# Ionic Liquids Today

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**Dye Sensitized Solar Cells:** **Alternative or complementary to photovoltaic solar cells?**

**"There's plenty of room at the bottom.":** **Nano-Materials**

**Content:**


I. **Editorial**
II. **Applications of Ionic Liquids**
III. **Clean-Tech Applications, part II: Dye-Sensitized Solar cells**
IV. **Nano-Materials**
V. **Community**
VI. **Tom Beyersdorff: My new materials.**


## I. Editorial

By Thomas Schubert.

# Some aspects of ionic liquids' commercialisation

Since our foundation in 2003 I was asked often "When we'll see the first industrial applications of ionic liquids?". Well, the answer is still very complex: If we take a close look at some classes of materials that are similar and/or structurally related with ionic liquids, like tensides, surfactants or phase-transfer-catalysts, we surely can identify industrial applications of ionic liquids that are much older than the term "ionic liquid". In fact, there's a considerable intersection, if we take the most common "liquid below 100°C"-definition. But of course this answer can not be sufficient. So the idea behind these questions is surely, which applications of ionic liquids were commercialised after the idea of ionic liquids and the generic term was born?

### The Global Players

At the horizon there's first evidence that ionic liquids will not end as curiosities in some chemist's labs: Chemical companies have identified ionic liquids as a potential market. On the one hand there are the global players, who added ionic liquids to their portfolios. E.g. BASF's BASIL™-process has the potential to become commercial successful and is a helpful and important milestone for the ionic-liquids-community. It stands for a number of applications, where ionic liquids are used as process chemicals. Another field, where we'll see ionic liquids soon, are electrochemical applications, where ionic liquids are used as performance chemicals.

## The Start-Ups

On the other hand there are small and mid-sized companies, who think successful about ionic liquids as well. Some striking examples electrolytes are e.g. the use of IL in dye-sensitized-solar-cells or for the aprotic deposition of metals, a field where a couple of start-up-companies are working on, but also chemicals for analytical applications like media for protein-crystallisation or Karl-Fischer-solvents (both IOLITEC), head-space-gas-chromatography, MALDI-TOF-materials and many more.

The flexibility and the innovative character of Start-Ups is at least comparable with those of the Global Players. In addition, the dialogue of potential users with a small and independent company like IOLITEC is easier, quicker and cheaper than a cooperation with a larger company.

## The users

Over the past years, a large number of materials, physical data and applications were published. To keep an overview is – especially for non-chemists – extremely difficult. As a consequence, those potential users are sometimes deterred by the overwhelming flood of materials and data. That's the reason, why Start-ups like IOLITEC can take advantage from their large number of ionic liquids on the shelf and their ionic liquids database. The identification of the material of choice for any customer's application can be offered as a service from Start-Ups quick and to cheap conditions.

I believe that a unique mix of properties of a certain material stands naturally for a certain application. For example, the negligible vapour-pressure, the wide electrochemical window and the sufficient conductivity is obviously interesting for the use in the aprotic electrochemical deposition of metals. Our intention is to work out this interface between properties and application better, to make a scientist's life a bit easier.

Nevertheless, a non-negligible number of colleagues from universities and from R&D-departments from companies were interested in ionic liquids and I predict that we haven't even seen the peak!

## Availability

Furthermore, I was also asked very often, if ionic liquids are already available on a larger scale. Again the answer is yes, but only if we take again the class surfactants and phase-transfer-catalysts. To my best knowledge , there's still no ionic liquid really available on a ton's scale today, if we exclude these "Zero-Generation-Ionic Liquids". But of course, I'm open to argue: Every colleague from a Global Player or from a Start-up is invited to correct me and may write about his company's activities in this bulletin!

In my opinion the availability is a barrier, but certainly not a long-term-problem: If there's a application with a known market, both, producers and users will surely find a way to make this material available. If this first step is done, the "Me too"-effect will do the rest.

**Price**

Since their introduction into the market as chemicals for use in laboratories the prices dropped continuously as a consequence from higher demand and more competition. If we take e.g. the most cited ionic liquid in literature, which is still (unfortunately) 1-butyl-3-methl-imidazolium hexafluorophosphate,[1] the price for one kg is now less than 50% than five years ago. And we're still just on the kilogram's-scale!

In other words, the journey for applications, where bulk-quantities are needed, will certainly go to lower, reasonable prices. The economy of scale will tore down barriers for the market entry, as soon as if money can be earned with industrial applications of ionic liquids! And this will be in the very near future…

# II. Applications of Ionic Liquids

By Tom Beyersdorff, Marcin Gonsior &Thomas Schubert.

**Beginning with the next issue of "Ionic Liquids Today", we'd like to honour the most interesting paper which will be released or is accepted in the period from 1st July to 15th September 2006. Every reader of this bulletin or publisher of a recent paper is invited to give suggestions via e-mail to info@iolitec.de. Our academic staff and the members of our Scientific Board will select one paper, which will be highlighted in the next issue.**

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## Inorganic Synthesis

**Ionothermal Synthesis of Molecular Sieves using ionic liquids & Microwaves (without nano-particles!):**

Y.-P. Xu, Z.-J. Tian, S.-J. Wang, Y. Hu, L. Wang, B.-C. Wang, Y.-C. Ma, L. Hou, J.-Y. Yu, L.-W. Lin, angew. Chem. 2006, 118, 4069-4074.

