

Design and Synthesis of Multifunctional Materials Based on an Ionic-Liquid Backbone**

Yuanjian Zhang, Yanfei Shen, Junhua Yuan,
Dongxue Han, Zhijuan Wang, Qixian Zhang, and
Li Niu*

Ionic liquids (ILs) have attracted an increasing amount of interest, owing to their low volatility, non-flammability, high chemical and thermal stabilities, high ionic conductivity, and broad electrochemical windows.^[1] Initial investigations concerning ILs focused on employing them as “green” solvents in chemical synthesis, catalysis, separation, and electrochemistry, for example.^[1a,2] Recently, ILs have emerged as templates or stabilizers for nanostructures,^[3] and as supported catalysts for organic and electrochemical reactions.^[4] Some task-specific ILs have also been designed,^[5] because the structures and properties of ILs can be easily tuned by selecting the appropriate combination of organic cations and anions (Scheme 1a).^[1] It is also possible to utilize one ionic component to deliver a unique function and the other to

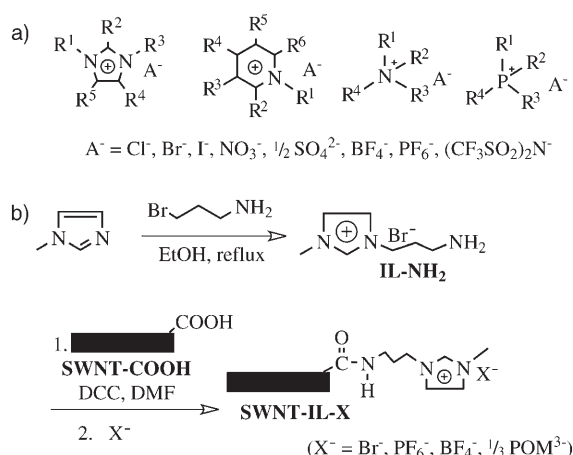
deliver a different and independent function. This concept would provide a facile and promising method to prepare multifunctional compounds. In contrast, to achieve this combination with a molecular compound would provide all sorts of synthetic challenges. However, to our knowledge, this type of flexibility of ILs has hardly been realized, as the majority of the applications of ILs are limited to employing them as novel solvents, catalysts, or surfactants.^[1–4]

Herein, we report a new concept for the preparation of multifunctional compounds by using an IL backbone. Single-walled carbon nanotubes (SWNTs) and counteranions such as Br[−], PF₆[−], BF₄[−], and polyoxometalates (POMs) can be deliberately coupled by using the imidazolium group, which is a common cation in ILs, as the backbone (Scheme 1). Preliminary results indicate that the individual properties of the SWNTs and the various counteranions are easily and successfully delivered into the resulting compounds.

Owing to their unique thermal, electronic, and mechanical properties, SWNTs have attracted a great deal of attention.^[6] It has been envisioned that the integration of SWNTs and other functional components would not only highlight the unique physical properties of SWNTs but would also lead to multifunctional materials.^[6b–k] Nevertheless, there are still many synthetic challenges.^[6f] As illustrated below with ILs, efficient coupling of SWNTs with other components is achieved in a simple anion-exchange reaction.

The preparation of SWNT-substituted imidazolium salts bearing various anions X (SWNT-IL-X) is illustrated in Scheme 1b. The characteristic G band and radical breathing mode (RBM) of the SWNT were observed by Raman spectroscopy after coupling (see Supporting Information), which indicates that the original properties of the SWNT are preserved in the final SWNT-IL-X, as reported previously.^[6] To determine whether the functions of the other components were also preserved in the SWNT-IL-X products, the properties of the X counteranions were investigated further.

