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Intermolecular Optical Electron Transfers in Polyether Hybrid Molten Salts of Mixed-Valent Ruthenium Complexes

Jason E. Ritchie and Royce W. Murray*

Kenan Laboratories of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27599

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This paper describes new, semisolid, room temperature, redox molten salts that have been synthesized[1] using our previously described tactic[1e] of combining methyl-terminated poly(ethylene glycol) ($MPEG_{MW=350}$) oligomers with electron donors and acceptors by direct attachment of the MPEG to a counterion of the redox ion. The new melts are listed in Table 1; Figure 1 shows an example structure. Further synthetic details and additional experiments will be presented in another report.[1ij]

We have here-to-fore studied[2] the electron-transfer chemistry of semisolid, MPEG-based redox melts using electrochemical measurements.[1] This paper turns to observations of optically driven electron transfer, or intervalent charge transfer (IVCT), in mixed-valent films of the redox melts, in which the enabling characteristic of the melts is the high redox site concentration. The melt $[Ru^{2.5+}(NH_3)_5py][MPEG_{350}SO_3]_{2.5}$ has $\sim$1M Ru sites, for example. Meyer[3b] and others[4] have speculated that a mixed-valent material of sufficiently high concentration should display IVCT bands. Indeed, the high local concentrations of ion pair systems lead to IVCT bands, as in the cases of $\{[Ru^{III}(NH_3)_5py]^{3+}, [Fe^{II}CN_6]^{4-}\}$[3ab], $\{[PQ]^{2+},[Fe^{II}CN_6]^{4-}\}$,[3c] $\{[Ru^{III}(NH_3)_5OH]^{3+}, [M^{II}(CN)_6]^{4-}\}$ (M = Ru, Fe),[3de] and concentrated, mixed-valent $K_{3.5}FeCN_6$ solutions.[5] In the undiluted melts described here, while all redox sites are, de facto, solvent separated ion pairs (where the “solvent” is MPEG), stronger ionic associations seem to also exist.

The new redox melts combine intrinsically high concentrations (i.e., no solubility limitations) with synthetic accessibility. These features open doors to a broadened range of electron transfer reactions, including intramolecular reactions between species of like charge. Additionally, it is possible to systematically vary parameters such as concentration and mixed valency proportions (varying the latter is not possible in binuclear mixed-valent systems). All of these directions are illustrated in this report.

Table 1 presents two groups of IVCT reactions. The first group, the top three entries, are mixed-valent redox melts designed as analogies to previously investigated[3c,6] dilute solution examples (see Table 1, footnotes *f*−*h*), aiming to establish general similarities or differences in behavior. As in the dilute solution results,[6] NIR bands attributable to an IVCT transition within the binuclear $Ru^{II}Ru^{III}$ complexes (the top one is the Creutz−Taube ion[6a]) appear only in mixed-valent melts (i.e., not in $Ru^{II}Ru^{II}$ or $Ru^{III}Ru^{III}$ melts). The IVCT band energies (E_{OP}), molar absorptivities (ϵ), and electronic coupling parameters (J) for the $Ru^{II}Ru^{III}$ melts are generally similar to the dilute solution results (see E_{OP} values in the footnotes for Table 1). Some differences are expected based on solvent effects.[4] Dis-similarities are found for the heteroredox viologen/ferrocyanide case, where the melt IVCT has a substantially lower energy relative to the dilute solution ion pair,[3c] and the C−T ion, where ϵ is smaller by more than 10-fold in the melt relative to dilute solution[6a] (signaling possibly a shift to Class II[7] behavior).

