C atoms

having one or more double bonds, which optionally may contain at least one Cl, Br or I atom and/or one or more oxygen or sulphur atoms,

a straight-chain or branched alkinyl group having 1 to 20 C atoms having one or more triple bonds, which optionally may contain at least

15

one Cl, Br or I atom and/or one or more oxygen or sulphur atoms and optionally may have a double bond,

or unsubstituted phenyl,

z is 1, 2, 3 or 4, x is 1, 2 or 3, y is 0, 1 or 2, v is 0, 1 or 2 and the sum of x+y+v is 2 or 3 and

20

in which Kt^{z+} denotes

an inorganic cation selected from the group of NO⁺, H⁺, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, or Mg²⁺, Cu⁺, Cu²⁺, Zn²⁺, Ag⁺, Ca²⁺, Y³⁺, Yb⁺³, La⁺³, Sc⁺³, Ce⁺³, Nd⁺³, Tb⁺³, Sm⁺³ or complex (ligands containing) metal cations

25

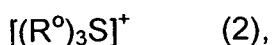
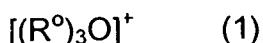
which include rare-earths, transitions or noble metals like rhodium, ruthenium, iridium, palladium, platinum, osmium, cobalt, nickel, iron, chromium, molybdenum, tungsten, vanadium, titanium, zirconium, hafnium, thorium, uranium, gold,

30

or an organic cation selected from the group of

5 a tritylium cation, in which the phenyl groups may be substituted by straight-chain or branched alkyl groups having 1 to 20 C atoms, straight-chain or branched alkenyl having 2 to 20 C atoms and one or more double bonds or straight-chain or branched alkynyl having 2 to 20 C atoms and one or more triple bonds,

10 an oxonium cation of formula (1) or a sulfonium cation of formula (2)



15 where R° each independently of one another denotes a straight-chain or branched alkyl group having 1-8 C atoms, non-substituted phenyl or phenyl which is substituted by R^{1*} , OR' , $N(R')_2$, CN or halogen and in case of sulfonium cations of formula (2) additionally denotes each independently $(R''')_2N$ and R' is independently of each other H,

20 non-fluorinated, partially fluorinated or perfluorinated straight-chain or branched C_1 - to C_{18} -alkyl, saturated C_3 - to C_7 -cycloalkyl, non-substituted or substituted phenyl, R^{1*} is independently of each other non-fluorinated, partially fluorinated or perfluorinated straight-chain or branched C_1 - to C_{18} -alkyl, saturated C_3 - to C_7 -cycloalkyl, non-substituted or substituted phenyl and R''' is independently of each other straight-chain or branched C_1 to C_6 alkyl;

25 an ammonium cation, which conforms to the formula (3)



where

30 R in each case, independently of one another, denotes H, OR' , $N(R')_2$, with the proviso that a maximum of one R in formula (3) is OR' or $N(R')_2$, straight-chain or branched alkyl having 1-20 C atoms, straight-chain or branched alkenyl having 2-20 C atoms and one or more double bonds,

straight-chain or branched alkynyl having 2-20 C atoms and one or more triple bonds,

5 saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by straight-chain or branched alkyl groups having 1-6 C atoms, where one or two R may be fully substituted by halogens, in particular -F and/or -Cl, and one or more of the substituents R may be partially substituted by halogens, in particular -F and/or -Cl, and/or by -OH, -OR', -CN, -N(R')₂, -C(O)OH, -C(O)OR', -C(O)R', -C(O)N(R')₂, -SO₂N(R')₂, -C(O)X, -SO₂OH, -SO₂X, -NO₂, -SR', -S(O)R', -SO₂R' and where one or two non-adjacent carbon atoms in R which are not in the α -position may be replaced by atoms and/or atom groups selected from the group -O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -C(O)-, -C(O)O-, -N⁺(R')₂-, -P(O)R'O-, -C(O)NR'-, -SO₂NR'-, -OP(O)R'O-, -P(O)(N(R')₂)NR'-, -P(R')₂=N- or -P(O)R'- where R' each independently is H, non-fluorinated, partially fluorinated or perfluorinated straight-chain or branched C₁- to C₁₈-alkyl, saturated C₃- to C₇-cycloalkyl, non-substituted or substituted phenyl and X each independently is halogen; a phosphonium cation, which conforms to the formula (4)