Original Title"Microwave-Enhanced Ionothermal Synthesis of Aluminophophate Molecular Sieves"

[1] The best application for this material is in my opinion: "Moderate storage and release of HF".


Just the buzzword "Nano" is missing: *Xu et al.* described a new microwave assisted method for the synthesis of molecular sieves via ionothermal synthesis. Advantages are the fast rate of crystallization, low synthesis-pressure and structural selectivity.

## Organic Synthesis

**Grignard Reactions in Ionic Liquids:**
K. Bica, P. Gartner, *Org. Lett.* **2006**, *8*, 733-735.
Original Title: "An Iron-Containing Ionic Liquid as Recyclable Catalyst for Aryl-Grignard Cross-Coupling of Alkyl Halides.
*Gartner and Bica* found that **1-butyl-3-methyl-imidazolium tetrachloroferrate*** is a very effective and air stable catalyst for the Grignard cross-coupling with primary and secondary alkyl halides bearing β-hydrogens, leading to the corresponding products in good yields. Since the reaction could be carried out biphasic, they were in the position to recycle the catalyst four times.
*** This material (IL-047) is available in our standard-portfolio!**

## Catalysis

**Enhancement of enantioselectivity and stability of Ru-BINAP in a phosphonium-ionic liquid:**
H.-T. Wong, Y.H. See-Toh, F.C. Ferreira, R. Crook, A.G. Livingston, *Chem. Comm.* **2006**, 2063-2065.
Original Title: "Organic solvent nanofiltration in asymmetric hydrogenation: enhancement of enantioselectivity and catalyst stability by ionic liquids"
Livingston et al. described a procedure for the use of the ionic liquid **trihexyl-(tetradecyl)-phosphonium chloride*** for the efficient recovery of the expensive Ru-BINAP-catalyst. In addition, they mentioned that the enhanced enantioselectivity is specific for the tested model reaction.
*** This material (IN-006) and as well R-BINOL KI-022 (see also: this issue, "VI Interesting new materials") is available in our standard-portfolio!**

## Physical Chemistry

**Carbon Composite Electrode for the detection of biomolecules:**
N. Maleki, A. Safavi, F. Tajabadi, *Anal. Chem.* **2006**, *78*, 3820-3826.
Original Title: "High Performance Carbon Composite Electrode Based on an Ionic Liquid as Binder"

The authors described an easy method for the construction of a **very sensitive carbon composite electrode**, for the **sensing of biomolecules** and other electroactive compounds using the ionic liquid *N*-octyl-pyridinium hexafluorophosphate. As a consequence from the unique surface properties of the electrode, the overpotential for biomolecules such as NADH is significantly lower than by using other electrodes.

## Analytical Chemistry

**Ionic Liquids as gate medium for the use in Scanning Tunneling Spectroscopy:**
T. Albrecht, K. Moth-Poulsen, J.B. Christensen, J. Hjelm, T. Bornholm, J. Ulstrup, J. Am. Chem. Soc. **2006**, *128*, 6574-6575.
Original Title: „Scanning Tunneling Spectroscopy in an Ionic Liquid"

*Bornholm*, *Ulstrup et al.* reported that they used successful **1-butyl-3-methyl-imidazolium hexafluorophosphate*** as a gate medium for tunnelling spectroscopy at the single molecule scale. As the authors mentioned, the method open new perspectives toward fundamental research and as well for **applications in molecular electronics**. The proof-of-principle was successfully demonstrated by using an Osmium-complex.
*** This material (IL-011) is available from our standard-portfolio (see also: this issue, "VI Interesting new materials")!**

## Polymers

**Polymerization in Ionic Liquids:**
V. Strehmel, A. Laschewsky, H. Wetzel, E. Görnitz, Macromol. **2006**, *39*, 923-930.
Original title: "Free Radical Polymerisation of n-Butyl Methacrylate in Ionic Liquids"
The authors use a series of imidazolium, pyridinium and ammonium-based ionic liquids as solvent for the polymerisation of a model monomer n-butyl methacrylate. In comparison to the polymerisation in conventional solvents like toluene (or bulk polymerisation) here using ILs higher molecular masses and higher polymerisation degrees were achieved.
Most of ILs used in this study you will find in our portfolio!

## Biotech

Effective asymmetric hydrogenation in ionic liquids:
T. Matsuda, Y. Yamagishi, S. Koguchi, N. Iwai, T. Kitazume, *Tetrahedron Lett.* **2006**, *47*, 4619-4622.
Original Titel: "An effective method to use ionic liquids as reaction media for asymmetric reduction by Geotrichum cadidum"
Matsuda et al. described a method, where an enzyme is used for the asymmetric reduction of ketones. Excellent enantioselectivities were observed when the cell was immobilized on water-absorbing polymer containing water.

## Reviews

**Physico-Chemical processes in imidazolium ionic liquids**
J. Dupont, P.A.Z. Suarez, *Phys. Chem. Chem. Phys.* **2006**, *8*, 2441-2452.

**Air and water stable ionic liquids in physical chemistry**
F. Endres, Z. El Abedin, *Phys. Chem. Chem. Phys.* **2006**, *8*, 2101-2115.

## III Cleantech applications, Part II: Dye-Sensitized-Solar-Cells

By Thomas Schubert.

