

Hybrid Redox Polyether Melts Based on Polyether-Tailed Counterions

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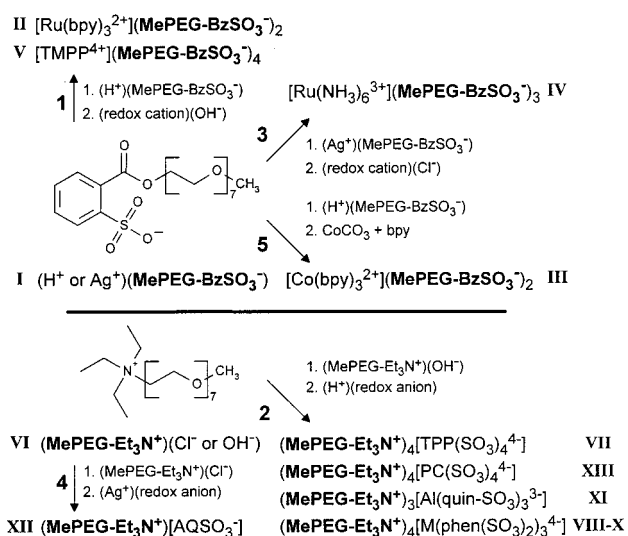
Abstract: Interesting ionic materials can be transformed into room temperature molten salts by combining them with polyether-tailed counterions such as polyether-tailed 2-sulfobenzoate (MePEG-BzSO₃⁻) and polyether-tailed triethylammonium (MePEG-Et₃N⁺). Melts containing ruthenium hexamine, metal trisbipyridines, metal trisphenanthrolines, and ionic forms of aluminum quinolate, anthraquinone, phthalocyanine, and porphyrins are described. These melts exhibit ionic conductivities in the 7 × 10⁻⁵ to 7 × 10⁻¹⁰ Ω⁻¹ cm⁻¹ range, which permit microelectrode voltammetry in the undiluted materials, examples of which are presented.

Introduction

We describe an apparently general synthetic route to room temperature melts of ionic substances that considerably enlarges the available library of electrochemically active, semisolid, polyether-based melts. Our previous investigations¹ of mass and charge transport in rigid media have relied on amorphous, highly viscous, room temperature melts (termed *hybrid redox polyether melts*) synthesized by covalently attaching polyether chains to redox active molecules. This approach can be challenging and is not applicable to many redox moieties. The new route follows the very recent work of Ohno *et al.*² and is based on using *polyether-tailed counterions*.

This paper describes new molten salts containing either polyether-tailed 2-sulfobenzoate (MePEG-BzSO₃⁻) or polyether-tailed triethylammonium (MePEG-Et₃N⁺) as counterions of ruthenium hexamine, metal trisbipyridines, metal trisphenanthrolines and ionic forms of aluminum quinolate, anthraquinone, phthalocyanine, and porphyrins. These generally quite viscous melts are prepared from readily available starting materials with neutralization and precipitation reactions (Scheme 1).³ The MePEG-BzSO₃⁻ anion was prepared by reacting 2-sulfobenzoic acid cyclic anhydride with MePEG, and the MePEG-Et₃N⁺ cation by reacting triethylamine with tosylated MePEG. The melts are prepared by neutralizing (#1) the hydroxide of a redox cation with (MePEG-BzSO₃⁻)(H⁺) [I] or (#2) the acid form of a redox anion with (MePEG-Et₃N⁺)(OH⁻) [VI], by precipitating (#3,4) AgCl from mixtures of silver and chloride salts of the tailed counterions and redox species, or by using a "one pot" reaction (#5) of a metal salt, ligand, and I. Examples of each method are presented in the Experimental Section. Stoichiometric

Scheme 1



proportions were used insofar as possible to facilitate product isolation. The approach of Scheme 1 offers a convenient synthetic generality in that the melting, or disorganizing, role of the polyether tail is compartmentalized to the counterion and thus readily extended to other interesting ionic moieties.

Experimental Section

Synthesis of (MePEG-BzSO₃⁻)(H⁺), I. A modified literature synthesis was used.⁵ To a 15 mL CHCl₃ mixture of 2-sulfobenzoic acid cyclic anhydride (7.5 g; 41 mmol; Aldrich) was added, dropwise over a 45 min period, a 25 mL CHCl₃ solution of MePEG (12.95 g; 37 mmol; Aldrich), which had been dried at ~70 °C under vacuum for ~12 h. The anhydride dissolved, yielding a clear, light yellow-brown solution. The solution was refluxed for ~2 h, filtered, flash-evaporated, and dried at ~70 °C under vacuum for several days, yielding a sweet smelling, pale yellow syrup. ¹H NMR in CDCl₃: δ 8.10 (m, 1H), 7.62 (m, 3H), 4.51 (t, 2H), 3.94 (t, 2H), 3.60 (m, 25H), 3.32 (s, 3H).