The wettability of ILs is unique. It has been reported that the Br[−] anions of imidazolium salts can easily be exchanged with BF₄[−] or PF₆[−], thereby modulating the wettability.^[1b,4e,5b] In order to investigate whether the tunable wettability derived from these anions could be delivered into SWNT-IL-X, SWNT-IL-Br was first assembled on a hydrophilic glass substrate as the outmost layer with the aid of polyethyleneimine (PEI) and poly(styrene-4-sulfonate) (PSS) by a typical layer-by-layer (LbL) process (glass/PEI/PSS/SWNT-IL-Br).^[4e] The anion was exchanged by submerging this film in 10 mM NaBF₄ or NaPF₆ for 4 hours and then rinsing thoroughly with water.^[5b] It was found that the water contact angle of the glass/PEI/PSS/SWNT-IL-Br multilayer could be tuned by this anion exchange, while for the glass/PEI/PSS multilayer in the control experiments no changes were observed (Figure 1). Because the wettability of an LbL multilayer is dominated by the outmost layer, the change in contact angle observed should be due only to anion exchange of the SWNT-IL-X.^[4e] In agreement with previous reports,^[4e,5b] the contact angle of SWNT-IL-PF₆ (49.7 ± 2.3°) is higher than that of SWNT-IL-BF₄ (45.8 ± 0.9°) and much higher than that of SWNT-IL-Br (39.8 ± 1.3°). Therefore, tunable wettability can also be successfully delivered into



Scheme 1. a) Cations and anions commonly used in ILs. b) The preparation of SWNT-IL-X.

[*] Y. Zhang, Y. Shen, J. Yuan, D. Han, Z. Wang, Q. Zhang, Prof. Dr. L. Niu
State Key Laboratory of Electroanalytical Chemistry
Changchun Institute of Applied Chemistry
and Graduate School of the Chinese Academy of Sciences
Chinese Academy of Sciences
Changchun 130022 (P.R. China)
Fax: (+86) 431-526-2800
E-mail: lniu@ciac.jl.cn

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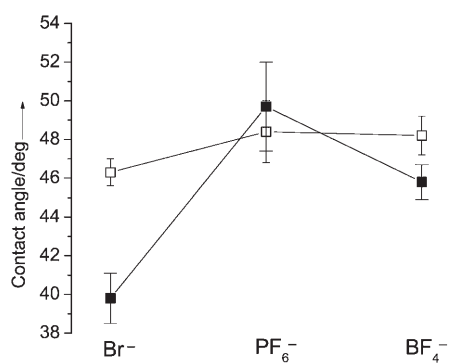


Figure 1. Effects of counteranions on the water contact angle of SWNT-IL-X (solid squares) and the control sample (hollow squares).

SWNT-IL-X ($X = \text{Br}^-$, PF_6^- , and BF_4^-) merely by exchanging the anion.

In this initial investigation, the ionic character of the IL is utilized to couple the SWNT to the other components. The ionic functionalization of SWNTs allows the counterion to be readily exchanged. Therefore, such an ionic feature might allow electrostatic interactions between SWNT-ILs and biological molecules, and could serve as the basis for developing biocompatible SWNT compounds. In general, the ionic functionalization of SWNTs in previous reports^[6j] was based on an acid–base reaction. Herein, the advantage of the IL is that its ionic character is not dependent on the pH, so its reactivity should be more general. Another advantage is the diversity of anions (organic/inorganic) and cations available (with various R groups, see Scheme 1), which makes it possible to integrate multiple functional components into one compound. For example, it should be possible to combine optical, electronic, and magnetic components in a single compound. Additionally, some IL properties are also unique. For instance, as discussed above, the wettability of SWNT-IL-X can be controlled merely by exchanging the Br^- anion with BF_4^- or PF_6^- , which is rarely seen for common SWNT composites and could be very useful for the phase-transfer of SWNTs in various solvents and their self-assembly at interfaces.^[6l]

To further illustrate this concept, the anion of phosphotungstic acid, $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ (H_3POM), a typical Keggin-type polyoxometalate (POM), was also coupled with an SWNT to construct a multifunctional compound for charge transfer. POMs have recently been extensively investigated in catalysis, electro- and photochromism, and medicine.^[7] They also undergo multiple consecutive and reversible multi-electron reductions into mixed-valence species (so-called heteropolyblues, HPBs), without decomposition. Therefore, their anion derivatives have been widely integrated into composite compounds by covalent^[7b,c] or ionic bonding.^[7d,e]

The integration of the POM and the SWNT is evident from the FTIR spectrum (Figure 2). The characteristic bands of the POM near 1082 ($\text{P}-\text{O}$), 963 ($\text{W}=\text{O}_{\text{ter}}$), and 894 cm^{-1} ($\text{W}-\text{O}-\text{W}$) are clearly observed in the spectrum of SWNT-IL-POM. Energy-dispersive X-ray (EDX) microanalysis further confirmed the complete exchange of Br^- for POM^{3-} in the resulting SWNT-IL-POM (see Supporting Information).

