**Fig. 1. A** Spectroscopic changes observed when TTF-C4P, **1**, (30 $\mu$M) is treated first with 1 molar equiv. of $BIQ^{2+}2PF_6^-$ and then with increasing quantities of THACl in $CHCl_3$ (up to 10 equivalents). The inset shows the EPR spectra of 1:1 mixture of TTF-C4P and $BIQ^{\bullet+}PF_6^-$ in $CHCl_3$ at r.t. and upon addition of THACl. **B** Cation induced reverse electron transfer seen upon the addition of up to 15 equiv. of TEACl to a 1:1 solution of TTF-C4P and $BIQ^{2+}2Cl^-$ in $CHCl_3$ (30 mM in each). Inset: EPR spectra of a 1:1 mixture of TTF-C4P and $BIQ^{2+}2Cl^-$ (1.1 x $10^{-4}$ M in each) in $CHCl_3$ at r.t. upon addition up to 5 molar equiv. of TEACl.



**Fig. 2.** (A) Single crystal X-ray structure of the supramolecular donor-acceptor complex of net stoichiometry [TTF-C4P]•$_2$•[BIQ$^{2+}$]•$_2$(Cl). (B) i) EPR spectra of a crystal of TTF-PQMes recorded at different angles at 4 K. ii) The angle variation of the $D$ value.

ments, isolation and characterization of the radical salts, [TTF-C4P]$^{\bullet+}$MeSO$_4^-$ and [BIQ]$^{\bullet+}$MeSO$_4^-$ The signals at ca. 751 and ca. 2000 nm were ascribed to TTF$^{\bullet+}$ and [TTF]$^{2+}$ radical cations derived from TTF-C4P. New spectral features at ca. 380 nm could also be assigned to the reduced radical BIQ$^{\bullet+}$ in this way.

Once produced, no further changes in these optical features were observed under ambient conditions. However, the deliberate addition of TEACl caused the intensity of the signals at ca. 751 and ca. 2000 nm to decrease and the peak at ca. 329 nm to be restored (Fig. 1B). These optical changes are thus fully consistent with the anion-induced formation of an electron transfer state consisting of BIQ$^{\bullet+}$ and [TTF-C4P]$^{\bullet+}$ and its subsequent cation-triggered reversal.

Electron paramagnetic resonance (EPR) spectroscopy confirmed that the underlying ET process was being "switched on" and "switched off" through the direct measurement of paramagnetic or radical species in solution via the addition of coordinating anions (e.g., Cl$^-$) and small cations (i.e., TEA$^+$), respectively (cf. insets to Fig. 1). There are two distinct radical signals corresponding to the radical cation of TTF-C4P, **1**, at $g$ = 2.0083, and the reduced radical of BIQ$^{2+}$, **2**, at $g$ = 2.0056.

The same mixed EPR spectra, containing signals for both [TTF-C4P]$^{\bullet+}$ and BIQ$^{\bullet+}$, were obtained when **1** was mixed with **2a**, **2b**, or **2c** in chloroform or when **1** was treated with **2d** or **2e** followed by THACl (see inset to Fig. 1A). On the other hand, the addition of two molar equiv. of TEACl, a chloride salt containing the small TEA$^+$ cation that is known to bind within the calix[4]pyrrole "bowl" of TTF-C4P, to the 1:1 mixture of **1** and **2c** in chloroform at 298 K caused the EPR signals for both [TTF-C4P]$^{\bullet+}$ and BIQ$^{\bullet+}$, to disappear nearly in their entirety (see inset to Fig. 1B).

Structural analysis of the third set of crystals revealed a supramolecular donor-acceptor assembly, wherein two anion-bound bowl-like TTF-C4P moieties tightly encapsulate a bis-imidazolium quinone guest in a 2:1 fashion (Fig. 2A). Based on the structural parameters, these capsule species are considered to be tightly coupled [TTF-C4P$^{\bullet+}$]$_2$[BIQ$^{\bullet+}$]2X– biradical systems (**1•3b** and **1•3c**; X = Br, Cl, respectively). This is the first time it has proved possible to isolate as a stable species a strongly coupled bimolecular radical ion pair involved in a bimolecular electron process prior to separation into the two radicals involved.
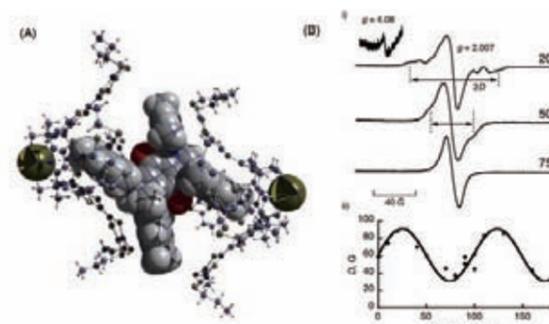
The existence of a tightly coupled biradical "capsule" was further confirmed by low temperature (4 K) EPR analyses of a single crystal of the [TTF-C4P$^{\bullet+}$]$_2$[BIQ$^{\bullet+}$]2Cl$^-$ salt (Fig. 2B). Typical triplet signals were observed at $g$ = 4.08 and 2.007 with zero-field splitting. The zero-field splitting parameter ($D$) observed when plotted against the angle of rotation for the single crystal, resulted in a sine curve which indicated the existence of an intramolecular radical ion pair.