Synthesis of (MePEG-Et₃N⁺)(tosylate⁻), VI. MePEG was converted to its tosylate form according to a previously published

(4) Some differences in calculated versus found elemental analysis are thought to arise either from water contaminant or from inaccuracy in the manufacturer's stated average 350 MePEG molecular weight, or both.

(5) Ito, K.; Ohno, H. *Solid State Ionics* 1995, 79, 300.

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(1) (a) Williams, M. E.; Masui, H.; Long, J. W.; Malik, J.; Murray, R. W. *J. Am. Chem. Soc.* 1997, 119, 1997. (b) Masui, H.; Murray, R. W. *Inorg. Chem.* 1997, 36, 5118. (c) Long, J. W.; Kim, I. K.; Murray, R. W. *J. Am. Chem. Soc.* 1997, 119, 11510. (d) Williams, M. E.; Crooker, J. C.; Pyati, R.; Lyons, L. J.; Murray, R. W. *J. Am. Chem. Soc.* 1997, 119, 10249.

(2) Ito, K.; Ohno, H. *Electrochem. Acta* 1998, 43, 1247.

(3) Abbreviations: AQSO₃⁻ (anthraquinone-2-sulfonate); phen(SO₃)₂⁻ (4,7-diphenyl-1,10-phenanthroline disulfonate); bpy (2,2'-dipyridine); BzSO₃⁻ (2-sulfobenzoate); Et₃N⁺ (triethylammonium); MePEG (poly(ethylene glycol) methyl ether, MW 350); PC(SO₃)₄⁻ (phthalocyanine tetrasulfonate); quin-SO₃⁻ (5-sulfoquinolate); TMPP⁴⁺ (*meso*-tetra-(*n*-methyl-4-pyridyl)porphyrin); TPP(SO₃)₄⁻ (*meso*-tetra(4-sulfonatophenyl)porphyrin).

Table 1. Glass Transition Temperatures and Ionic Conductivities of Hybrid Redox Polyethers with Polyether-Tailed Counterions

melt no.	melt	T_G (°C)	$\sigma_{\text{ION}}(25^\circ\text{C})$ ($\Omega^{-1}\text{cm}^{-1}$)
I	(MePEG-BzSO ₃ ⁻)(H ⁺)	-47	5.3×10^{-6}
II	[Ru(bpy) ₃ ²⁺](MePEG-BzSO ₃ ⁻) ₂	-13	1.1×10^{-8}
III	[Co(bpy) ₃ ²⁺](MePEG-BzSO ₃ ⁻) ₂	-10	1.5×10^{-8}
IV	[Ru(NH ₃) ₆ ³⁺](MePEG-BzSO ₃ ⁻) ₃	-34	4.4×10^{-7}
V	[TMPP ⁴⁺](MePEG-BzSO ₃ ⁻) ₄	-63	7.1×10^{-8}
VI	(MePEG-Et ₃ N ⁺)(tosylate ⁻)	-65	7.6×10^{-5}
VII	(MePEG-Et ₃ N ⁺) ₄ [TPP(SO ₃) ₄ ⁴⁻]	-43	6.8×10^{-8}
VIII	(MePEG-Et ₃ N ⁺) ₄ [Fe(phen(SO ₃) ₂) ₃ ⁴⁻] ^a	-26	6.9×10^{-9}
IX	(MePEG-Et ₃ N ⁺) ₄ [Ru(phen(SO ₃) ₂) ₃ ⁴⁻] ^b	-3	6.1×10^{-10}
X	(MePEG-Et ₃ N ⁺) ₄ [Co(phen(SO ₃) ₂) ₃ ⁴⁻] ^c	-20	7.4×10^{-10}
XI	(MePEG-Et ₃ N ⁺) ₃ [Al(quin-SO ₃) ₃ ³⁻]	-40	2.6×10^{-7}
XII	(MePEG-Et ₃ N ⁺)[AQSO ₃ ⁻]	-46	4.7×10^{-6} ^d
XIII	(MePEG-Et ₃ N ⁺) ₄ [PC(SO ₃) ₄ ⁴⁻]	-49	4.6×10^{-7}