Recently, the dramatic increase of the oil-price reminded us that fossil fuels are a limited source on our planet. As surely everybody knows, the consumption of oil, gas and coal produces the greenhouse gas $CO_2$, which stands for global warming, causing dramatic climatic changes. In contrast to that, solar energy is clean and in unlimited supply. It can be transformed in thermal energy that can be used to heat, to cool (see also Issue 01/06) or to produce electric energy in solar-thermal power plants.

Another possibility to use solar energy is to generate electricity directly by using the photovoltaic effect in silicon-based solar-cells. In the very early 90s *Grätzel* and *O'Regan* developed an alternative to photovoltaic cells, the so-called *dye-sensitized solar cells (DSCs)*, using a photoactive dye to transform light into electricity in a similar way as in the photosynthesis.

Starting with the first model cells reported,[1] the DSCs have attracted continuously attention as an alternative to the established photovoltaic conversion of solar energy. Though the energy-efficiency is lower compared with photovoltaic cells, DSCs have one real adavantage: they are transparent. As a consequence, they can be used architecturally in different way than PV cells: the vision of a window producing electricity is close to become reality.

DSCs today typically consist of three adjacent thin layers sandwiched between two transparent conductive oxide (TCO) electrodes:

1. a high band-gap nanocrystalline semiconductor which is coated with a dye sensitizer for absorption in the visible region,
2. a platinized counter electrode to collect the electrons,
3. a redox electrolyte.

In fig. 1 (next page) you'll find a typical design of DSC.

To achieve an optimum efficiency many combinations of semi-conducting materials and dyes were tested, but titanium dioxide together with ruthenium bipyridinyl complexes mark today the state-of-the-art: together with the set-up from fig. 1 power conversion efficiencies up to 10.6% were recently achieved, using the $I_3^-/I^-$-redox-couple.[2]

Though there might be still space to advance semiconductors and sensitizers, scientists search as well to find new redox-couples-electrolyte combinations. Some authors used redox-couples in combination with organic solvents,[3] in other publications polymer-gel-electrolytes were described.[4] The most promising results were achieved by using ionic liquids.

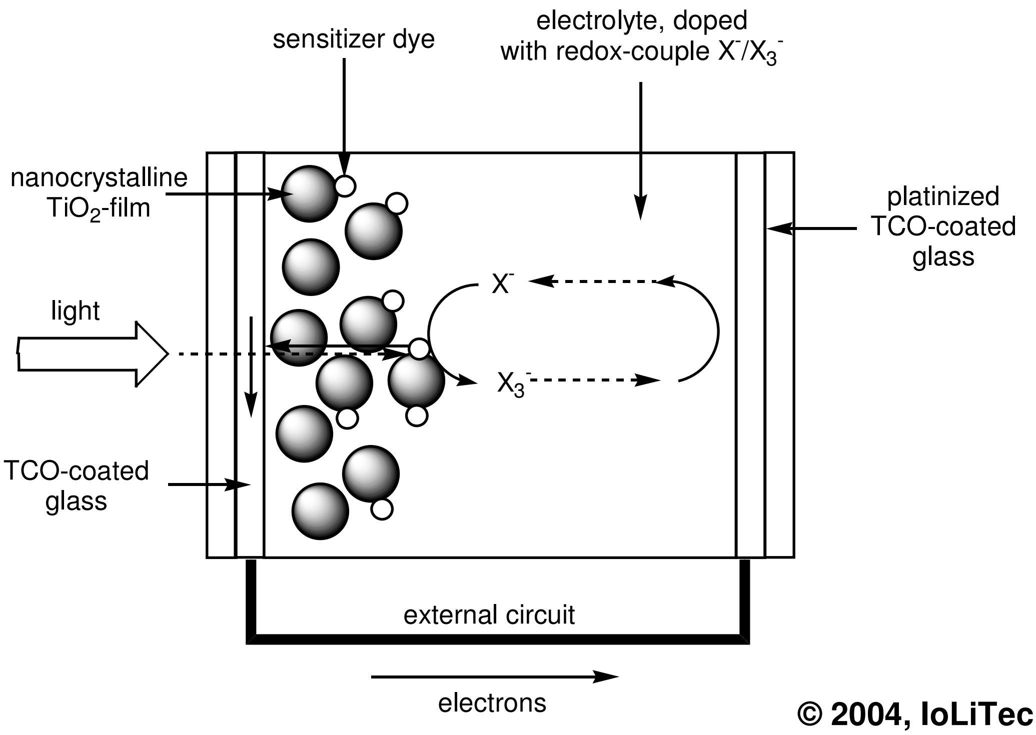


**Fig. 1:** Design of a typical DSC.

## Ionic Liquids in DSCs

Ionic liquids are non-aqueous electrolytes that combine the advantage of thermal and electrochemical stability with conductivity and a negligible vapour-pressure. They were identified very early as an alternative to common electrolyte systems again by *Grätzel* from the ETH Lausanne, who introduced a couple of ionic liquids, e.g. the well-established bis(trifluomethanesulfonyl)imide-, trifluoroacetic acid-, thiocyanates and iodide-based materials, for their use in DSCs.[5]

As described above, actual research focuses on new redox-couple/electrolyte-combinations. Well established are the $I_3^-/I^-$ systems, but also pseudo-halide-systems, such as $(SCN)_3^-/SCN^-$ and $(SeCN)_3^-/SeCN^-$ were recently reported.[6] Another interesting approach is to use nano-tube-ionic-liquids composites.[7]

**DSCs' road to commercialisation: BMBF-funded project COLORSOL**

In this context, we'd like to announce that the German Bundesministerium für Bildung, Forschung und Wissenschaft (BMBF) has just started the project COLORSOL, that focus on the development of this high-potential technology to a complete product.

