Synthesis and Characterization of Imidazolium Perrhenate Ionic Liquids

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Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

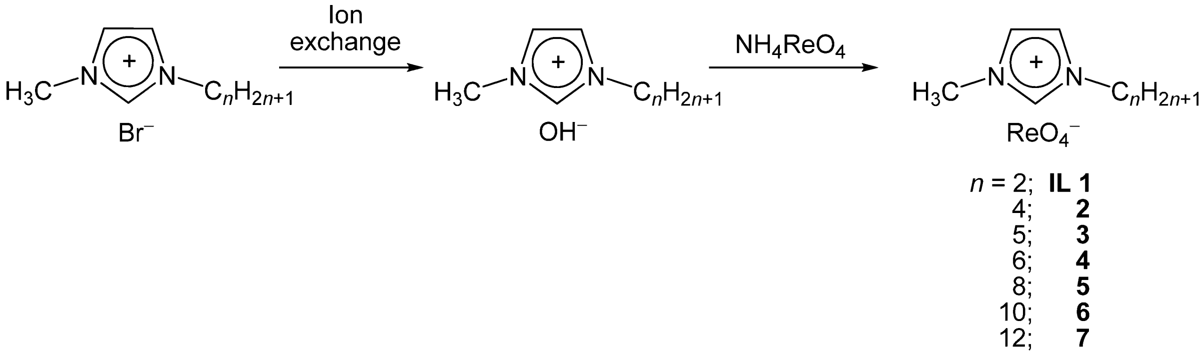
A series of air- and water-stable imidazolium perrhenate-based room-temperature ionic liquids [(RT)ILs] of the type $[C_n\text{mim}][ReO_4]$ ($C_n\text{mim} = 1\text{-}C_nH_{2n+1}\text{-3-methylimidazolium}$, $n = 2, 4, 5, 6, 8, 10, 12$) have been synthesized and characterized by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and elemental analysis (EA). The effect of the variation of the alkyl chain length on physical properties such as melting point, thermal stability, density, and conductivity was examined.

Key words: Ionic Liquids, Physical Properties, Perrhenate, Rhenium, Synthesis

Introduction

Room-temperature ionic liquids – in the following denoted as (RT)ILs – have been known since the middle of the 20th century [1]. However, broader interest arouse only during the last two decades [2]. Particularly during the last decade research on ionic liquids grew almost exponentially and both novel types and new applications appear on an almost daily basis [3 – 7]. Thus far, more than 40,000 research articles on ionic liquids have been published [8]. This is not really surprising, considering their extremely versatile chemical composition giving rise to a quite diverse set of chemical and physical properties in comparison to classical (“conventional”) organic solvents. Particularly their low miscibility with non-polar, organic solvents, low volatility, low flash point, at least in several cases low toxicity [9 – 12], thermal stability and high polarity have contributed to the attraction of ILs and their labeling as “green” alternatives to conventional solvent systems [13]. Pioneering contributions came from several groups [14 – 18] and many others joined in quickly to unravel a seemingly novel and, as it appears, still today largely undiscovered area of chemistry [19 – 21]. Furthermore, studies of ILs and SILPs (Supported Ionic Liquid Phases) [22] as reaction media for two- or multi-phase-catalyzed reactions made applications of ILs an additional and very prominent research area. In some cases, ILs have already found applications in industrial catalytic processes [23].

We had been using ionic liquids, among other purposes, as solvents for olefin epoxidation catalysis and observed in some cases a significant increase of catalytic activity [24 – 28]. The catalysts applied were usually high oxidation state organometallics, such as compounds containing Re(VII) or Mo(VI) [13] We also observed that under certain circumstances (*i. e.* immobilization on special carrier materials) usually inactive inorganic compounds, such as perrhenates, show at least moderate catalytic activity [29]. These observations tempted us to synthesize ionic liquids containing the perrhenate ion. The synthesis of such compounds and their properties are reported in this work.



Scheme 1. Synthesis of imidazolium perrhenate ionic liquids **1**–**7**.

Results and Discussion

Synthesis

A series of air- and moisture-stable perrhenate-containing ILs **1**–**7** (Scheme 1) was synthesized *via* exchange of bromide by hydroxide anions on an ion exchange resin, subsequent addition of NH_4ReO_4 and stirring at 70 °C for 24 h.