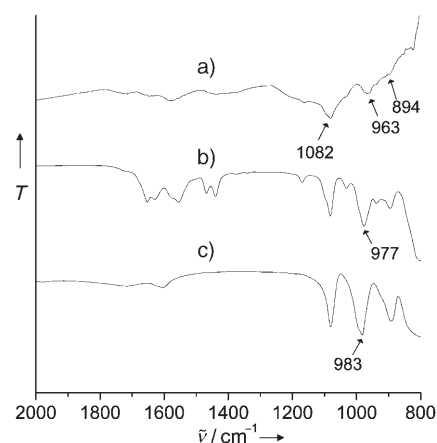


Figure 2. FTIR spectra of SWNT-IL-POM (a), IL-POM (b), and H_3POM (c).

Interestingly, a red-shift of approximately 20 cm^{-1} with respect to the $\text{W}=\text{O}_{\text{ter}}$ vibration in H_3POM is observed for the SWNT-IL-POM, while a red-shift of only 6 cm^{-1} is observed for the IL-bearing POM (IL-POM). As SWNTs readily accept electrons,^[6g] electron delocalization between the SWNT and the POM might occur, which would decrease the electron density of $\text{W}=\text{O}_{\text{ter}}$ and result in the distinct red-shift. On the basis of this unique interaction between the SWNT and the POM, and considering their individual properties, SWNT-IL-POM might find applications in electron donor–acceptor systems.

Cyclic voltammetry (CV) was further used to investigate the redox/charge activity of SWNT-IL-POM. The surface-confined SWNT-IL-POM shows three couples of sharp and well-defined redox waves due to the POM cluster (Figure 3a). A plot of the cathodic peak current (I) as a function of the scan rate (ν) is linear up to 2 Vs^{-1} , while the peak potentials remain nearly constant (Figure 3b). The small difference in the anodic and cathodic peak potentials ($\Delta E_p < 60 \text{ mV}$) implies that the redox response remains practically reversible. It is therefore reasonable to assume that the rich redox activity of the POM has been successfully transferred to SWNT-IL-POM by a simple anion-exchange reaction.

It has been reported that the characteristics of the cyclic voltammograms of POM microparticles attached to electrode surfaces depend on the conductivity, solubility, and dissolution kinetics of the adhered solid and the electrogenerated products.^[7f] In order to illustrate the unusual redox/charge-transfer activity of SWNT-IL-POM, a set of control CV experiments with a POM-modified SWNT, a POM-modified SWNT-COOH, and IL-POM in 0.5M H_2SO_4 were also performed (see Supporting Information). Owing to the synergistic effect of each component, only the cyclic voltammogram of SWNT-IL-POM gave sharp and well-defined redox waves. The cyclic voltammograms of the POM-modified SWNT and the POM-modified SWNT-COOH are dominated by the charging current of the SWNT, as only a small amount of the POM is absorbed physically on the SWNT. This indicates that the IL on the SWNT plays an important role in effectively immobilizing the POM through

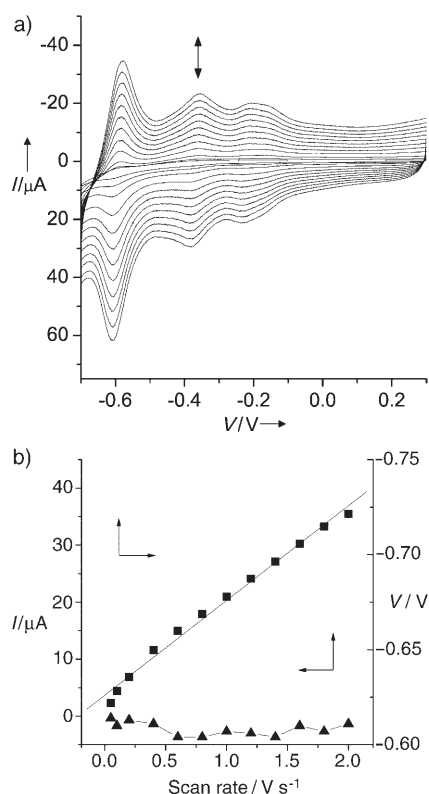


Figure 3. a) Cyclic voltammograms of an SWNT-IL-POM-modified glassy carbon (GC) electrode ($d = 3$ mm) in $0.5\text{ M H}_2\text{SO}_4$ at scan rates of $0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8,$ and 2.0 V s^{-1} (from inner to outer). b) Plot of the peak current (squares) and peak potential (triangles) of the third reduction wave as a function of scan rate. Reference electrode: Ag/AgCl (saturated KCl); counter electrode: Pt.