^a With $\approx 20\%$ excess tailed counterion, relative to ideal 4:1 stoichiometry. ^b With $< 2\%$ excess tailed counterion. ^c With $\approx 5\%$ excess tailed counterion. ^d Extrapolation to 25 °C from activation plot over range 30–55 °C.

procedure.⁶ The tosylate was then refluxed in an excess of triethylamine for ~ 48 h under nitrogen; removal of excess solvent by flash-evaporation gave a clear, amber oil. ¹H NMR in CDCl₃: δ 7.65 (d, 2H), 7.05 (d, 2H), 3.95 (m, 2H), 3.53 (m, 33H), 3.3 (s, 3H), 2.3 (s, 3H), 1.3 (t, 9H).

The tosylate anion was replaced with either hydroxide or chloride anions by using Dowex 1X8-400 ion-exchange resin (Aldrich) prepared according to standard procedures. The (MePEG-Et₃N⁺)(OH⁻) and (MePEG-Et₃N⁺)(Cl⁻) were used as dilute solutions obtained directly from the ion exchange column.

Synthesis of Electroactive Molten Salts. Each molten salt listed in Table 1 was synthesized by combining the parent salt with a tailed-counterion as described in Scheme 1. An example of each reaction type—precipitation (#1,2), neutralization (#3,4), and “one pot” (#5)—is described below; details concerning the remaining melts are given in Supporting Information.

Synthesis of [Ru(bpy)₃²⁺](MePEG-BzSO₃⁻)₂, II. Literature synthesis⁷ was followed to prepare [Ru(bpy)₃]Cl₂. The chloride salt (0.2258 g; 0.3 mmol) was dissolved in a minimum amount of H₂O, and Ag₂O (0.0695 g, 0.3 mmol + $\sim 15\%$ excess, Aldrich) was added. The mixture was stirred for ~ 2 h and passed through a Gelman PTFE 0.2 μm syringe filter. The clear red-orange filtrate was neutralized with a 10 mL aqueous solution of the acid form of I (0.3205 g, 0.6 mmol), the solution was flash-evaporated, and the resulting melt was redissolved in acetone, causing unreacted Ru(bpy)₃Cl₂ to precipitate. Filtering off the solid, the solution was flash-evaporated and dried at ~ 70 °C under vacuum for ~ 12 h to yield a clear, viscous red-orange oil. Spectroscopic purity: MW calcd 1634, found 1666. ¹H NMR in CDCl₃: δ 8.60 (d, 6H), 7.95 (t, 8H), 7.70 (d, 6H), 7.35 (m, 12H), 4.42 (t, 4H), 3.82 (t, 4H), 3.60 (m, 48H), 3.35 (s, 6H). Anal. calcd for RuC₇₄H₉₄O₂₄N₆S₂: C, 54.97; H, 5.90; N, 5.14. Found: C, 52.98; H, 6.03; N, 5.00.⁴

Synthesis of (MePEG-Et₃N⁺)[AQSO₃⁻], XII. To a boiling 40 mL aqueous solution of anthraquinone-5-sulfonic acid sodium salt monohydrate (1.0 g, 3.0 mmol, Aldrich) was added AgNO₃ (0.52 g, 3.4 mmol, Aldrich). After being stirred for ~ 1 h, the pale yellow solution was slowly cooled to room temperature, and then to 0 °C in an ice bath, precipitating the silver salt. Converting a 25 mL aqueous solution of (MePEG-Et₃N⁺)(tosylate⁻) (1.7 g, 2.8 mmol) to its chloride salt as described above, an excess of insoluble anthraquinone silver salt was added and the mixture heated to boiling with stirring for 30 min. The mixture was filtered hot to remove the precipitate, then cooled to 0 °C and again filtered to remove AgCl and unreacted anthraquinone silver salt, leaving a pale yellow solution. Flash-evaporation gave a viscous yellow oil. ¹H NMR in CDCl₃: δ 8.75 (s, 1H), 8.25 (m, 4H), 7.75 (m, 2H), 3.95 (m, 2H), 3.55 (m, 32H), 3.3 (s, 3H), 1.35 (t, 9H).

(6) Long, J. W.; Kim, I. K.; Murray, R. W. *J. Am. Chem. Soc.* **1997**, *119*, 11510.

(7) Meyer, T. J.; Salmon, D. J.; Sullivan, B. P. *Inorg. Chem.* **1978**, *17*, 334.