The second group of examples in Table 1 are mixed-valent $[Ru(NH_3)_5py]$ and $[Ru(NH_3)_6]$ complex melts, in which the IVCT electron transfers are intermolecular. The IVCT band energy is 8800 cm^{-1} for a (1:1) melt containing equal quantities of $[Ru^{2+}(NH_3)_5py]$ and $[Ru^{3+}(NH_3)_5py]$ complexes (i.e., $[Ru^{2.5+}(NH_3)_5py][MPEG_{350}SO_3]_{2.5}$); this energy is similar to that of a $[Ru^{2.5+}(NH_3)_6]$ melt (9100 cm^{-1}) but somewhat lower than that of the binuclear 4,4′-bpy redox melt (Table 1, 10100 cm^{-1}). Again, the IVCT band is seen only in mixed-valent melts (Figure 1).

In further measurements, the relative proportions of $[Ru^{2+}(NH_3)_5py]$ and $[Ru^{3+}(NH_3)_5py]$ complexes (Figure 1) and the concentration of a 1:1 mixture (by diluting with $MPEG_{750}$, Figure 2) were varied. These changes exert noticeable effects (Table 1) on the IVCT band, which exhibits an increase in ϵ and a shift to higher energy when the electron donor/acceptor ratio differs from 1:1 and when the overall concentration of a 1:1 melt becomes diluted. In all cases, the IVCT band shape seems to be non-Gaussian.

We preliminarily assign the energy changes to changes in the strong ion pairing interactions in the highly concentrated melts, between the two cationic complexes and their sulfonate counterions. It is known[4,8] in binuclear complexes, that unequal (asymmetrical) counterion interactions with the donor and acceptor states can lead to increases in E_{OP}. For the non-1:1 mixed-valent melt compositions, the loss of the initial relative symmetry in the melt’s network of ion pairing interactions in a 1:1 mixture of $[Ru^{2+}(NH_3)_5py]$ and $[Ru^{3+}(NH_3)_5py]$ is postulated to enhance counterion association with the latter ion, and to yield the enlarged E_{OP} transition energies seen in Figure 1.

Dilution of a 1:1 mixture of the $[Ru^{2+}(NH_3)_5py]$ and $[Ru^{3+}(NH_3)_5py]$ complexes moves the IVCT band to higher energy (Figure 2). The band vanishes at high dilution. Strikingly, the apparent molar absorptivity (ϵ) of the mixed-valent mixture increases with dilution, by nearly 4-fold; intuitively, dilution should depress ϵ. The result implies that dilution (Table 1) may in fact not be uniform. High local concentrations of adjacent Ru^{II} and Ru^{III} sites could persist by microphase segregation, and/or by formation of $\{[Ru^{2+}(NH_3)_5py], [MPEG_{350}SO_3]^{-}, [Ru^{3+}(NH_3)_5py]\}$ ion pair aggregates. The ion pairing symmetry must be degraded in the diluted melt, the relatively strengthened interaction

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[2] The inorganic complexes are prepared using literature procedures[3b] and isolated as hexafluorophosphate salts. Ru^{III} complexes are prepared by bubbling Cl_2/N_2 through an aqueous solution of the Ru^{II} complex; mixed valent forms are made by combining Ru^{II} and Ru^{III} complexes as the chloride salts. The resulting mixed valent aqueous solution is passed through an ion exchange column to replace chloride with hydroxide; this solution is titrated with aqueous MPEG-SO_3H to neutral pH. The water is removed by evaporation and the melt is stored in an inert atmosphere glovebox. Mixed-valent materials are handled under N_2 or Ar.

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Table 1. Summary of Optical Electron-Transfer Results