Partners:

- Fraunhofer-Institut für Arbeitswirtschaft und Organisation (IAO), Stuttgart
- Fraunhofer-Institut für Solare Energiesysteme (ISE), Freiburg,
- Borderstep Institut für Innovation und Nachhaltigkeit GmbH, Kleinmachnow,
- Pröll KG, Weißenburg i. Bay.,
- Engco Advanced Technologies GmbH, Stuttgart,
- Ionic Liquids Technologies GmbH & Co. KG (Io Li Tec), Denzlingen,
- BGT Bischoff Glastechnik AG, Bretten,
- Bundesverband Deutscher Fertigbau e. V. (BDF), Bonn.

**IOLITEC's related products:**

The following ionic liquids are known for the use in DSCs are currently available:

a) 1-methyl-3-propyl-imidazolium iodide
b) 1,2-dimethyl-3-propyl-imidazolium iodide
c) 1-ethyl-3-methyl-imidazolium thiocyanate
d) 1-ethyl-3-methyl-imidazolium dicyanimide
e) 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide (not in the U.S.)

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**References:**

[1] B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737-740.
[2] M. Grätzel, *J. Photochem. Photobiol. C: Photochem. Rev.* **2003**, *4*, 145.
[3] G. Oskam, B.V. Bergeron, G.J. Meyer, P.C. Searson, *J. Chem. Phys. B* **2001**, *105*, 6867.
[4] J.R. Durrant, S.A. Haque, *Nature Mater.* **2003**, *2*, 402-407.
[5] P. Bonhote, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, *35*, 1168.
[6] H. Usui, H. Matsui, N. Tanabe, S. Yanagida, *J. Photochem. Photbiolog. A: Chemistry*, **2004**, 164, 97-101.
[7] P. Wang, S.M. Zakeeruddin, J.-E. Moser, R. Humphry-Baker, M. Grätzel, *J. Am. Chem. Soc.* **2004**, *126*, 7164-7165.

## IV Nano-materials: now available from IoLiTec

By Marcin Gonsior.

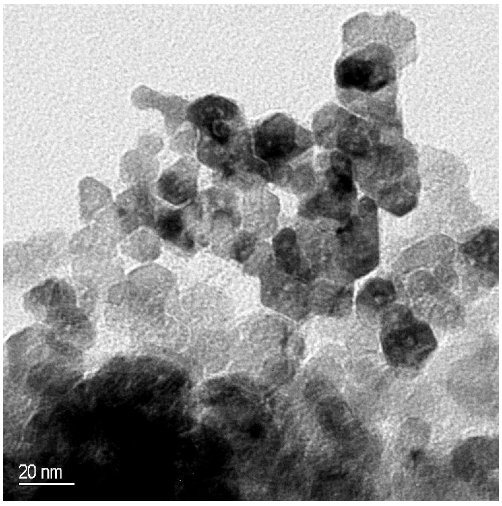
With beginning of the 3rd quarter, Iolitec's platform for Nano-materials launches on our web-site (www.iolitec.de). In cooperation with the group from Prof. Hempelmann, University of Saarland, the production and distribution of nano-materials is now put into practice as a substantial part of our Nanotec/Coatings division.

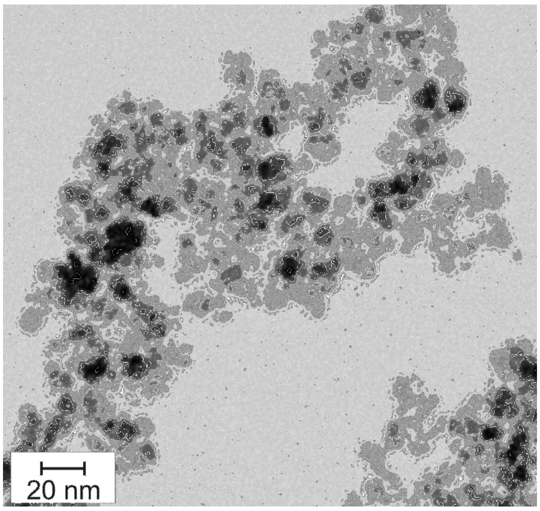
Available are nanopowders of various forms and sizes of crystallites, e.g. 10 nm for nano-Ag or 12 to 100 nm for nano-ZnO. These powders can be purchased directly from IoLiTec. We offer materials from research lab quantities to pilot plant scale. Typical amounts of 25, 50 and 100 g are in stock and can be shipped within 1-2 weeks. On request, we're in the position to scale up the production for selected products to 50 kg/month.

Available are the following **Nano-materials as powders or dispersions**:

**Nano-Metal-Oxides: $Fe_2O_3$, $Fe_3O_4$, ZnO, CuO, AgO, $SnO_2$, $Al_2O_3$, $ZrO_2$**

**Metal-nanopowders: Cu, Pd, Ag, Au and their alloys**




**Left: Nano-particles Zinc Oxide, right: Nano-particles of Magnetite.**

# Selected applications of nano-particles: a short review

***Nanofluids*** – several metal particles, e.g. Cu, can be used as high-performance heat transfer fluids.

***Plastic Additives*** – the implemantation of nano-particles into polymers can cause lower weights than the addition of traditional filling-materials. In addition, some physical, especially mechanical properties can be improved by using nano-particles as additives. Another striking example is the use of Nano-Ag to achieve antibacterial properties. This is interesting for the use in plastic products i.e. medical device, textile or packaging industry.