The ILs **1**–**5** are liquids at room temperature, whereas **6** and **7** exhibit melting points of 38 °C and 48 °C, respectively (see Table 3 below). All ILs can be handled in air and stored in desiccators prior to use without decomposition.

NMR spectroscopic characterization

The ILs **1**–**7** were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy (in [D$_6$]DMSO). Compared to the corresponding imidazolium bromide precursor the protons of the products **1**–**7** (see Fig. 1) are somewhat shifted, particularly the imidazolium ring protons (Table 1). The NMR spectra of **1**–**7** show no impurities detectable by NMR (Supporting Information available online; see the note at the end of the paper for availability). Similarly, some ^{13}C NMR shift changes for the carbon atoms of both the imidazolium ring and the alkyl chain in ILs **1**–**7** can be observed (Table 1). These shift changes are in agreement with a modified coordination situation.

Vibrational spectroscopy

The characteristic IR absorption bands of the $[ReO_4]^-$ anion are shown in Table 2. The ν(Re=O) vibrations are found in the region 848 – 913 cm^{-1}. The bands of the imidazolium moiety can be assigned to C–C, C=N, and C–H bonds in the ring, the C–N and C–H methyl bonds, and the C–C and C–H bonds of the alkyl chain.

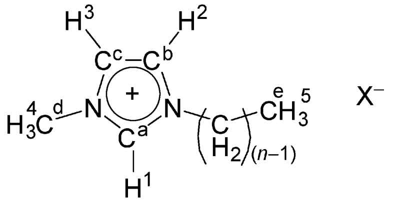


Fig. 1. Assignments of proton and carbon NMR signals of the imidazolium bromides and perrhenates **1**–**7** (X = Br, ReO_4).

The imidazolium ring C=C and C=N stretching vibrations are found between 1450 and 1572 cm^{-1}. The bands arising from ring C–H torsion vibrations are also observed in the region between 1000 and 620 cm^{-1}. The methylene groups can be observed in the region 3200 – 2000 cm^{-1}. The $\nu(CH_2)$ and $\nu(CH_3)$ stretching vibrations of the substituted alkyl groups show up in the 2800 – 3000 cm^{-1} region, and in the region from 2000 to 3000 cm^{-1} a very broad band ascribed to the aliphatic C–H vibration modes of the methyl and methylene groups is present. The ν(CH) stretching vibrations of the imidazolium CH groups are located in the region 3000 – 3200 cm^{-1} [30, 31]. The characteristic bands between 1000 and 1500 cm^{-1} are mainly assigned to methyl and methylene bending, to symmetric and asymmetric ring stretching and ring C–H bending modes [32].

The Raman spectra of the ILs **1**–**7** show the typical ReO_4 peaks of the symmetric and asymmetric stretching modes, appearing at 960 – 962 cm^{-1}. The symmetric and antisymmetric deformation modes appear at

Table 1. Comparison of ^{1}H and ^{13}C shifts of ILs **1**–**7** and their bromide precursors in [D$_6$]DMSO (δ in ppm).

