ELECTROGENERATED CHEMILUMINESCENCE.
ON THE ELECTROGENERATED CHEMILUMINESCENCE (ECL)
OF TETRAKIS(PYROPHOSPHITO)DIPLATINATE(II), $Pt_2(P_2O_5H_2)_4^{4-}$

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The electroreduction of $Pt_2(P_2O_5H_2)_4^{4-}$ (or A^{4-}) in MeCN (0.1 M Bu_4NBF_4) at a Pt electrode occurs at potentials where background reduction occurs and results in green light emission characteristic of $A^{4-}*$. A reaction mechanism involving electron transfer between A^{5-} and a reduction product of Bu_4N^+ is proposed. The emission that occurs at a mercury cathode shows a new band at ≈ 607 nm.

There have been many studies of the spectroscopic properties and electronic states of $Pt_2(P_2O_5H_2)_4^{4-}$ (abbreviated as A^{4-}) [1,2], following the isolation [3] and determination of the structure [4] of this species. Interest in this anion can be traced to the intense photoluminescence found in both solution and the solid state, as well as its interesting structure, which involves dimeric face-to-face square planes. The excited states involve metal–metal bond excitation characteristics [1,2] that are different from those of many luminescent metal complexes (e.g., the ruthenium (II) chelates) previously studied by ECL [6] that involve metal–ligand charge transfers. ECL generally involves the production of excited states via electron transfer reactions of electrogenerated species [7] and ECL studies can provide information about the energetics and mechanisms of these reactions.

In a recent communication [8], Volger and Kunkely described ECL of A^{4-} in an acetonitrile (MeCN) solution, which they ascribed to the electron transfer reaction between the reduced form (A^{5-}) and the oxidized form (A^{3-}) leading to A^{4-*}. In our work on this system, we have found that it is only necessary to reduce the tetra-*n*-butylammonium (TBA) salt :

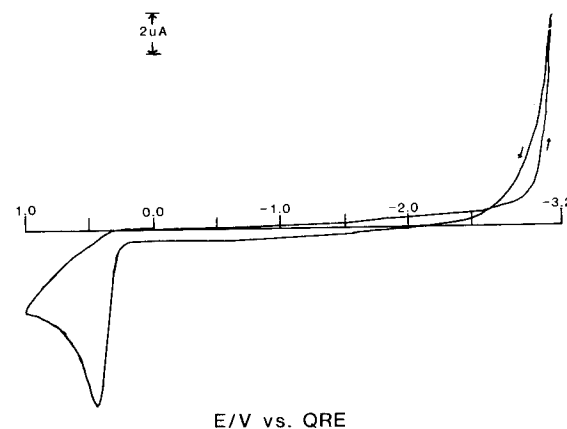* Contribution No. 7225 from the Arthur Amos Noyes Laboratory, California Institute of Technology.

E/V vs. QRE

Fig. 1. Cyclic voltammogram of 1 mM $(TBA)_4Pt_2(P_2O_5H_2)_4$ in 0.1 M $TBABF_4$/MeCN. Scan started at 0 V in the negative direction. Scan rate = 100 mV/s. Electrode area = 3.1 mm^2.

of A^{4-} in MeCN at potentials near the background limit of the solvent to generate ECL. As shown in fig. 1, there is no apparent peak for the reduction of A^{4-} before the background reduction of supporting electrolyte, $TBABF_4$. However, the reduction to A^{5-} is believed to occur at ≈-2.9 V versus a silver quasi-reference electrode (QRE) from the related ECL data. Oxidation of A^{4-} occurs in an irreversible wave with

an anodic peak potential at +0.45 V versus QRE.

Volger and Kunkely [8] observed ECL in MeCN under similar conditions by applying 4 V ac at 280 Hz. They concluded that the ECL was from electron transfer between A^{3-} and A^{5-} via the sequence

$$A^{4-} \rightarrow A^{3-} + e, \tag{1}$$

$$A^{4-} + e \rightarrow A^{5-}, \tag{2}$$

$$A^{3-} + A^{5-} \rightarrow A^{4-*} + A^{4-}. \tag{3}$$
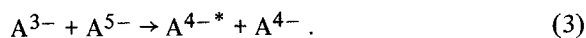
In our controlled potential experiments, an intense green emission was observed at a platinum disk electrode with potential pulses between +0.7 and −3.0 V, but also with pulses to −3.0 V from any potential between 0 and −2 V versus QRE. Thus emission is produced just on stepping to potentials where only reduction of the TBA salt ‡ of A^{4-} and supporting electrolyte occurs without anodic electrogeneration of an oxidant. The observed emission is essentially the same as the photoluminescence spectrum (fig. 2); the emission peak occurs in both cases at 512 nm and the apparent broader band in the ECL shown probably arises from the wider slit used in obtaining the ECL spectrum.