***High Performance Abrasives*** – application by chemical mechanical planarization (CMP) technologies, e.g. semicondutor polishing. The following nano-particles are used for CMP processes: $TiO_2$, $CeO_2$, $ZrO_2$, $Al_2O_3$, $SiO_2$.

***Nano-Composites*** – surface modification of nanoparticles aims in increasing compatibility with a matrix material, mostly organic polymers. $SiO_2$, $Al_2O_3$, Mn, Al, Ti as well as semiconductors like CdTe, CdSe are used in such inorganic-organic composite-materials.

***Catalysts*** – due to their nanometer size, nano-powders provide high surface area if they are compared with usual catalysts. This property is responsible for the excellent catalytic performance of these materials. Typically examples are nano-metal powders: Au, Ag, Pd, Ru, Cu. These metals are usually dispersed on a solid substrate – a metal oxide (see above!).

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**You haven't found the nanoparticles for your special needs?** Please contact us! We provide basic information about nano-particles, their characteristics and/or applications. In addition, we offer also custom made nano-particles synthesized by using modern techniques in ionic liquids. For more information please visit to our website www.iolitec.com ! Our homepage will systematically be updated considering a growing interest in nanomaterial applications.

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# V Community

## News

**IOLITEC's Co-founder of Andreas Bösmann waves good-bye**
Andreas Bösmann, who founded IOLITEC together with Thomas Schubert, left the company at the end of March 2006. IOLITEC's staff, IOLITEC's financial consultant Peter Unkelbach and IOLITEC's Managing Director Thomas Schubert say "thank you!" for having a good time together and wishing all the best for his new job at the University of Erlangen!

**IOLITEC partner of the project "COLORSOL"**
IOLITEC is partner in the BMBF-funded project COLORSOL, which focus on the commercialisation of DSCs. In this context, Ionic Liquids are used as electrolytes.

**Congratulations: New Director at Freiburg's Fraunhofer Institute for Solar Energy Systems**
Prof. Dr. Eicke R. Weber is the new director at the FhG ISE in Freiburg. He took the office from Prof. Dr. Joachim Luther, who went on pension at the and of June. With 3 R&D-projects, the FhG ISE is one of IOLITEC's most important research partners.

## Upcoming exhibitions and conferences:

**July, 30th-August, 4th:** **18th International Symposium on Fluorine Chemistry,** Bremen.

**August, 10th-13th:** **Transatlantic Symposium "Frontiers in Chemistry",** Durham, New Hampshire, USA.
IOLITEC's Managing Director, Dr. Thomas Schubert, was invited as one of 30 German delegates to discuss with leading chemists from the United States and from Great Britain.

**September, 4th-6th:** **12. Deutscher Fluortag,** Schmitten, Germany.

**September, 15th-18th:** **232rd ACS Meeting,** San Francisco, USA.
Meet IOLITEC's Managing Director, Dr. Thomas Schubert, at the symposium on the physical chemistry of ionic liquids. If you're interested, please visit his talk "**The Effect of Impurities on the Physical and (Electro-)chemical properties of Ionic Liquids**" and IOLITEC's Poster at the corresponding poster session "Ion Chromatography – a Valuable Method for the Quality Control of Ionic Liquids".

**September, 16th-22nd:** **Euchem conference on Molten Salts and Ionic Liquids ,** Hammamet, Tunesia.

**October, 8th-11th:** **Green Solvents for Processes,** Friedrichshafen, Germany.

## VI Interesting New Materials

By Tom Beyersdorff.

## IOLITEC supports strategic research in the DFG-funded program SPP1191: 10%-discount for all participants!

With the beginning of the program every participant of the DFG-program SPP 1191 receives a discount of 10% on our ionic liquids and key intermediates (except our special offers).

## New materials:

### Weakly coordinating anions: WCAs

In co-operation with **Professor Krossing** from the University of Freiburg/Germany, we expanded our portfolio by 4 salts of weakly-coordinating anions (WCAs), namely salts of the tetrakis(perfluoro-t-butoxy)aluminate-anion $[Al(OC(CF_3)_3)_4]^-$. In contrast to other WCAs e.g. $PF_6^-$, $BF_4^-$, $SbF_6^-$, or $[Sb(OTeF_5)]^-$, which are sensitive against moisture, these anions are stable in the presence of water and even of $HNO_3$!

WCAs play an important role in i.e. catalysis since they are able to stabilize highly reactive cationic species due to their low basicity.

Krossing *et al.*[2] were able to stabilize a large number of reactive cations such as $PX_4^+$, $P_2X_5^+$ and $P_5X_2^+$ (X=Br, I) in the presence of the $[Al(OC(CF_3)_3)_4]^-$ anion.

They were also able to isolate complexes cations such as $Ag(P_4S_3)^+$ and $Ag(P_4S_3)_2^+$ in combination with the the $[Al(OC(CF_3)_3)_4]^-$ anion.[3,4]

In addition, RT stable salts of the tris(ethene)silver-cation were obtained by stabilization with the $[Al(OC(CF_3)_3)_4]$-anion.[5] Krossing *et al.*[6] also synthesized and characterized various cationic Bronsted acid complexes of the perfluorinated alkoxyaluminates.