10

15

$$[P(R^2)_4]^+ \quad (4),$$

20 where

R^2 in each case, independently of one another, denotes

H, OR' or N(R')₂.

straight-chain or branched alkyl having 1-20 C atoms,

25 more double bonds

straight-chain or branched alkynyl having 2-20 C atoms and one or

more triple bonds,

saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms

30 having 1.6 C atoms

where one or two R^2 may be fully substituted by halogens, in particular

E and/or *Cl*, and one or more of the substituents *R*² may be partially

-i and/or -oi, and -s.

substituted by halogens, in particular -F and/or -Cl, and/or by -OH, -OR', -CN, -N(R')₂, -C(O)OH, -C(O)OR', -C(O)R', -C(O)N(R')₂, -SO₂N(R')₂, -C(O)X, -SO₂OH, -SO₂X, -NO₂, -SR', -S(O)R', -SO₂R' and where one or two non-adjacent carbon atoms in R² which are not in the α-position may be replaced by atoms and/or atom groups selected from the group -O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -C(O)-, -C(O)O-, -N⁺(R')₂-, -P(O)R'O-, -C(O)NR'-, -SO₂NR'-, -OP(O)R'O-, -P(O)(N(R')₂)NR'-, -P(R')₂=N- or -P(O)R'- where R' each independently is H, non-fluorinated, partially fluorinated or perfluorinated straight-chain or branched C₁- to C₁₈-alkyl, saturated C₃- to C₇-cycloalkyl, non-substituted or substituted phenyl and X each independently is halogen;

a uronium cation, which conforms to the formula (5)



where R³ to R⁷ each, independently of one another, denote H, where H is excluded for R⁵, straight-chain or branched alkyl having 1 to 20 C atoms, straight-chain or branched alkenyl having 2-20 C atoms and one or more double bonds, straight-chain or branched alkynyl having 2-20 C atoms and one or more triple bonds, saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms, which may be substituted by straight-chain or branched alkyl groups having 1-6 C atoms, where one or two of the substituents R³ to R⁷ may be fully substituted by halogens, in particular -F and/or -Cl, and one or more of the substituents R³ to R⁷ may be partially substituted by halogens, in particular -F and/or -Cl, and/or by -OH, -OR', -N(R')₂, -CN, -C(O)OH, -C(O)OR', -C(O)R', -C(O)N(R')₂, -SO₂N(R')₂, -C(O)X, -SO₂OH, -SO₂X, -SR', -S(O)R', -SO₂R', -NO₂ and where one or two non-adjacent carbon atoms in R³ to R⁷ which are not in the α-position may

be replaced by atoms and/or atom groups selected from the group -O-,
-*S*-, -S(O)-, -SO₂-, -SO₂O-, -C(O)-, -C(O)O-, -N⁺(R')₂-, -P(O)R'O-,
-C(O)NR'-, -SO₂NR'-, -OP(O)R'O-, -P(O)(N(R')₂)NR'-, -P(R')₂=N- or
-P(O)R'- where R' each independently is H, non-fluorinated, partially
5 fluorinated or perfluorinated straight-chain or branched C₁- to C₁₈-alkyl,
saturated C₃- to C₇-cycloalkyl, non-substituted or substituted phenyl
and X each independently is halogen;

a thiuronium cation, which conforms to the formula (6)