ECL arising only upon reduction has been observed

‡ $K_4Pt_2(P_2O_5H_2)_4$ was prepared by the method of Che et al. [2]. The TBA salt of A^{4-} was obtained by metathesis of $K_4Pt_2(P_2O_5H_2)_4$ and TBACl in H_2O. The lithium salt was obtained from $(TBA)_4Pt_2(P_2O_5H_2)_4$ and $Li\,CF_3SO_3$.
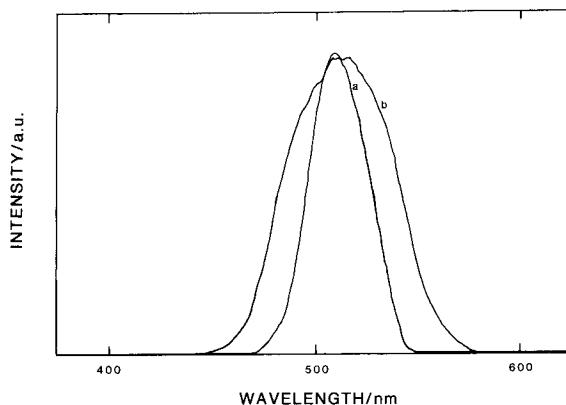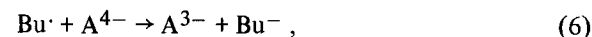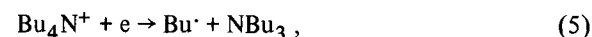

Fig. 2. (a) Photoluminescence spectrum (λ_{exc} = 370 nm); (b) ECL spectrum generated by applying +0.7 V to −3.0 V at 30 Hz at a Pt disk electrode. The solution was the same as in fig. 1.

previously with $Ru(bpy)_3^{2+}$ and reducible aromatic hydrocarbons upon simultaneous reduction of the compound and $S_2O_8^{2-}$ [9]. The mechanism of excited state formation in that work involved generation of an oxidant, SO_4^-, upon reduction of $S_2O_8^{2-}$, which subsequently underwent an electron transfer reaction with the reduced form of the luminescor. Thus, in explaining the emission upon reduction of A^{4-}, we must search for an oxidant which is sufficiently energetic to produce A^{4-*} upon reaction with A^{5-}.
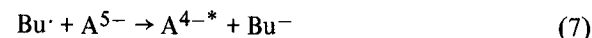
One possible source of this strong oxidant is from the reduction of the supporting electrolyte, because the electrochemical reduction of quaternary ammonium salts is thought to produce the corresponding alkyl or aryl radical (R·) and the amine [10]:

$$R_4N^+ + e \rightarrow R· + R_3N. \tag{4}$$

Since ECL is observed when a reductive background reactions occurs, we invoke participation of a Bu_4N^+ reduction product in the ECL processes and assume that the reduction potential of the butyl radical (Bu·) is sufficiently positive to generate the excited state of A^{4-}:

$$A^{4-} + e \rightarrow A^{5-}, \tag{2}$$

$$Bu_4N^+ + e \rightarrow Bu· + NBu_3, \tag{5}$$

$$Bu· + A^{4-} \rightarrow A^{3-} + Bu^-, \tag{6}$$

or

$$Bu· + A^{5-} \rightarrow A^{4-*} + Bu^- \tag{7}$$

If this reaction scheme is correct, the potential of the half-reaction of $Bu· + e \rightarrow Bu^-$ must be more positive than −0.4 V versus QRE, from the energetics of reaction (7) [7].

The scheme in reactions (5) through (7) requires a quaternary ammonium ion, so that replacement of the R_4N^+ with a different supporting electrolyte cation (provided that the required negative potential for reduction of A^{4-} can be attained) should lead to a loss of ECL. To try to test this possibility, the Li^+ salt of A^{4-} was prepared (see footnote ‡) and this was incorporated into a layer of protonated poly(4-vinyl-pyridine) on a Pt electrode surface [11]. This electrode was immersed in MeCN solution of 0.1 M $LiCF_3SO_3$. No light was detected for any potential step width (to −3.0 V versus QRE) or sequence, i.e. a bipolar step
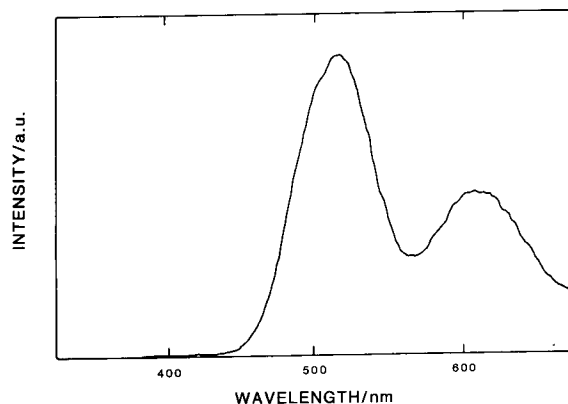
Fig. 3. ECL spectrum generated by applying −0.5 to −3.2 V at 30 Hz at mercury pool electrode. The solution was the same as in fig. 1.

sequence. When $TBABF_4$ was added to this solution, the distinctive green ECL emission appeared upon reduction. No ECL could be generated for an MeCN solution of Li_4A with $LiCF_3SO_3$ as supporting electrolyte. These results cannot be considered strong evidence for the proposed mechanism, however, since the reduction of Li^+ at a Pt electrode in aprotic solvents is known to produce passivating layers under some conditions [12].

Some passivation of the Pt electrode upon reduction of A^{4-} also occurs with $TBABF_4$. Thus only two or three emission pulses were seen when the potential was stepped between −0.5 and −3.0 V. Continuous light emission could be attained (or a non-emitting electrode reactivated) by bringing the electrode to sufficiently positive potentials (>0.7 V) [13]. The ECL spectrum in fig. 2 was obtained with continuous pulsing between 0.7 and −3.0 V for this reason.

In an attempt to overcome the problems of Pt electrode passivation, we tried a mercury pool electrode as a cathode. Continuous ECL emission was observed at Hg for at least one hour under pulsing between −0.5 and −3.2 V; however, there was a remarkable change in the color of the emission from green to orange. The ECL spectrum with a Hg cathode (fig. 3) shows a new peak at 607 nm in addition to the original one at 512 nm. The nature of the new emissive species formed at Hg is not known.

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