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[2] M. Gonsior, I. Krossing, L. Müller, I. Raabe, *Chem. Eur. J.* **2002**, 4475-4492.
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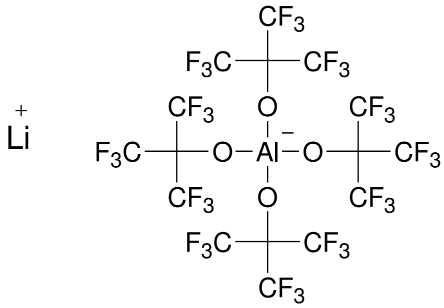
[4] I. Krossing, L. van Wüllen, *Chem. Eur. J.* **2002**, 700-711.
[5] I. Krossing, A. Reisinger, *Angew. Chem..* **2003**, 5903.
[6] I. Krossing, A. Reisinger, *Eur. J. Inorg. Chem.* **2005**, 1979-1989.

# *Lithium tetrakis(perfluoro-t.-butoxy)aluminate: Li [Al(pftb)$_4$]*



The salt Li[Al(pftb)$_4$] is a useful precursor for the introducing of the [Al(pftb)$_4$]-anion into various other salts by metathesis.

Li-Salts of WCAs are used as substitute for $LiClO_4$ in Li-catalysed Diels-Alder-reactions, 1,4-conjugate-additions and pericyclic rearrangement-reactions.[7,8,9] Also radical polymerisations have been catalysed by these kind of salts.

The use of Li [Al(pftb)$_4$] as electrolyte support in the Li-ion-batteries is limited since the mobility of large ions are insufficient for this application. However, a good performance has been achieved in polymer-based Li-ion-batteries using a Poly(ethylenoxide)-matrix.[10]

**Our special offer:***

| | | |
|---|---|---|
| **Li [Al(pftb)$_4$] (99%):** | **KI-018-1 g** | **550,00 €** |
| | **KI-018-5 g** | **2475,00 €** |
| | **KI-018-10 g** | **4455,00 €** |

[7] R. Braun, J. Sauer, *Chem. Ber.*, **1986**, *119*, 1269.
[8] P. A. Grieco, J. J. Nunes, M. D. Gaul, *J. Am. Chem. Soc.*, **1990**, *112*, 4595.
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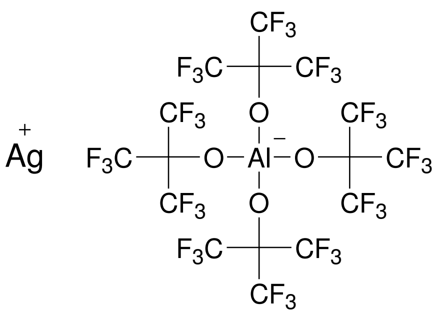
[10] H. Tokuda, S. Tabata, M. A. B. H. Susan, H. Hayamizu, M. Watanabe, *J. Phys. Chem. B*, **2004**.

### Silver tetrakis(perfluoro-t-butoxy)aluminate: Ag [Al(pftb)$_4$]



This silver salt is facile starting material to introduce the [Al(pftb)$_4$] anion and it can be used in most chlorinated alkanes. It has also been described to catalyse i.e. a variety of hetero-Diels-Alder-reactions.[11,12]

If combined with various alkyl iodides synthetic useful alkyl-cations can be generated *in situ* by precipitation of AgI.

$$R–I + Ag\,[Al(pftb)_4] \rightarrow R^+\,[Al(pftb)_4]^- + Ag\text{-}I$$

Gonsior[13] used this silver-complex among others to stabilize a large number of reactive phosphenium- and arsenium-intermediates during his PhD-studies.

**Our special offer:***

| | | |
|---|---|---|
| **Ag [Al(pftb)$_4$] (99%):** | **KI-019-1 g** | **650,00 €** |
| | **KI-019-5 g** | **2975,00 €** |
| | **KI-019-10 g** | **5400,00 €** |

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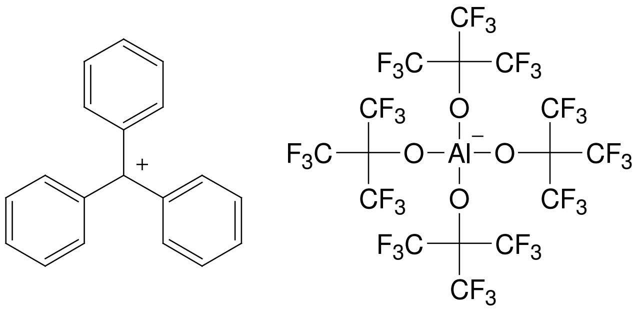
11 S. Saitoin, *Lewis Acids in Organic Synthesis*, *Ed.* H. Yamamoto, Wiley-VCH Weinheim, Germany, **2000**, 9.

12 N. J. Patmore, C. Hague, J. H. Cotgreave, M. F. Mahon, C. G. Frost, A. S. Weller, *Chem. Eur. J.*, **2002**, *8*, 2088.

13 M. Gonsior, „ From cationic silver complexes to reactive Phosphenium- and Arsenium-intermediates stabilized by weakly coordinating anions”, Dissertation, Göttingen: Cuvillier, **2005**, ISBN 3-86537-583-9.