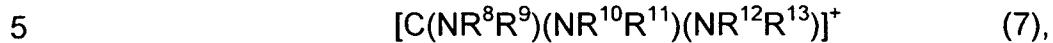


where

R³ to R⁷ each, independently of one another, denote
H, where H is excluded for R⁵,
straight-chain or branched alkyl having 1 to 20 C atoms,
15 straight-chain or branched alkenyl having 2-20 C atoms and one or
more double bonds,
straight-chain or branched alkynyl having 2-20 C atoms and one or
more triple bonds,
saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms,
20 which may be substituted by straight-chain or branched alkyl groups
having 1-6 C atoms, where one or two of the substituents R³ to R⁷ may
be fully substituted by halogens, in particular -F and/or -Cl, and one or
more of the substituents R³ to R⁷ may be partially substituted by
halogens, in particular -F and/or -Cl, and/or by -OH, -OR', -N(R')₂, -CN,
25 -C(O)OH, -C(O)OR', -C(O)R', -C(O)N(R')₂, -SO₂N(R')₂, -C(O)X, -
SO₂OH, -SO₂X, -SR', -S(O)R', -SO₂R', -NO₂ and where one or two non-
adjacent carbon atoms in R³ to R⁷ which are not in the α -position may
be replaced by atoms and/or atom groups selected from the group -O-,
-*S*-, -S(O)-, -SO₂-, -SO₂O-, -C(O)-, -C(O)O-, -N⁺(R')₂-, -P(O)R'O-,
-C(O)NR'-, -SO₂NR'-, -OP(O)R'O-, -P(O)(N(R')₂)NR'-, -P(R')₂=N- or
30 -P(O)R'- where R' each independently is H, non-fluorinated, partially
fluorinated or perfluorinated straight-chain or branched C₁- to C₁₈-alkyl,

saturated C₃- to C₇-cycloalkyl, non-substituted or substituted phenyl and X each independently is halogen;

a guanidinium cation, which conforms to the formula (7)



where

R⁸ to R¹³ each, independently of one another, denote

H, -CN, N(R')₂, -OR',

straight-chain or branched alkyl having 1 to 20 C atoms,

10 straight-chain or branched alkenyl having 2-20 C atoms and one or more double bonds,

straight-chain or branched alkynyl having 2-20 C atoms and one or more triple bonds,

saturated, partially or fully unsaturated cycloalkyl having 3-7 C atoms,

15 which may be substituted by straight-chain or branched alkyl groups having 1-6 C atoms, where one or two of the substituents R⁸ to R¹³ may be fully substituted by halogens, in particular -F and/or -Cl, and one or more of the substituents R⁸ to R¹³ may be partially substituted by

halogens, in particular -F and/or -Cl, and/or by -OH, -OR', -N(R')₂, -CN,

20 -C(O)OH, -C(O)OR', -C(O)R', -C(O)N(R')₂, -SO₂N(R')₂, -C(O)X, -

SO₂OH, -SO₂X, -SR', -S(O)R', -SO₂R', -NO₂ and where one or two non-adjacent carbon atoms in R⁸ to R¹³ which are not in the α -position may be replaced by atoms and/or atom groups selected from the group -O-,

-S-, -S(O)-, -SO₂-, -SO₂O-, -C(O)-, -C(O)O-, -N⁺(R')₂-, -P(O)R'O-, -

25 C(O)NR'-, -SO₂NR'-, -OP(O)R'O-, -P(O)(N(R')₂)NR'-, -P(R')₂=N- or

-P(O)R'-, where R' each independently is H, non-fluorinated, partially

fluorinated or perfluorinated straight-chain or branched C₁- to C₁₈-alkyl, saturated C₃- to C₇-cycloalkyl, non-substituted or substituted phenyl

and X each independently is halogen;