Synthesis of [Co(bpy)₃²⁺](MePEG-BzSO₃⁻)₂, III. Co(CO₃)₂·xH₂O (0.1397 g; 1.065 mmol + $\sim 10\%$ excess; Aldrich) was suspended in 5 mL of 25% H₂O in CH₃OH and a solution of the acid form of I (1.14 g; 2.134 mmol) in 5 mL of 25% H₂O in CH₃OH was added. To this mixture, with stirring under nitrogen, was added dropwise a solution of 2,2'-dipyridine (0.5 g; 3.201 mmol; Aldrich) in 2 mL of 25% H₂O in CH₃OH. Upon refluxing for ~ 1 h, most of the solid dissolved and the solution became brown. Filtering through Celite-545 (Fisher) and washing with CH₃OH, the filtrate was flash-evaporated and dried at ~ 70 °C under vacuum for ~ 24 h, yielding a viscous, clear brown oil. Spectroscopic purity: MW calcd 1592, found 1597. Anal. Calcd for CoC₇₄H₉₄O₂₄N₆S₂: C, 56.42; H, 6.05; N, 5.28. Found: C, 54.43; H, 6.12; N, 5.05.⁴

Additional Synthetic Information. H₂O was purified by a Barnstead Nanopure System Model 4754. Polyethylene glycol methyl ether ($M_N = 350$ g/mol, MePEG, Aldrich) was dried in a vacuum oven at 60 °C immediately prior to use. Triethylamine (Aldrich) was dried through an activated alumina column. *p*-Toluene sulfonyl chloride (Aldrich) was stored in a desiccator under nitrogen. Neutralizations were monitored with an Orion Model 601A pH meter and a Corning Semi-Micro Combination pH electrode or a Corning PS-30 pH Meter. ¹H NMR spectra were obtained on a Bruker AC-200 MHz NMR. Spectroscopic purities were determined with a Unicam UV-4 spectrometer ($\lambda_{\text{MAX,Ru}} = 450$ nm; $\lambda_{\text{ANAL,Co}} = 295$ nm) with extinction coefficients measured from methanol solutions of the respective metal trisbipyridine chloride salts. Elemental analyses were provided by Galbraith Laboratories (Knoxville, TN), with calculated analyses based on vendor's specification of average 350 MW of MePEG.⁴

Differential Scanning Calorimetry (DSC). Thermal analyses of 15–20 mg melt samples (loaded under N₂ into preweighed Al DSC pans) were conducted using a Seiko DSC220-CU differential scanning calorimeter at heating/cooling rates of 10 °C/min, under a stream of dry N₂. Samples were dried at ~ 70 °C under vacuum for ≥ 12 h. The glass transition temperature, T_G , taken as the average inflection temperatures on the DSC heating and cooling curves, varies substantially (from -3 to -65 °C) in Table 1, contrary to previous results⁸ on less structurally diverse materials.

Ionic Conductivity. Ionic conductivities of thin, drop-cast melt films were measured (Solartron Model SI 1260 Impedance Analyzer and 1267 electrochemical interface) on microlithographically fabricated Pt interdigitated array (IDA) electrodes, generously donated by O. Niwa of Nippon Telephone and Telegraph. The IDA, consisting of 50 “finger” pairs, each 3 μm wide and 2 μm apart, was mounted on a temperature controlled stage (Lakeshore 330 Autotuning Temperature Controller) with heat conductive paste (Buehler 0.05 μm alumina suspended in Dow-Corning high vacuum grease) and placed under vacuum. Impedance measurements from 2 MHz to 1 Hz were performed at 0 V DC bias and 10 to 100 mV AC amplitude. Film resistance was taken from the real axis of the complex impedance semicircle and converted to σ_{ION} by using the calibrated IDA cell constant.

Viscosity Measurements. Temperature-dependent viscosities are measured on ca. 1 g of dried material, under N₂, using a cone-plate rheometer (Brookfield Model DV-III, CP52 cone) and a constant temperature circulator bath (Brookfield Model EX-100/FTC-350A).