mixed-valent melt[a]	C_R[b] (M)	E_{OP} (cm^{-1})	ϵ[d] (cm^{-1} M^{-1})	fwhm (cm^{-1})	J[e] (cm^{-1})
$[Ru^{II}(NH_3)_5(pyz)Ru^{III}(NH_3)_5]$ $(MPEG_{350}SO_3)_5$	0.52	6300[f]	180	1800	130
$[Ru^{II}(NH_3)_5(4,4'\text{-bipy})Ru^{III}(NH_3)_5$ $(MPEG_{350}SO_3)_5$	0.49	10100[g]	250	2000	140
$[PQ^{2+}PEG_{600}]_2$ $[Fe^{II}(CN)_6]$	0.75	14000[h]	71	5300	210
$[Ru^{2.5+}(NH_3)_5py]$ $(MPEG_{350}SO_3)_{2.5}$	0.50	8800	210	2300	110
$[Ru^{2.33+}(NH_3)_5py]$ $(MPEG_{350}SO_3)_{2.33}$	0.35[i]	10100	300	1500	120
$[Ru^{2.67+}(NH_3)_5py]$ $(MPEG_{350}SO_3)_{2.67}$	0.32	9100	320	1800	120
$[Ru^{2.5+}(NH_3)_6]$ $(MPEG_{350}SO_3)_{2.5}$	0.50	9100	210	1800	100
$[Ru^{2.5+}(NH_3)_5py]$ $(MPEG_{350}SO_3)_{2.5}$ + 1:1 PEG_{750}	0.23	9500	410	1800	110
$[Ru^{2.5+}(NH_3)_5py]$ $(MPEG_{350}SO_3)_{2.5}$ + 1:2 PEG_{750}	0.16	10000	550	1600	110
$[Ru^{2.5+}(NH_3)_5py]$ $(MPEG_{350}SO_3)_{2.5}$ + 1:4 PEG_{750}	0.090	11400	750	1600	110
$[Ru^{2.5+}(NH_3)_5py]$ $(MPEG_{350}SO_3)_{2.5}$ + 1:6 PEG_{750}	0.065	11400	770	1400	98

[a] pyz = pyrazine; MPEGXXX is monomethyl poly(ethylene glycol) of indicated average MW; $MPEG_{350}SO_3^-$ is illustrated in Figure 1; $PQ^{2+}PEG_{600}$ is 4,4′-dimethyldipyridyl coupled to PEG_{600} as described before,[1h] py = pyridine. [b] Concentration of the reduced species. [c] E_{OP} is the energy at λ_{MAX} of the IVCT band. [d] Apparent molar absorptivity at λ_{MAX}, calculated using the concentration of the least abundant complex (i.e., that of $[Ru^{3+}(NH_3)_5py]$ in the $[Ru^{2.33+}(NH_3)_5py][MPEG_{350}SO_3]_{2.33}$ melt). [e] Electronic coupling term calculated as outlined by Hush and Meyer.[4,10] [f] E_{OP} = 6400 cm^{-1} and $\epsilon \approx 5000$ in dilute solution.[6a] [g] E_{OP} = 9700 cm^{-1} in dilute solution.[6b] [h] IVCT band for $PQ^{2+}/FeCN_6^{4-}$ in water occurs at 18900 cm^{-1}.[3c] ΔE^o = 0.533 V in melt vs 0.81 V in H_2O. [i] Concentration of the minority, oxidized species.

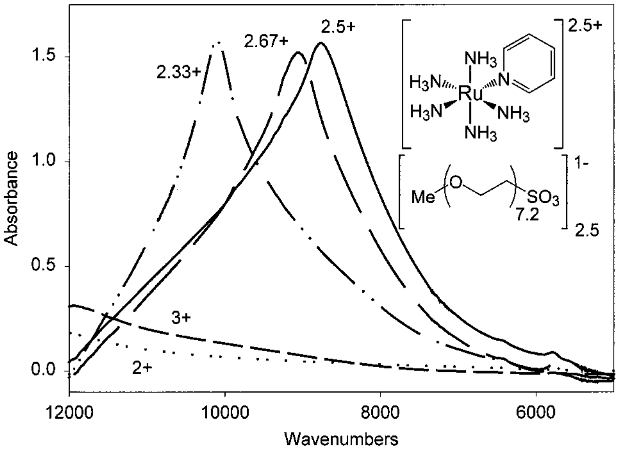

Figure 1. Optical absorbance spectra of indicated mixed-valent states of $[Ru^{n+}(NH_3)_5py][MPEG_{350}SO_3]_n$, from n = 2+ to 3+.