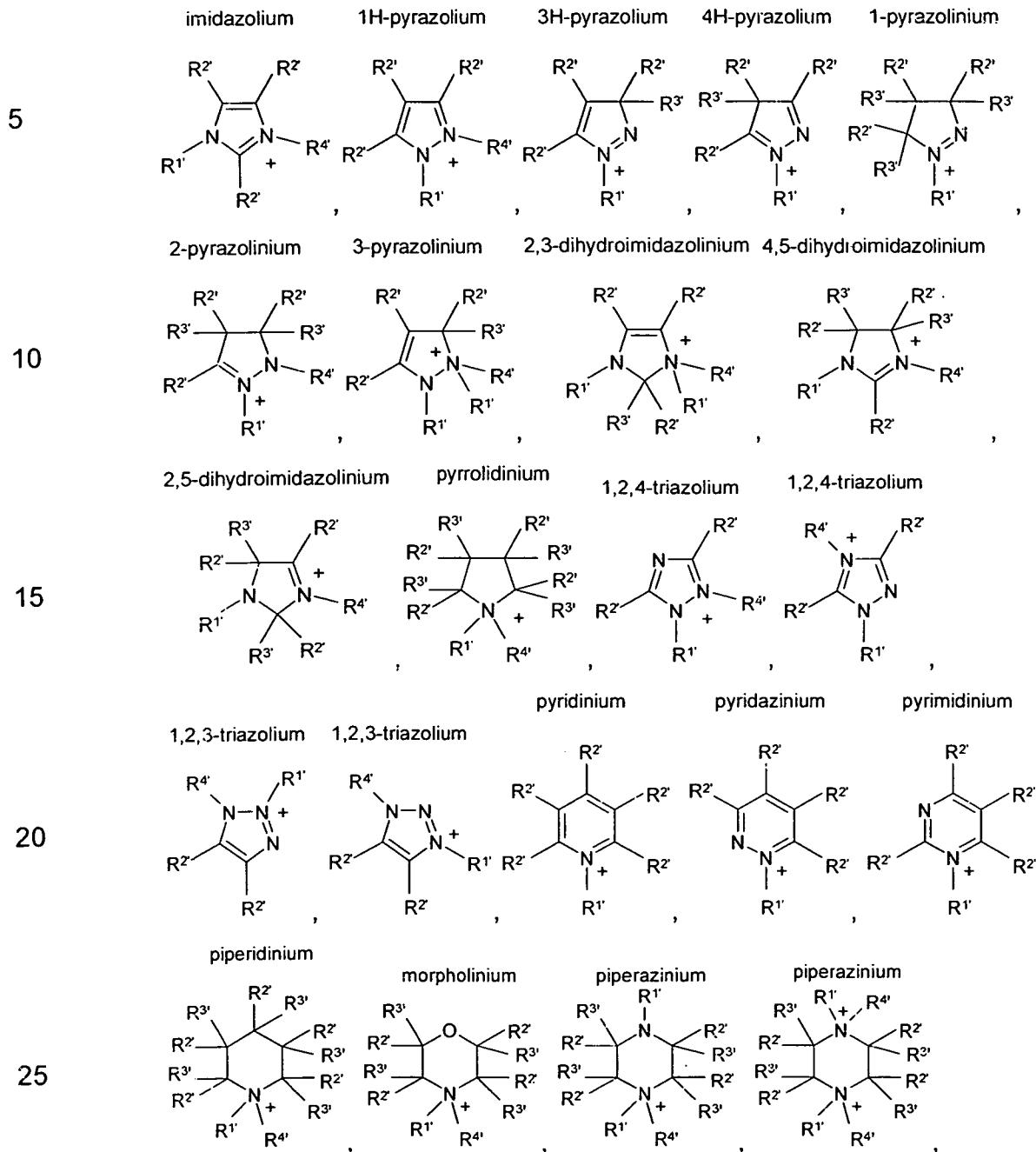
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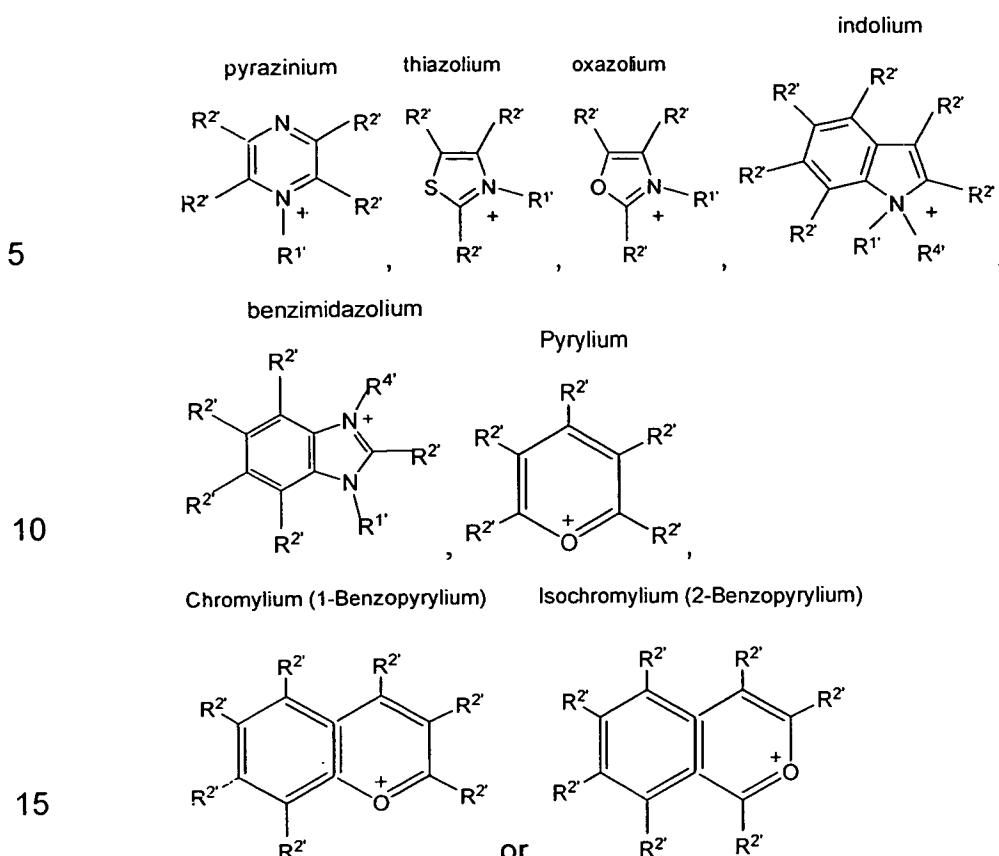
a heterocyclic cation which conforms to the formula (8)