**Triphenylcarbenium tetrakis(perfluoro-*tert*-butoxy)aluminate: $Ph_3C$ [Al(pftb)$_4$]**




This compound is of great interest in homogenous catalysis. Metallocenes of the formula $[(Cp)2M(CH_3)]^+$ that are active catalysts, require a stable weekly coordinating anion, which is very important for the activity and selectivity of i.e. the polymerization. $Ph_3C$ [Al(pftb)$_4$] generates very reactive catalysts of a well defined composition[14]:

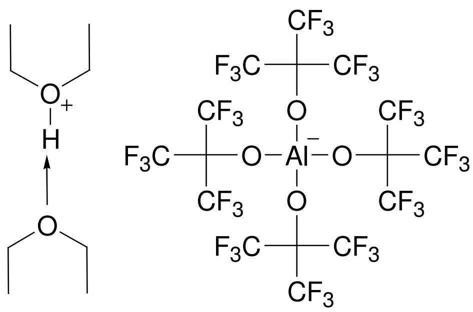
$$(Cp)_2Zr(CH_3)_2 + Ph_3C\,[Al(pftb)_4] \rightarrow (Cp)_2Zr(CH_3)^+\,[Al(pftb)_4]^- + MeCPh_3$$

**Our special offer:***

| | | |
|---|---|---|
| **Ph3C [Al(pftb)$_4$]:** | **KI-018-1 g** | **650,00 €** |
| | **KI-018-5 g** | **2975,00 €** |
| | **KI-018-10 g** | **5400,00 €** |

[14] E. Y.-X. Chen, T. J. Marks, *Chem. Rev.*, **2000**, *100*, 1391.

**Diethyloxonium tetrakis(perfluoro-tert.-butoxy)aluminate monoetherate: $H(OEt_2)_2$ [Al(pftb)$_4$]**



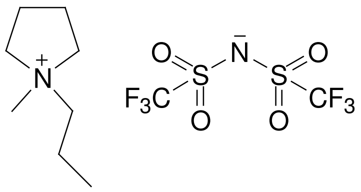

This protonated ether can be usen as a facile $H^+$-source since the reaction by-product diethylether can easily be removed from the reaction mixture. With this compound the [Al(pftb)$_4$] anion can easily be introduced to carboxylate salts.

**Our special offer:***

| | | |
|---|---|---|
| **Li [Al(pftb)$_4$] (99%):** | **KI-018-1 g** | **700,00 €** |
| | **KI-018-5 g** | **3150,00 €** |
| | **KI-018-10 g** | **5670,00 €** |

## *New Ionic Liquids and Special offers*

**1-Methyl-1-propyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide: [PrMPyrr] $NTf_2$**



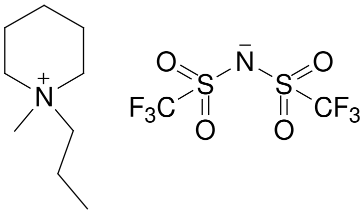
An interesting new material:

It is characterized by a conductivity of 3.4 mS/cm and a viscosity of 68 cP. The high thermal and electrochemical stability (ECW almost 5.0 V) qualify this Ionic Liquid to be a promising solvent for electrochemical applications.

## *Our special offer:**

| | | |
|---|---|---|
| **[PrMPyrr] $NTf_2$ (99%):** | **IL-044-50 g** | **95,00 €** |
| | **IL-044-100 g** | **170,00 €** |
| | **IL-044-250 g** | **380,00 €** |
| | **IL-044-500 g** | **650,00 €** |
| | **IL-044-1 kg** | **1150,00 €** |

**1-Methyl-1-propyl-piperidinium bis(trifluoromethylsulfonyl)imide: [PrMPip] $NTf_2$**




Recently Yang *et al.*[15] reported the first electrochemical deposition and dissolution of magnesium on a silver substrate from a 1 M-solution of $Mg(OTf)_2$ in [PrMPip] $NTf_2$. The same Ionic Liquid has been investigated by Sakaebe *et al.*[16] as electrolyte in Li-ion batteries using a Li/$LiCoO_2$ cell. The system showed high intercalation capacities and high coulombic efficiencies for $LiCoO_2$ cathode using [PrMPip] $NTf_2$.

Both examples show the great potential of this Ionic Liquid! The physical properties are:

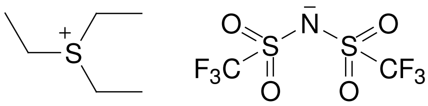
| | |
|---|---|
| Viscosity | 170 cP |
| Conductivity | 1.4 mS/cm |
| ECW | 5.5 V |

**Our special offer:***

| | | |
|---|---|---|
| **[PrMPip] $NTf_2$ (99%):** | **IL-045-50 g** | **105,00 €** |
| | **IL-045-100 g** | **190,00 €** |
| | **IL-045-250 g** | **380,00 €** |
| | **IL-045-500 g** | **685,00 €** |
| | **IL-045-1 kg** | **1200,00 €** |

[15] Y. NuLi, J. Yang, J. Wang, J. Xu, P. Wang, *Electrochemical and Solid-State Letters* **2005**, C166-C169.
[16] H. Sakaebe, H. Matsumoto, *Electrochem. Comm.* **2003**, 594-598.

**Triethylsulfonium bis(trifluoromethylsulfonyl)imide: [S222] $NTf_2$**



Not always ammonium or imidazolium:

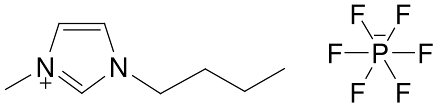
S222 $NTf_2$ is an interesting material based on a sulfonium cation!