On the basis the above findings, we propose that reversible, anion-induced electron transfer takes place in accord with Scheme 1. Specifically, the use of a BIQ$^{2+}$ salt containing a co-ordinating anion or the addition of THACl to chloroform solutions of TTF-C4P and BIQ$^{2+}$ salts with non-coordinating anions leads first to conformational "flipping" and stabilization of the calix[4]pyrrole cone conformation. This is followed by formation of a capsule-like donor acceptor complex, either **3** or **3'**, followed by fast electron transfer. The initial, within-the-capsule electron transfer is then followed by reversible separation of the two positively charged radical species in question. The net result is the formation of [TTF-C4P]$^{\bullet+}$ and BIQ$^{\bullet+}$ as electron transfer products under a reversible equilibrium process.

We have found that reversible electron transfer can be achieved using other electron acceptors. We thus believe that the ion-switched strategy reported herein may be generalized to provide working devices useful for light harvesting, ion sensing, energy storage, among other applications

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## Design, Synthesis, and Electorchemistry of Room-Temperature Ionic Liquids Functionalized with Propylene Carbonate

The following is a comment on the published paper shown on the preceding page.

# How to Create Fairy-tale Green Functional Solvents for Future Technology?

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## Introduction

It is not an exaggeration to say that solvent, which is one of the most important reaction media, supports many modern technologies. However physicochemical properties of the conventional solvent such as organic solvent and aqueous solution is not enough to create future technologies that are required to work under severe condition. In addition, some solvents, especially volatile organic compounds (VOCs), are not earth-friendly. Therefore now it is hoped that next-generation green functional solvent is developed by a process suited to large-scale production. We believe room-temperature ionic liquid (RTIL) will take over the next-generation solvent's seat. RTIL is a nonvolatile liquid salt having a liquid phase at 298 K and combines various features, e.g., high ionic conductivity ($\leq$ 120 mS cm$^{-1}$), wide liquidus temperature range (173 ~ 450 K), wide electrochemical windows ($\leq$ 5.8 V), negligible vapor pressure ($\leq$ 5 × 10$^{-9}$ torr), and easily tunable physicochemical properties [1]. Focusing on the unique features, many applications have been proposed so far. Those are electrolytes for Li secondary battery and low-temperature PEM fuel cell, reaction solvents for organic synthesis and nanoparticle preparation, extract agents for rare metal ions and CO$_2$, lubricants for space technology, and so on (Figure 1). There is no longer any doubt that RTIL contribute to create future science and technologies [2].
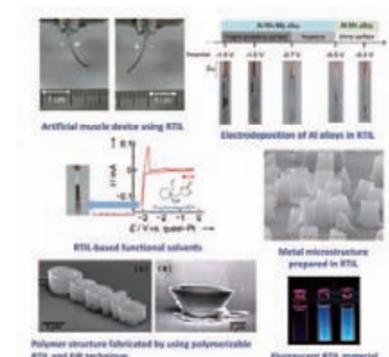


**Figure.1** Examples of RTIL-based technologies.

It is interesting to note that most RTIL can be classified into seven families on the basis of their cationic structures, as depicted in Figure 2 along with typical side chains and anions. However it is difficult to synthesize large quantities of RTIL with high purity because we cannot exploit a distillation process for the RTIL purification due to the nonvolatility of the RTIL once the RTIL is synthesized. Current our greatest challenge is to establish a highly practical and scalable approach for next-generation green functional solvent, especially RTIL, directly leading to development of future science and technologies.
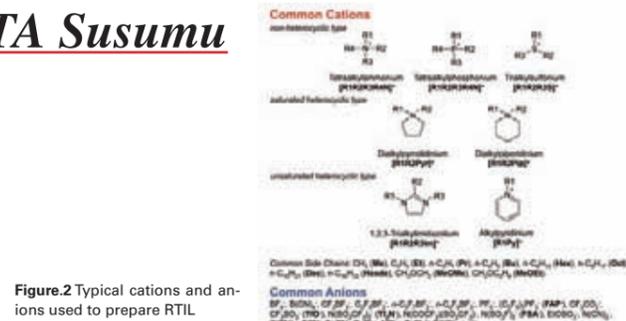