Electrochemical Measurements. Cyclic voltammetry and potential step chronoamperometry of the undiluted melts were performed with use of a locally built low-current potentiostat interfaced to an IBM-compatible computer through a Keithly DAS-HRES 16-bit A/D board.⁹ A thin film of each melt was drop-cast onto a three-electrode assembly, consisting of a 10 or 25 μm diameter Pt working, 24 gauge wire Pt counter electrode, and a 0.5 mm wire Ag quasireference electrode, enclosed in a cylindrical epoxy housing with polished tip exposing the electrode surfaces. Temperature-dependent measurements were made possible with a Brookfield Model EX-100/FTC-350A circulating bath and cooler and a thermocouple-monitored jacketed cell. The electrode

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(9) Applied potential manipulated via in-house software developed by R. Terrill; picostat [measures currents < 1 pA] designed by S. Woodward, UNC-CH.

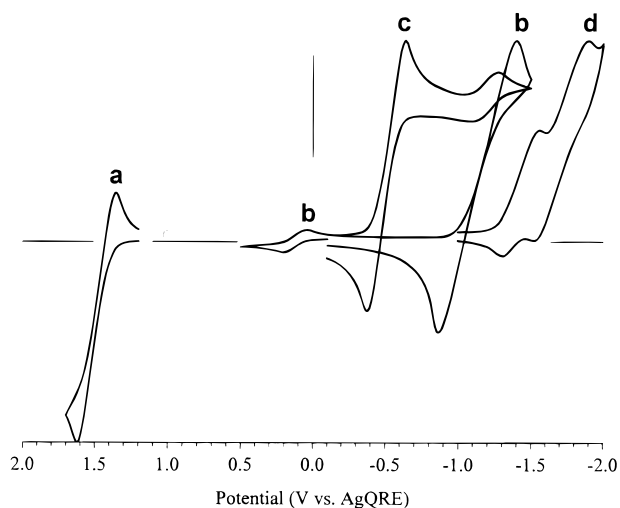


Figure 1. Cyclic voltammetry (potential scan rate ν) at Pt microdisk electrode (radius r) in undiluted melts: (a) $[\text{Ru}(\text{bpy})_3]^{2+}(\text{MePEG-BzSO}_3^-)_2$; (b) $[\text{Co}(\text{bpy})_3]^{2+}(\text{MePEG-BzSO}_3^-)_2$; (c) $(\text{MePEG-Et}_3\text{N}^+)-[\text{AQSO}_3^-]$; (d) $(\text{MePEG-Et}_3\text{N}^+)_3[\text{Al}(\text{quin-SO}_3)_3]^{3-}$. Current scale bar = 0.3, 0.6, 20, 2 nA; $r = 5.6, 5.6, 13.5 \mu\text{m}$; temperature = 65, 65, 60, 60 °C; $\nu = 2, 5, 2, 25 \text{ mV/s}$, for curves a–d, respectively. Ag wire quasi-reference electrode; exact comparisons of potentials between different melts should not be attempted from these data. The $\Delta E^\circ = 1.28 \text{ V}$ separation between the Co(II/III) and Co(II/I) couples is the same as observed in a dilute acetonitrile solution.

and each prepared sample were maintained under vacuum for several days prior to, and during, measurements.

Results and Discussion

The Scheme 1 reactions produce molten salts that are ionically conductive at or slightly above room temperature. Table 1 lists their ionic conductivities (σ_{ION}) and glass transition temperatures (T_{G}). Above T_{G} , all are amorphous melts except **XII**, which is partially crystalline and melts at 27 °C. Values of σ_{ION} vary widely, reflecting combined effects of ionic bulk and charge, as well as sample purity. σ_{ION} is highest for the native melts **I** and **VI**, so that preparations containing more than stoichiometric amounts of these counterions exhibit higher σ_{ION} (and lower T_{G}), as illustrated by the metal phenanthroline [**VIII–X**] melt data (compare Fe, Ru).¹⁰ Comparing melts **VI** and **XII** shows that increasing anion bulk depresses σ_{ION} and increases T_{G} . Data for the other melts probably reflect some combination of redox ion bulk and charge effects. Similarity of ion bulk and charge leads to almost identical ionic conductivities in the pairs of metal trisbipyridine and porphyrin melts.