Compound	H^1	H^2	H^3	H^4	$n\times$ (CH_2)$_{n-1}$	H^5
[C$_2$mim]Br	9.38 (1H, s)	7.89 (1H, d)	7.78 (1H, d)	3.87 (3H, s)	4.25 – 4.19 (2H, q)	1.39 (3H, t)
1	9.08 (1H, s)	7.75 (1H, d)	7.66 (1H, d)	3.85 (3H, s)	4.21 – 4.16 (2H, q)	1.42 (3H, t)
[C$_4$mim]Br	9.37 (1H, s)	7.87 (1H, d)	7.79 (1H, d)	3.87 (3H, s)	4.19 – 4.15 (2H, t) 1.78 – 1.71 (2H, m) 1.25 – 1.20 (2H, m)	0.86 (3H, t)
2	9.04 (1H, s)	7.71 (1H, d)	7.65 (1H, d)	3.85 (3H, s)	4.17 – 4.14 (2H, t) 1.80 – 1.73 (2H, m) 1.29 – 1.23 (2H, m)	0.89 (3H, t)
[C$_5$mim]Br	9.37 (1H, s)	7.88 (1H, d)	7.79 (1H, d)	3.87 (3H, s)	4.21 – 4.17 (2H, t) 1.79 – 1.76 (2H, m) 1.31 – 1.15 (4H, m)	0.83 (3H, t)
3	9.03 (1H, s)	7.71 (1H, d)	7.64 (1H, d)	3.86 (3H, s)	4.17 – 4.13 (2H, t) 1.81 – 1.77(2H, m) 1.33 – 1.18 (4H, m)	0.85 (3H, t)
[C$_6$mim]Br	9.53 (1H, s)	7.96 (1H, d)	7.87 (1H, d)	3.89 (3H, s)	4.23 – 4.19 (2H, t) 1.77 – 1.73 (2H, m) 1.19 (6H, m)	0.77 (3H, t)
4	9.04 (1H, s)	7.72 (1H, d)	7.65 (1H, d)	3.86 (3H, s)	4.17 – 4.14(2H, t) 1.78 – 1.74(2H, m) 1.25 (6H, m)	0.84 (3H, t)
[C$_8$mim]Br	9.37 (1H, s)	7.88 (1H, d)	7.80 (1H, d)	3.88 (3H, s)	4.21 – 4.17(2H, t) 1.80 – 1.75(2H, m) 1.22 (10H, m)	0.83 (3H, t)
5	9.09 (1H, s)	7.76 (1H, d)	7.69 (1H, d)	3.85 (3H, s)	4.17 – 4.13 (2H, t) 1.78 – 1.75 (2H, m) 1.26 (10H, m)	0.86 (3H, t)
[C$_{10}$mim]Br	9.45 (1H, s)	7.91 (1H, d)	7.83 (1H, d)	3.88 (3H, s)	4.22 – 4.18 (2H, t) 1.75 (2H, m) 1.19 (14H, m)	0.80 (3H, t)
6	9.14 (1H, s)	7.75 (1H, d)	7.68 (1H, d)	3.85 (3H, s)	4.16 – 4.13 (2H, t) 1.77 (2H, m) 1.22 (14H, m)	0.84 (3H, t)
[C$_{12}$mim]Br	9.217	7.813	7.744	3.865	4.194 – 4.145 (2H, t) 1.776 (2H, m) 1.240 (18H, m)	0.855 (3H, t)
7	9.09 (1H, s)	7.76 (1H, d)	7.70 (1H, d)	3.85 (3H, s)	4.17 – 4.13 (2H, t) 1.76 (2H, m) 1.25 (18H, m)	0.86(3H, t)

Compound	C^a	C^b	C^c	C^d	$n\times$ (CH$_2$)$_{n-1}$	C^e
[C$_2$mim]Br	136.84	124.04	122.52	36.34	44.68	15.75
1	136.74	124.10	122.48	36.22	44.75	15.61
[C$_4$mim]Br	137.10	124.10	122.82	36.36	48.99, 31.95, 19.30	13.84
2	137.00	124.11	122.76	36.22	49.17, 31.93, 19.36	13.77
[C$_5$mim]Br	137.09	124.10	122.82	36.36	49.24, 29.67, 28.16, 22.06	14.31
3	136.99	124.10	122.74	36.21	49.47, 29.64, 28.20, 22.07	14.20
[C$_6$mim]Br	137.09	124.01	122.79	36.38	49.18, 31.10, 29.99, 25.65, 22.42	14.34
4	137.00	124.11	122.76	36.22	49.47, 31.11, 29.93, 25.73, 22.42	14.31
[C$_8$mim]Br	137.10	124.10	122.82	36.35	49.27, 31.72, 30.11, 29.05, 28.92, 26.05, 22.61	14.47
5	136.93	124.07	122.72	36.21	49.26, 31.72, 29.97, 29.01, 28.92, 26.08, 22.51	14.39
[C$_{10}$mim]Br	137.12	124.06	122.80	36.36	49.23, 31.85, 30.07, 29.50, 29.43, 29.25, 29.00, 26.07, 22.65	14.43
6	137.02	124.12	122.77	36.23	49.44, 31,88, 30.01, 29.51, 29.42, 29.27, 28.99, 26.12, 22.68	14.40
[C$_{12}$mim]Br	136.577	123.562	122.292	35.838	48.37, 31.88, 29.55, 29.13, 29.11, 29.07, 28.95, 28.81, 28.52, 25.58, 22.16	13.940
7	137.01	124.14	122.80	36.27	49.41, 31.86, 29.96, 29.59, 29.57, 29.51, 29.39, 29.27, 28.95, 26.08, 22.65	14.46

Table 2. Selected IR (KBr) data (cm^{-1}) for ILs **1**–**7**. Abbreviations: sym = symmetric; asym = asymmetric.