where

HetN^{2+} denotes a heterocyclic cation selected from the group





where the substituents

R^1 to R^4 each, independently of one another, denote H ,

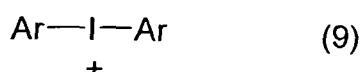
20 straight-chain or branched alkyl having 1-20 C atoms,
straight-chain or branched alkenyl having 2-20 C atoms and one or
more double bonds,
straight-chain or branched alkynyl having 2-20 C atoms and one or
more triple bonds,

25 and
R² denote additionally F, Cl, Br, I, -CN, -OR', -N(R')₂, -P(O)(R')₂, -P(O)(OR')₂, -P(O)(N(R')₂)₂, -C(O)R', -C(O)OR', -C(O)X, -C(O)N(R')₂, -SO₂N(R')₂, -SO₂OH, -SO₂X, -SR', -S(O)R', -SO₂R' and/or NO₂, with the proviso that R¹, R³, R⁴ are in this case independently of each other H
30 and/or a straight-chain or branched alkyl having 1-20 C atoms, straight-chain or branched alkenyl having 2-20 C atoms and one or more double bonds.

where one to three substituents R^1 to R^4 may be fully substituted by halogens, in particular -F and/or -Cl, and one or more substituents R^1 to R^4 may be partially substituted by halogens, in particular -F and/or -Cl, and/or by -OH, -OR', $N(R')_2$, -CN, -C(O)OH, -C(O)OR', -C(O)R', -C(O)N(R')₂, -SO₂N(R')₂, -C(O)X, -SO₂OH, -SO₂X, -SR', -S(O)R', -SO₂R', -NO₂, but where R^1 and R^4 cannot simultaneously be fully substituted by halogens and where, in the substituents R^1 to R^4 , one or two non-adjacent carbon atoms which are not bonded to the heteroatom may be replaced by atoms and/or atom groups selected from the -O-, -S-, -S(O)-, -SO₂-, -SO₂O-, -C(O)-, -C(O)O-, -N⁺(R')₂-, -P(O)R'O-, -C(O)NR'-, -SO₂NR'-, -OP(O)R'O-, -P(O)(N(R')₂)NR'-, -P(R')₂=N- or -P(O)R'-,