ionic bonding. Only two weak redox waves were observed in the cyclic voltammograms of IL-POM. Hence, it can be concluded that the SWNT is also important for this unusual redox/charge-transfer activity, because of its unique electronic properties. In fact, there are three possible causes for this unusual charge-transfer activity in SWNT-IL-POM: the high electron conductivity of the SWNT, the ionic conductivity of the IL, and the redox conductivity of the POM. Furthermore, in conjunction with the electron delocalization between the SWNT and the POM, SWNT-IL-POM might be considered for future applications in ionic devices (for example, photoelectrochemical cells, fuel cells, and double-layer capacitors).^[1c,6g] Therefore, a multifunctional architecture for charge transfer has been prepared by deliberately combining the useful functions of SWNTs, ILs, and POMs into one compound.

In summary, an SWNT and species such as Br^- , PF_6^- , BF_4^- , and POMs have been successfully coupled onto an IL backbone. The resulting compounds retain the original properties of each component and display unusual tunable wettability and charge-transfer activity. Moreover, this principle could also be extended to the deliberate combination of other independent components into multifunctional compounds. No longer simply “green” solvents, the full exploitation

of this feature of ILs will shed light on the design and synthesis of multifunctional compounds.

Experimental Section

Pristine SWNTs (single-walled volume content $> 50\%$, length $5\text{--}15\text{ }\mu\text{m}$, diameter $< 2\text{ nm}$) were produced by a chemical vapor deposition (CVD) process and were obtained from Shenzhen Nanotech Port Co. Ltd., China, in purified form. Unless otherwise stated, reagents were of analytical grade and were used as received.

SWNT-IL-X was synthesized by an amidation reaction between the carboxylic-acid functionalized SWNT (SWNT-COOH) and the amine-terminated IL (IL-NH₂).^[6h,j,k] IL-NH₂ was prepared by treating 1-methylimidazole (0.02 mol) with 2-bromopropylamine hydrobromide (0.02 mol) by refluxing in ethanol (50 mL) under nitrogen for 24 h and then purified by recrystallization.^[5a] ESI-MS (H₂O): m/z 140 [M^+]; $^1\text{H NMR}$ (D₂O): $\delta = 8.74$ (s, 1 H), 7.48 (s, 1 H), 7.42 (s, 1 H), 4.29 (t, $J(\text{H,H}) = 7.2\text{ Hz}$, 2 H), 3.02 (t, $J(\text{H,H}) = 7.8\text{ Hz}$, 2 H), 2.23 ppm (m, 2 H). IL-NH₂ is soluble in ethanol, DMF, and DMSO, very soluble in water, and stable in air. SWNT-COOH was prepared by refluxing the pristine SWNTs in 3 M HNO_3 . SWNT-IL was prepared by ultrasonically treating a solution of SWNT-COOH (5 mg), IL-NH₂ (10 mg), and dicyclohexylcarbodiimide (DCC, 10 mg) in DMF (10 mL) for 15 min and then vigorously stirring at 50°C for 24 h. Unreacted SWNTs were removed by centrifugation. SWNT-IL-Br was subsequently filtered through a nylon membrane with $0.22\text{-}\mu\text{m}$ pores and thoroughly washed with DMF, ethanol, and water. The covalent bonding between SWNT-COOH and IL-NH₂ was demonstrated by FTIR spectroscopy (see Supporting Information). EDX microanalysis showed that the molar ratio of carbon atoms in the SWNTs to the imidazolium salt was approximately 15:1, which is similar to that reported previously.^[6f] SWNT-IL-POM was prepared by vigorously stirring an aqueous solution of SWNT-IL-Br and excess H₃POM overnight; SWNT-IL-POM was collected by centrifugation and thoroughly washed with water. It is insoluble in water, and its stability depends on the POM cluster. POM-modified SWNT and SWNT-COOH were prepared similarly by stirring the SWNT or SWNT-COOH in H₃POM aqueous solution.

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