IL	Imidazolium ring					Alkyl groups				$[\text{ReO}_4]^-$	
	ν(RC–H)		ν(C=C)	ν(C=N)	ν(C–H)	ν(C–H)		νMe(C–H)		Re=O (ν_{sym})	Re=O (ν_{asym})
1	3149m	3108m	1572m	1450m	1169s	2986m	2970m	1450m	1383w	909	848
2	3150m	–	1560m	1459m	1166s	2962m	2874m	1459m	1384w	905	848
3	3148m	3109m	1571m	1466m	1166s	2958m	2933m	1459m	1382w	906	853
4	3150m	–	1561m	1459m	1166s	2957m	2859m	1459m	1383w	908	848
5	3149m	–	1560m	1458m	1165s	2957m	2856m	1458m	1382w	913	848
6	3112m	–	1565m	1464m	1163s	2962m	2856m	1464m	1383w	902	862
7	3149m	3062m	1572m	1473m	1179s	2949m	2850m	1473m	1383w	910	861

Table 3. Physical data of ILs **1**–**7**. ILs **6** and **7** are solid at 25 °C and below.

ILs	M. p. / glass trans. temp. (°C)	Density (g cm^{-3})		Dec. temp. (°C)	Specific conductivity (mS cm^{-1})		Molar conductivity ($\text{S cm}^2\,\text{mol}^{-1}$)	
		20 °C	25 °C		20 °C	25 °C	20 °C	25 °C
1	−15.2	2.163	2.157	397.5	6.180	7.580	1.032	1.270
2	−76.5	1.969	1.963	399.8	1.767	2.230	0.349	0.442
3	−73.9	1.856	1.851	397.0	1.107	1.473	0.241	0.321
4	−61.1	1.799	1.794	394.8	0.855	1.096	0.198	0.255
5	9.2	1.663	1.658	380.9	0.607	0.806	0.163	0.217
6	38.3	a	1.527	382.0	a	a	a	a
7	48.3	a	1.433	383.9	a	a	a	a

324 – 335 cm^{-1}. The results are similar to that of aqueous ReO_4^- at 971 and 331 cm^{-1} [33].

Physical properties of compounds 1–7

The imidazolium perrhenate compounds **1**–**7** exhibit melting points below 50 °C (see Table 3), justifying the denotation "ionic liquids". The ionic compounds **1**–**5** are liquids at room temperature, and glass transition processes can be detected below room temperature according to differential scanning calorimentry (DSC) data. ILs **6** and **7** have melting points of 38.3 and 48.3 °C, respectively. The thermogravimetric analysis (TGA) data indicate that all compounds show negligible volatility and high thermal stability with decomposition onset temperatures between 380 and 400 °C (Fig. 2).

Increasing the alkyl chain length from ethyl to octyl to dodecyl increases the hydrophobicity of the ionic liquids. Densities and conductivity, however, decrease. ILs **1**–**4** show good solubility in water, whereas octyl, decyl and dodecyl moieties are responsible for the hydrophobicity of the ILs **5**–**7**. It is well-known that to a large extent the water miscibility is governed by nature of the anion (*e. g.* BF_4 *vs.* NTf_2) [13]. However, it is also possible to modify solubility *via* the cations (*e. g.* with short alkyl substituents *vs.* long, fatty chains) [34 – 36]. Compounds **1**–**7** are soluble in polar organic solvents such as CH_2Cl_2, acetone, acetonitrile, and ethanol.