where R' each independently is H, non-fluorinated, partially fluorinated or perfluorinated straight-chain or branched C₁- to C₁₈-alkyl, saturated C₃- to C₇-cycloalkyl, non-substituted or substituted phenyl and X each independently is halogen or

a iodonium cation which conforms to the formula (9)



where

the aryl group Ar denotes each independently of each other aryl with 6 to 30 C atoms which is non-substituted or substituted with at least a straight-chain or branched alkyl group having 1 to 20 C atoms, a straight-chain or branched alkenyl group having 2 to 20 C atoms and one or more double bonds, a straight-chain or branched alkynyl group having 2 to 20 C atoms and one or more triple bonds, R¹⁺, NO₂, SR', N(R')₂, CN and/or halogen and

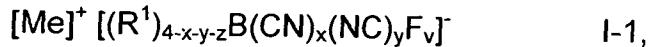
where R^1 each independently is non-fluorinated, partially fluorinated or perfluorinated straight-chain or branched C_1 - to C_{18} -alkyl, saturated C_3 - to C_7 -cycloalkyl, non-substituted or substituted phenyl

5 and halogen is F, Cl, Br or I,

with the proviso that potassium (18-crone-6) tricyano-*n*-octylborate and tetraethylammonium phenyl-tricyanoborate are excluded.

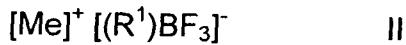
10 2. A compound of formula I according to claim 1, characterized in that R^1 in formula I is each independently a straight-chain or branched alkyl group having 1 to 4 C atoms, which optionally may contain at least one Br atom or at least one CN group or at least one oxygen atom or a straight-chain or branched alkenyl having 2 to 4 C atoms.

15 3. Process for the preparation of a compound of formula I according to claim 1 in which $[Kt]^{z+}$ is an alkali metal cation, z denotes 1 and the sum of $x+y+v$ denotes 3, which denotes a compound of formula I-1,



20 in which $[Me]^+$ denotes an alkali metal cation and R^1 , x , y and v have a meaning according to claim 1,

comprising the reaction of a compound of formula II



25 in which $[Me^1]^+$ denotes an alkali metal cation and R^1 has a meaning according to claim 1 with trialkylsilylcyanide, in which the alkyl groups are each independently of one another straight-chain or branched alkyl having 1 to 8 C atoms.

30 4. Process for the preparation of a compound of formula I according to claim 1 in which $[Kt]^{z+}$ is an organic cation and the sum of $x+y+v$ denotes 3,

comprising the reaction of a compound of formula III



in which $[Kt]^{z+}$ denotes the organic cation and R^1 has a meaning according to claim 1 with trialkylsilylcyanide, in which the alkyl groups are each independently of one another straight-chain or branched alkyl having 1 to 8 C atoms.

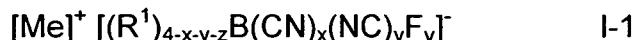
5. Process for the preparation of a compound of formula I according to claim 1 in which $[Kt]^{z+}$ is alkali metal cation, z denotes 1 and the sum of $x+y+v$ denotes 2, comprising the reaction of a compound of formula IV



10 in which R^1 has a meaning according to claim 1 with trialkylsilylcyanide in the presence of an alkali metal fluoride, wherein the alkyl groups within the trialkylsilylcyanide are each independently of one another straight-chain or branched alkyl having 1 to 8 C atoms.