**Figure.2** Typical cations and anions used to prepare RTIL

## Strategy

Alkyl carbonates are often employed as solvents for the study of energy-storage devices, e.g., lithium secondary batteries, and some of those including propylene carbonate (PC) and diethyl carbonate have already been put to practical use in modern electronics technology such as in mobile phones and laptop computers. However, all of these organic solvents potentially have safety drawbacks related to their flammable and volatile nature that can lead to explosions and/or fire accidents. RTIL is expected to be a new class of solvents for next-generation rechargeable high-energy density batteries, because RTILs possess unique "salt-like" properties [1,2]. Some of these properties are highly advantageous in electrochemical applications such as high electrochemical stability, negligible vapor pressure, and resistance to combustion. Thus, we anticipated that chemically combining an appropriate carbonate and organic salt may remove some of the undesirable properties of alkyl carbonates and provide uniquely functionalized RTIL for energy-storage devices, particularly lithium secondary battery systems (Figure 3).
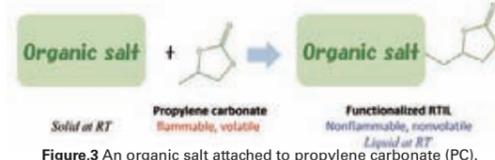


**Figure.3** An organic salt attached to propylene carbonate (PC).

## Synthetic process

The synthesis (Scheme 1) started from inexpensive, commercially available reagents, piperidine and epichlorohydrin, which afforded epoxypropylpiperidine 2 by using a modified Heywood-Phillips procedure [3]. The TBAI catalyzed cyclic carbonation of 2 then provided the desired carbonate 3 in 86% yield [4]. Both reactions were successfully operated under solvent-free, large-scale conditions (~250 mmol). Subsequently, exposing carbonate 3 (~175 mmol) with four equivalents of methyl iodide in acetone gave the analytically pure salt 1a in quantitative yield. This simple three-step approach did not require any chromatographic purification and enabled large-scale synthesis of the functionalized salt 1a. Indeed, more than 400 g of the salt was easily prepared; however, subsequent anion exchange of 1a did not give the desired RTIL.
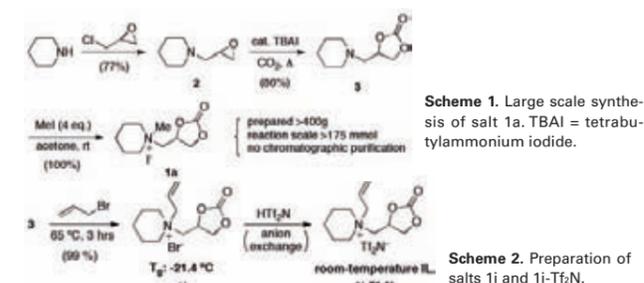


**Scheme 1.** Large scale synthesis of salt 1a. TBAI = tetrabutylammonium iodide.



**Scheme 2.** Preparation of salts 1i and 1i-Tf$_2$N.

To test the generality of this route as well as to explore a low-melting/room-temperature ionic liquid, the other piperidinium salt analogues of 1 were continuously prepared from carbonate 3 (Table 1). For practical reasons, all examples were operated under neat conditions. Interestingly, among the examples, the salt 1c (entry 3) displayed the lowest melting point (100-102 ℃) and, compared to the other alkyl groups (entries 1-5), a "three-carbon" propyl chain is obviously a critical length to yield a low-temperature melt in this salt system. In fact, this is a common behavior of organic salts, e.g., 1-alkyl-3-methylimidazolium tetrafluoroborate [1]; that is, the propyl group created a sterically hindered environment around the cation leading to the appropriate ion-ion separation, which eventually lowered the melting point of 1c. Although anion exchange of 1c may help to lower the melting point further, due to the lack of reactivity of the propyl halide, a more reactive "three-carbon" chain reactant, allyl halide, was then employed (Scheme 2). Treatment of 3 with allyl bromide instantly afforded salt 1i in excellent yield, even under large-scale neat conditions (~120 mmol). Furthermore, 1i showed only a glass transition temperature at -21.4 ℃ without a true melting point. Anion exchange of 1i with bis(trifluoromethanesulfonyl)amine (HTf$_2$N) finally provided the RTIL, 1i-Tf$_2$N.