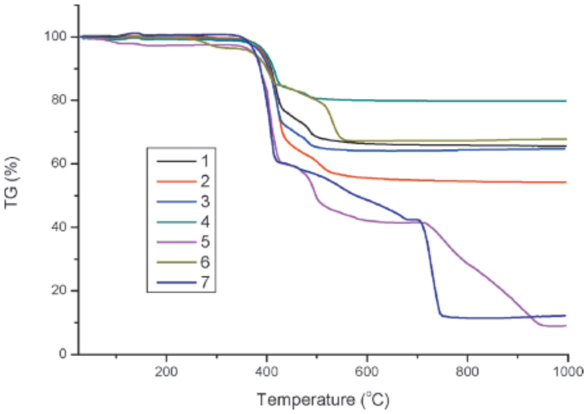


Fig. 2 (color online). Degradation of ILs **1**–**7** measured by TGA (10 K min^{-1}, 25 – 1000 °C, N_2 flow).

Experimental Section

General remarks

All preparations were performed under laboratory atmosphere. All reagents and solvents employed were commercially available and were of analytical grade. NH_4ReO_4 (99.99 %) was purchased from Zhuzhou KETE Industries Co. Ltd. Anion-exchange resin (type 717) was purchased from Shanghai Chemical Reagent Co. Ltd. and activated by the usual method. Characterization and microanalyses of the obtained products were performed in the Institute of Rare and Scattered Elements Chemistry of Liaoning University in China and the Mikroanalytisches Laboratorium of the Technische Universität München. ^{1}H and ^{13}C NMR were measured in [D$_6$]DMSO with a mercury-VX 300 spectrometer or a 400-MHz Bruker Avance DPX-400 spectrometer (resonance frequencies for ^{1}H: 400 MHz, ^{13}C: 100 MHz). IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer or a Perkin–Elmer FT-IR spectrometer using KBr as the matrix. ESI-MS spectra were measured on a Finnigan LCQ Classic mass spectrometer. The Raman spectra were measured on a Microscopic Confocal Raman Spectrometer (RM 2000) produced by Renishaw.

Laser radiation was provided by a semiconductor laser (785 nm) and was passed through a line filter and a cylindrical lens and focused onto the NMR tube containing the sample. The laser power at the sample was approximately 0.90 mW. Scattered light was collected at a 90° angle from the excitation beam. The light was dispersed *via* an 1800 line mm^{-1} grating and detected via a liquid nitrogen-cooled CCD. Thermogravimetry coupled with mass spectroscopy (TG-MS) was conducted utilizing a Netzsch TG209 system; typically about 10 mg of each sample were heated from 25 to 1000 °C at 10 K min^{-1}. Differential Scanning Calorimetry (DSC) was performed on a Q 2000 series DSC instrument. Typically about 2 mg of sample was heated from -100 to 150 °C at 10 K min^{-1}. Conductivity of pure liquids at 20 °C and 25 °C was measured by a Mettler Toledo SG7 conductometer. Density was measured by an Anton Paar DMA4500 densimeter. The content of water in the ILs was measured using a Karl Fischer moisture titrator (ZSD-2 type).

*General preparation of ionic liquids **1–5** and **7***

1-Alkyl-3-methylimidazolium bromides [C$_n$mim]Br were synthesized according to literature processes [37–41]. Then aqueous 1-alkyl-3-methylimidazolium hydroxides [C$_n$mim][OH] were prepared from [C$_n$mim]Br by use of activated anion-exchange resin over a 100 cm column. (The products are not particularly stable and should be used immediately after preparation). 1.2 equiv. of NH$_4$ReO$_4$ was added, and the solution was heated to 70 °C for 24 h, followed by a complete removal of the residual water under reduced pressure. The excess of NH$_4$ReO$_4$ was removed by extraction of the ionic liquid with dichloromethane. Colorless (**1–4** and **7**) and brown (**5**) solid (**7**) ionic liquids were obtained, dried in vacuum desiccators under reduced pressure for 24 h at 80 °C and stored in desiccators prior to use.

*Preparation of ionic liquid **6***

1-Decyl-3-methylimidazolium bromide [C$_{10}$mim]Br was synthesized according to the literature [37–41]. Then a solution of 1-decyl-3-methylimidazolium bromide in water and ethanol (volumetric ratio 1/1.5) was slowly added on the ion exchange resin (pH = 7). The product was washed slowly off the column with the mixture of water and ethanol until the pH of the eluent remained equal to 7, affording the desired product [C$_{10}$mim][OH]. Subsequently, 1.2 equiv. of NH$_4$ReO$_4$ was added, and the solution was heated to 70 °C for 24 h. The slurry was kept for 10 min, the solution decanted, and the residue dried under reduced pressure. IL **6** (a colorless solid at room temperature) was obtained by extraction of the mixture with dry dichloromethane. The solvent was distilled off in an evaporator and the residue dried under oil pump vacuum.