High conductivity (5.1 mS/cm), low viscosity (38 cP) and thermal as well as electrochemically (ECW ~7.0 V) stability make this Ionic Liquid a promising solvent for electrochemical applications.

**Our special offer:***

| | | |
|---|---|---|
| **[S222] $NTf_2$ (99%):** | **IL-030-50 g** | **90,00 €** |
| | **IL-030-100 g** | **170,00 €** |
| | **IL-030-250 g** | **370,00 €** |
| | **IL-030-500 g** | **645,00 €** |
| | **IL-030-1 kg** | **1100,00 €** |

## 1-Butyl-3-methyl-imidazolium hexafluorophosphate: [BMIM] $PF_6$




Recently Ulstrup, Bjornholm *et al.*[17] used BMIM $PF_6$ as an electrochemical gate medium for tunnel-scanning spectroscopy (see also: this issue, "The world of Ionic Liquids", Analytical Chemsitry).

At the Achema 2006 Gubicza *et al.*[18] presented the results of various biocatalytic as well as metal-catalyzed reactions and the reuse of the catalyst in BMIM $PF_6$. They showed that catalyst recycling was successfully achieved using BMIM $PF_6$ in both cases.

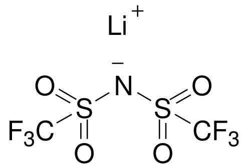
**Our special offer:***

| | | |
|---|---|---|
| **[BMIM] $PF_6$ (99%):** | **IL-011-50 g** | **60,00 €** |
| | **IL-011-100 g** | **105,00 €** |
| | **IL-011-250 g** | **230,00 €** |
| | **IL-011-500 g** | **380,00 €** |
| | **IL-011-1 kg** | **600,00 €** |

[17] T. Albrecht, K. Moth-Poulsen, J. B. Christensen, J. Hjelm, T. Bjornholm, J. Ulstrup, *J. Am. Chem. Soc.* **2006**, 6574-6575.

[18] L. Gubicza, T. Frater, K. Belafi-Bako, *Presentation at Achema* **2006**, "Reuse of Lipase Enzymes In Ionic Liquid Solvents.

**Lithium bis(trifluoromethylsulfonyl)imide: Li $NTf_2$**



Li $NTf_2$ is a widely used Li-source for batteries as well as a $NTf_2$-source for Ionic Liquids, which are characterized by in most cases by high thermal and electrochemical stability combined with relatively high conductivity.

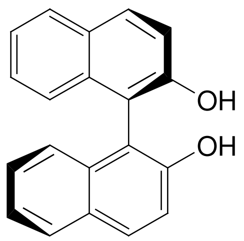
**Our special offer:***

| | | |
|---|---|---|
| **Li $NTf_2$ (>98%):** | **KI-001-100 g** | **130,00 €** |
| | **KI-001-250 g** | **220,00 €** |
| | **KI-001-500g** | **400,00 €** |
| | **KI-001-1 kg** | **700,00 €** |
| | **KI-001-2,5 kg** | **1400,00 €** |
| | **KI-001-5 kg** | **2500,00 €** |

**Chiral Specialties:**

With respect to customers who are not only interested in Ionic Liquids but also catalytic asymmetric transformations we added two widely used chiral specialties to our portfolio.

**R-(+)-1,1'-Bi-(2-naphthol): R-BINOL**




BINOL is probably one of the most popular chiral auxilies used in homogeneous catalytic asymmetric reactions.
It is widely used as ligand in asymmetric catalysis or as precursor for BINAP-ligands. Its lithium aluminium hydride derivatives are extensively used for the asymmetric reduction of ketones.

**Analytic data:**

Assay: >99% (NMR)

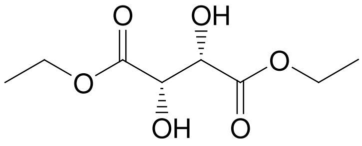
Enantimeric Excess: 98%

Optical rotation: [α]20/D=+33,0°; c=1 in THF

**Our special offer:***

| | | |
|---|---|---|
| **R-BINOL (>99%):** | **KI-022-10 g** | **100,00 €** |
| | **KI-022-50 g** | **450,00 €** |
| | **KI-022-100 g** | **765,00 €** |
| | **KI-022-250 g** | **1600,00 €** |
| | **KI-022-500 g** | **2560,00 €** |

**D-(-)-Diethyltartrate: (-)-DET**




(-)-Det can be used as ligand in asymmetric Sharpless-epoxidations or as precursor for Seebach´s TADDOL-ligands.

**Analytic data:**

Assay: >99% (NMR)

Enantimeric Excess: 98%

Optical rotation: [α]20/D= -7,2°; c=2,95 in EtOH

**Our special offer:***

| | | |
|---|---|---|
| **(-)-DET (>99%):** | **KI-023-25 g** | **35,00 €** |
| | **KI-023-50 g** | **66,50 €** |
| | **KI-023-100 g** | **125,00 €** |
| | **KI-023-250 g** | **265,00 €** |
| | **KI-023-500 g** | **400,00 €** |
| | **KI-023-1 kg** | **650,00 €** |

*** All special offers are valid until August 15th , 2006. All prices are FOB Denzlingen, costs for shipping and handling and custom charges are not included in the prices.**

## Impressum


*Ionic Liquids Today* will be released 4 times a year.

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