Microelectrode voltammetry has been shown¹ to yield insights into electron transfer dynamics in semisolid electroactive melts. Figure 1 shows illustrative microelectrode voltammograms in several of the new molten salts (undiluted). Except for the Co(III/II) reaction (more positive wave of Curve b; this reaction has a very small electron self-exchange rate), all of the currents are expected to be enhanced by coupling between physical diffusion (D_{PHYS}) of the redox ion and electron self-exchange reactions (rate constant k_{EX} , $\text{M}^{-1} \text{s}^{-1}$) in the mixed valent melt layers next to the electrode. Expressed as an apparent diffusion coefficient, D_{APP} , this enhancement is given¹¹ as

$$D_{\text{APP}} = D_{\text{PHYS}} + k_{\text{EX}}\delta^2 C/6 \quad (1)$$

where δ (cm) is the center-to-center spacing between donor and acceptor sites of total concentration C (M). On the basis of potential step chronoamperometry of the Co(III/II) reaction in melt **III**, D_{PHYS} of the Co complex is ca. $8 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ at 25 °C. For comparison, the D_{PHYS} value for a comparable Co complex containing an equal number of ethylene oxide units but attached to the ligand^{1a} is $3 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ at 25 °C. The D_{PHYS} value for another Co complex (two tri(propylene oxide) chains per bpy ligand) is $4 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ at 25 °C.¹² These small D_{PHYS} values reflect the large viscosities (ca. 4×10^6 , 2×10^6 , and $1.5 \times 10^7 \text{ cP}$ at 25 °C, respectively) of these molten salts.

Combining, as before,¹ D_{PHYS} with the D_{APP} values measured for the Co(II/I) and Ru(III/II) couples in their bipyridine melts (**III** and **II**) (5.8×10^{-10} and $3.9 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, respectively) gives $k_{\text{EX}} = 2.6 \times 10^5$ and $1.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for these semisolid state electron transfer reactions, respectively. As mentioned above, D_{PHYS} for the Co complex **III** is determined from its Co(III/II) couple. This D_{PHYS} is used to represent D_{PHYS} of the Ru complex in the calculation of the Ru(III/II) k_{EX} value, since the metal complexes **II** and **III** are isostructural. These measurements demonstrate a capacity for mass transport and electron transfer dynamics measurements in the new melts, and also show that comparisons should be possible with dynamics for metal trisbipyridine^{1a,b,13} and porphyrin^{1c,14} melts in which the polyether chains are attached to the ligands of the redox moiety (i.e., ligand-tailed melts).

Voltammetry of melt **XII** (Figure 1c) shows two chemically reversible reductions, the second of which gives a smaller current and seems to also be electrochemically quasireversible (larger ΔE_{PEAK}). This unusual behavior has been observed for other species reduced in sequential, nominally one electron steps, in both dilute solution¹⁵ and melts;¹⁶ the complex combination of ionic and electronic migration and ion pairing influences apparently operating will be analyzed in a future publication.¹⁷

The aluminum quinolate molten salt [**XI**] exhibits two, incompletely reversible, one electron reduction steps separated by ca. 350 mV (Figure 1d), and a third step (not shown) more negative by 350 mV. A dilute acetonitrile solution also gives three equally spaced (by 350 mV) reduction steps. Aluminum quinolate is a promising constituent of organic light-emitting diodes,¹⁸ and further study of the physical, electron transfer, and luminescent properties of the melt and glassy versions of this material is underway.¹⁷

The ionic melts presented herein illustrate the wide variety of interesting organic, inorganic, and organometallic ions that we believe will be accessible¹⁹ in a molten salt form by reactions such as those in Scheme 1. The target ions need not be

(12) Measurements of material with $\approx 5\%$ excess ligand as determined by NMR. Crooker, J. C. Unpublished results, UNC-CH, 1998.

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(10) Excess tailed counterion determined from ¹H NMR by comparing integrations of the phenanthroline aromatic protons to that of the ethylene oxide protons (42:115 stoichiometric ratio).

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electroactive ones. Further variations in the polyether chain length and the nature of the counterion headgroup and indeed that of the oligomeric tail offer the flexibility for adjusting melt properties over an even wider range than shown here. Developing the relationships between melt structure and physical/electrochemical properties may ultimately permit synthesis of

(19) (a) Other than the derivatized counterion work presented here and in the works of Ito *et al.*,² other routes to organic molten salts appear to be limited to imidazolium^{19b} and butylpyridinium^{19c} based materials. For example: (b) Sun, I. W.; Hussey, C. L. *Inorg. Chem.* **1989**, 28, 2731. (c) Karpinski, Z. J.; Nanjundiah, C.; Osteryoung, R. A. *Inorg. Chem.* **1984**, 23, 3358.

semisolid, amorphous materials with a predictive handle on desired physical, electronic, and optical properties.

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Supporting Information Available: Synthetic schemes, elemental analyses, spectroscopic purity, and 200 MHz ¹H NMR spectral characterization for Scheme 1 melts not discussed above (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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