Compounds **1–7** were characterized by FT-IR, ^{1}H and ^{13}C NMR spectroscopy (for the full NMR data see Table 1), ESI-MS, and elemental analysis. The glass transition temperatures, melting points (DSC), and decomposition temperatures (TGA) were determined and can be found in the Supporting Information.

1: $C_6H_{11}N_2O_4Re$ (361.37). – IR (KBr): ν = 909, 848 cm^{-1} (Re=O). – MS ((+)-ESI): m/z = 111.0 (calcd. 111.2 for $C_6H_{11}N_2$, [M]$^+$). – Elemental analysis for $C_6H_{11}N_2O_4Re$ (%): calcd. C, 19.94, H, 3.07, N, 7.75; found C, 19.85, H, 2.98, N, 7.71.

2: $C_8H_{15}N_2O_4Re$ (389.42). – IR (KBr): ν = 905, 848 cm^{-1} (Re=O). – MS ((+)-ESI): m/z = 139.1 (calcd. 139.2 for $C_8H_{15}N_2$, [M]$^+$). – Elemental analysis for $C_8H_{15}N_2O_4Re$(%): calcd. C, 24.67, H, 3.88, N, 7.19; found C, 25.21, H, 4.12, N, 7.17.

3: $C_9H_{17}N_2O_4Re$ (403.45). – IR (KBr): ν = 906, 853 cm^{-1} (Re=O). – MS ((+)-ESI): m/z = 153.1 (calcd. 153.2 for $C_9H_{17}N_2$, [M]$^+$). – Elemental analysis for $C_9H_{17}N_2O_4Re$ (%): calcd. C, 26.79, H, 4.25, N, 6.94; found: C, 26.48, H, 4.24, N, 6.90.

4: $C_{10}H_{19}N_2O_4Re$ (417.48). – IR (KBr): ν = 908, 848 cm^{-1} (Re=O). – MS ((+)-ESI): m/z = 167.1 (calcd. 167.3 for $C_{10}H_{19}N_2$, [M]$^+$). – Elemental analysis for $C_{10}H_{19}N_2O_4Re$ (%): calcd. C, 28.77, H, 4.59, N, 6.71; found C, 28.74, H, 4.69, N, 6.64.

5: $C_{12}H_{23}N_2O_4Re$ (445.53). – IR (KBr): ν = 913, 848 cm^{-1} (Re=O). – MS ((+)-ESI): m/z = 195.2 (calcd. 195.3 for $C_{12}H_{23}N_2$, [M]$^+$). – Elemental analysis for $C_{12}H_{23}N_2O_4Re$ (%): calcd. C, 32.35, H, 5.20, N, 6.29; found C, 31.69, H, 4.92, N, 5.80.

6: $C_{14}H_{27}N_2O_4Re$ (473.58). – IR (KBr): ν = 902, 862 cm^{-1} (Re=O). – MS ((+)-ESI): m/z = 223.3 (calcd. 223.4 for $C_{14}H_{27}N_2$, [M]$^+$). – Elemental analysis for $C_{14}H_{27}N_2O_4Re$ (%): calcd. C, 35.51, H, 5.75, N, 5.92; found C, 35.91, H, 5.88, N, 6.07.

7: $C_{16}H_{31}N_2O_4Re$ (501.64). – IR (KBr): ν = 910, 861 cm^{-1} (Re=O). – MS ((+)-ESI): m/z = 251.3 (calcd. 251.4 for $C_{16}H_{31}N_2$, [M]$^+$). – Elemental analysis for

$C_{16}H_{31}N_2O_4Re$ (%): calcd. C, 38.31, H, 6.23, N, 5.58; found C, 37.93, H, 6.28, N, 5.52.

Supporting information

Further characteristic data including pictures of various spectra of ILs **1**–**7** are given as Supporting Information available online (DOI: 10.5560/ZNB.2013-3032).

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