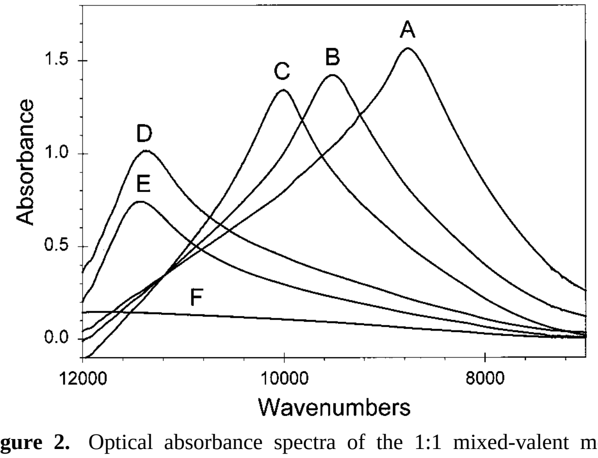

Figure 2. Optical absorbance spectra of the 1:1 mixed-valent melt $[Ru^{2.5+}(NH_3)_5py]$ $(MPEG_{350}SO_3)_{2.5}$: (A) neat melt, C_{RuII} = 0.50 M (Figure 1, 2.5+ case), and diluted w:w with PEG_{750}; (B) 1:1 dilution, 0.23 M; (C) 1:2 dilution, 0.16 M; (D) 1:4 dilution, 0.090 M; (E) 1:6 dilution, 0.065 M; and (F) 1:9 dilution.

with the $[Ru^{3+}(NH_3)_5py]$ complex producing an increase in E_{OP}. The change in the optical barrier is quite substantial; the shift from 8800 cm^{-1} to 11400 cm^{-1} corresponds to a 31 kJ/mol increase, relative to the neat 1:1 melt.

Marcus has recently outlined three different kinds of ion-pairing effects on thermal and optical electron transfers.[9] Redox polyether hybrids are semisolids with high viscosities (η ranges from 10^4 to 10^7 cP)[1] and low diffusivities,[1] and thus sluggish counterion nuclear motions. In that context, we suggest that the observed optical electron transfers can be viewed in the "Class I: Electron-Transfer First" category,[9] in which electron transfer precedes ionic migration. That is, in the melt's ionic network, the IVCT reaction causes the strong ionic interaction between the $[MPEG_{350}SO_3]^-$ counterion and $[Ru^{3+}(NH_3)_5py]$ to be replaced, following optical electron transfer, by a weaker, less stabilizing, interaction between that counterion and a now more distant $[Ru^{3+}(NH_3)_5py]$ complex. In this interpretation, the changes in free energy ΔG^o of the weakened interaction are reflected in Figures 1 and 2 as changes in E_{OP} brought about by alterations in the energetics of ionic association of the $[Ru(NH_3)_5py]$ complexes existing prior to the optical electron transfer.

The NIR bands in Figures 1 and 2 are clearly non-Gaussian in shape. Thermal measurements[1] show that the redox melts are amorphous. In the dis-ordered and near-solid materials, the non-Gaussian shapes may reflect a super position of IVCT bands arising from donor/acceptor pairs having an essentially frozen distribution of ion association geometries and electron transfer paths and distances. While the electronic coupling values (J) presented in Table 1 are probably affected by the non-Gaussian IVCT band shape, they are generally similar to other class II mixed-valent materials.[7]

Finally, the present work has relevance to understanding the large thermal electron-transfer energy barriers observed in our previous electrochemical studies of redox melts with related structures.[1b] The ion association analysis of the optical electron transfers implies commensurate ion association contributions to thermal energy barriers, which are being pursued[1j] in electrochemical studies of the present redox melts. This observation does not, however, rule out possible, concurrent solvent dynamics contributions to energy barriers in the melts, which have been identified in one case.[1d,g]

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