15

6. Process for the preparation of a compound of formula I according to claim 1 in which $[Kt]^{z+}$ is another cation than the used alkali metal cation in the starting material in a salt-exchange reaction, characterized in that an alkali metal salt of formula I-1



20 in which $[Me]^+$ is an alkali metal cation and R^1 , x , y , v and the sum of $x+y+v$ have a meaning according to claim 1 is reacted with a compound of formula V

KtA $\quad V,$

25

in which Kt has a meaning of an organic cation or an inorganic cation other than the alkali metal cation of the compound of formula I-1 and

A denotes F^- , Cl^- , Br^- , I^- , OH^- , $[HF_2]^-$, $[CN]^-$, $[SCN]^-$, $[R_1COO]^-$, $[R_1OC(O)O]^-$, $[R_1SO_3]^-$, $[R_2COO]^-$, $[R_2SO_3]^-$, $[R_1OSO_3]^-$, $[BF_4]^-$,

30 $[PF_6]^-$, $[HSO_4]^{1-}$, $[NO_3]^-$, $[(R_2)_2P(O)O]^-$, $[R_2P(O)O_2]^{2-}$, $[(R_1O)_2P(O)O]^-$, $[(R_1O)P(O)O_2]^{2-}$, $[(R_1O)R_1P(O)O]^-$, tosylate, malonate which may be substituted by straight-chain or branched alkyl groups having 1 to 4 C

atoms, $[\text{HOCO}_2]^-$ or $[\text{CO}_3]^{2-}$ (merely for the synthesis of other compounds of formula I-1 having an other alkali metal cation than the starting material),

in which R_1 is each independently of another a straight-chain or

5 branched alkyl group having 1 to 12 C atoms and

R_2 is each independently of one another a straight-chain or branched perfluorinated alkyl group having 1 to 12 C atoms and where electroneutrality should be taken into consideration in the formula of the salt KtA .

10

7. An electrolyte formulation comprising at least one compound of formula I according to claim 1 or 2.

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8. An electrochemical and/or optoelectronic device comprising an electrolyte formulation according to claim 8.

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9. Use of compounds of formula I according to claim 1 or 2 in which $[\text{Kt}]^{z+}$ is an organic cation or H^+ and z is 1, 2, 3 or 4 as media for chemical reactions, as catalyst and/or as media in catalytical processes, as

20 conducting salts, as components of electrolytes for the application in electrochemical cells, as components of supporting electrolytes for electrochemical processes, as surfactants, as phase-transfer catalysts, as entrainer, as extractant; as antistatic additive, as plasticiser; as heat-transfer-medium, as modifier for membranes and textile materials; as

25 lubricant, as additive to lubricant compositions or to other engineering fluids; as hydraulic fluid, as additive to hydraulic fluids.

30

10. Use of a compound of formula I according to claim 1 or 2 in which $[\text{Kt}]^{z+}$ is Li^+ as conducting salt and/or component of electrolytes.

11. Use of compounds of formula I according to claim 1 or 2 in which $[\text{Kt}]^{z+}$ is an inorganic cation as catalyst, as conducting salts, as components

of electrolytes for the application in electrochemical cells, as components of supporting electrolytes for electrochemical processes, as surfactants, as phase-transfer catalysts or as antistatic additive.

5 12. Use of compounds of formula I-1



in which Me is an alkali metal cation and R^1 , x, y, v and the sum of $x+y+v$ have a meaning according to claim 1 or 2 for the synthesis of compounds of formula I according to claim 1 or 2 in which $[\text{Kt}]^{z+}$ is an organic cation and z is 1, 2, 3 or 4.

10 13. Use of compounds of formula I according to claim 1 or 2 in which $[\text{Kt}]^{z+}$ is a cation of formula (2), (5), (6), (9), tritylium, pyrylium, 1-benzopyrylium or 2-benzopyrylium as cationic polymerization initiator, photo-polymerization initiator or photo-acid generator.

15 14. Curable composition comprising at least one compound of formula I with cations of formula (2), (5), (6), (9), tritylium, pyrylium, 1-benzopyrylium or 2-benzopyrylium according to claim 1 or 2 and at least one polymerizable compound.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/002859

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F5/02 H01M6/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07F H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/222584 A1 (WELZ-BIERMANN URS [DE] ET AL) 5 October 2006 (2006-10-05) page 8; claims 20,21; example 15 -----	1-14
A	US 4 307 182 A (DALZELL REX J ET AL) 22 December 1981 (1981-12-22) column 6; table I; compound 2 -----	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 October 2012	06/11/2012

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Authorized officer

Bourghida, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/002859

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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