**Table 1.** Synthesis of a series of piperidinium salts 1.

## Physicochemical properties

Although we have successfully prepared several ILs, 1a-Tf$_2$N (m.p. 92.0 ℃), 1c, 1i, and 1i-Tf$_2$N, having melting point below 100 ℃, only 1i-Tf$_2$N was a true RTIL. The viscosity exceeded 30000 cP at 35 ℃ and the conductivity was considerably-low. The thermal stability and electrochemical stability were also assessed in this investigation. Figure 4 displays thermoanalytical data of 1i and 1i-Tf$_2$N, estimated by means of thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The decomposition temperature, T$_d$, was given at 76.4 ℃ for 1i and 286.9 ℃ for 1i-Tf$_2$N, with the assumption that the decomposition begins at the temperature where 1 wt.% loss was detected. The higher decomposition temperature, i.e., higher thermal stability, of 1i-Tf$_2$N can be reasonably explained by the lower nucleophilicity of the anion, [Tf$_2$N]$^-$. Differential scanning calorimetry (DSC) clarified that these salts do not have melting points, but have glass transition temperatures at -21.4 ℃ (1i) and -24.3 ℃ (1i-Tf$_2$N). The former salt had almost no fluidity at 25 ℃ due to the strong cation-anion interactions compared to 1i-Tf$_2$N, but the latter was a barely fluidic salt. Thus, we concluded that 1i-Tf$_2$N has a wide liquidus temperature range exceeding 300 ℃.
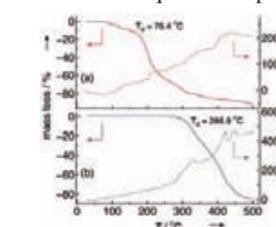


**Figure 4.** Results of thermogravimetric analysis (TGA) and differential thermal analysis (DTA). (a)1i and (b) 1i-Tf$_2$N. The rate of temperature increase was 10 ℃ min$^{-1}$.

The electrochemical stability of 1i-Tf$_2$N was studied by using linear sweep voltammetry which was carried out at 45 ℃ to avoid unfavorable voltammograms resulting from the large IR drops that appeared below this temperature. The electrochemical window at a glassy carbon (GC) and a Pt electrode were ca. 4.5 V and 5.0 V, respectively.

## Li deposition/stripping in the RTIL.

Figures 5a shows a cyclic voltammogram recorded at a copper wire electrode in 91.0-9.0 mol % [1i-Tf$_2$N]-[LiTf$_2$N] binary RTIL system. A very sharp deposition wave with an associated stripping wave appeared at ca. -3.0 V. In addition to this, a very small redox couple, which may be related to the formation of solid-electrolyte interphase layer, also appeared at ca -2.0 V. As shown in Figure 5b, controlled-current electrolysis at -100 μA for 600 sec yielded a light gray electrodeposit of Li metal deposited on the Cu substrate. No additives were used. This result implies that the [1i-Tf$_2$N]-[LiTf$_2$N] binary RTIL system is a promising solvent for next-generation lithium secondary battery systems.
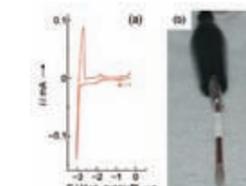


**Figure 5.** (a) A cyclic voltammogram recorded at a Cu wire electrode in 91.0-9.0 mol % [1i-Tf$_2$N]-[LiTf$_2$N]. The temperature was 85 ℃. The sweep rates were 10 mV sec$^{-1}$. (b) A photograph of the Cu wire electrode after the electrodeposition experiment at -100 μA. The temperature was 85 ℃. The electrodeposition time was 600 sec

## Conclusion

We could establish a highly practical and scalable approach for a series of piperidinium salts having a propylene carbonate moiety. All three-step reactions were carried out under solvent-free/neat conditions and no chromatographic purification was required. Controlling the length of alkyl chain as well as the type of counter anion successfully afforded a RTIL. This novel RTIL possesses wide thermal stability and Li metal deposition ability. Thus, those positive aspects of the melt in both synthesis and electrochemistry hold great promise as a candidate next-generation green functional solvent.

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