

ELECTROGENERATED CHEMILUMINESCENCE.  
XVI. ECL OF PALLADIUM AND PLATINUM  
 $\alpha, \beta, \gamma, \delta$ -TETRAPHENYLPORPHYRIN COMPLEXES

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The electrochemistry of the Pt(II) and Pd(II) complexes with  $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin (TPP) in dichloromethane solutions containing 0.1 M tetra-*n*-butylammonium perchlorate is characterized by one-electron transfers to form both oxidized and reduced species. The electron transfer reactions between these electrogenerated species lead to the emission of light. The radiating species has been identified as the lowest triplet state of the Pt(TPP) or Pd(TPP) by comparison with results of previous spectroscopic studies.

In recent publications [1] we reported electro-generated chemiluminescence (ECL) of  $\text{Ru}(\text{bipy})_3^{2+}$  (where bipy is 2,2'-bipyridine) arising from the reaction of the electrogenerated +3 species with either the +1, 0 or -1 species to yield the emitting excited triplet state. We wish to report here findings of similar electrochemical and ECL behavior for the metalloporphyrins M(TPP) where M is Pt or Pd and TPP is  $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin. These metalloporphyrins are uncharged complexes of Pd(II) and Pt(II) and the free base porphine formed with the loss of two protons. The cyclic voltammetric behavior of Pd(TPP) and Pt(TPP) in methylene chloride solution containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte, is shown in fig. 1; peak potentials for the different waves, as well as for TPP itself [2] are given in table 1. The peak current values at these scan rates and concentrations if compared with those of known one-electron processes demonstrates that processes I-IV and VII correspond to one-electron transfers.

When the potential of a platinum electrode, immersed in a  $\text{CH}_2\text{Cl}_2$  solution of Pd(TPP) was cycled at a frequency of 0.5 Hz between  $E_{\text{pa}}$  (II) (production of the +1 species) and  $E_{\text{pc}}$  (IV) (production of the -1 species), low intensity ECL was generated which corresponds very closely to the luminescence spectrum

of this solution at liquid nitrogen temperatures (fig. 2). The intensity of the ECL emission upon continuous cycling at 0.5 Hz was quite steady with the light spikes alternating between a larger one during a reduction half-cycle and a smaller one during the oxidation half-cycle. Low level ECL which quickly dies away is observed when the electrode is stepped between  $E_{\text{pa}}$  (I) and  $E_{\text{pc}}$  (IV). Low level ECL emission was also obtained for Pt(TPP) when the potential of the platinum electrode was cycled at 0.5 Hz between  $E_{\text{pa}}$  (I) or (II) and  $E_{\text{pc}}$  (IV) through (VII); ECL was not observed when the anodic limit of the square wave was  $E_{\text{pa}}$  (III). The Pt(TPP) ECL extended from about 625 to 725 nm with the maximum located at 656 nm. For Pt(TPP) the larger light spikes originate from the reduction half-cycle.

Previous spectroscopic studies of the Pd(TPP) and Pt(TPP) by Eastwood and Gouterman [3] demonstrated that the observed luminescence at 688 nm for Pd(TPP) and 654 nm for Pt(TPP) can be assigned to emission from the triplet state of these species. The close agreement of the ECL emission to that obtained upon photoexcitation suggests that the major emission in ECL is also from the triplet state. For Pd(TPP) the energy levels of the lowest excited singlet state and lowest triplet state are 2.25 and 1.80 eV, respectively. The free energy available from the reaction of the +1

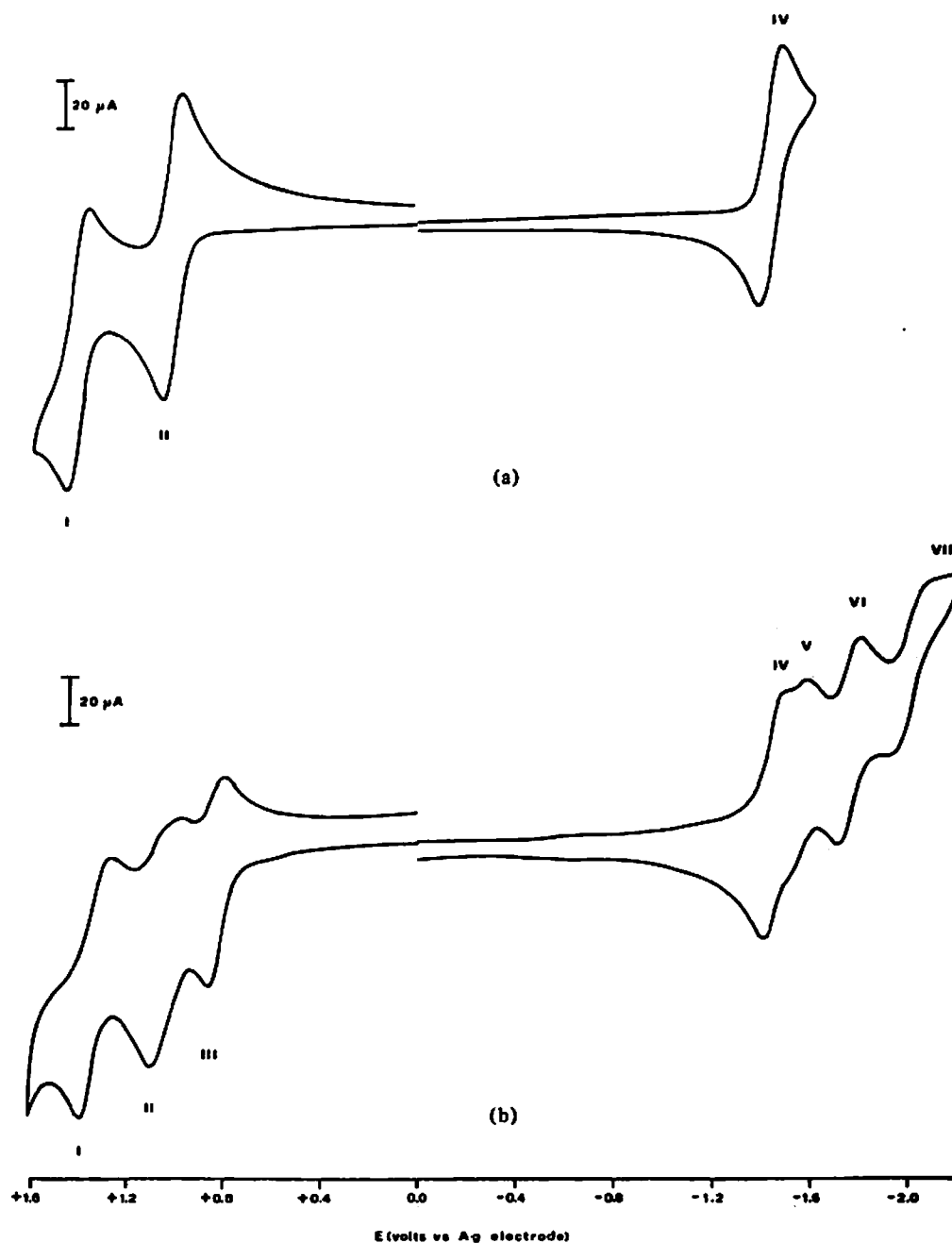


Fig. 1. Cyclic voltammogram of (a) 1.7 mM Pd(TPP), (b) 2 mM Pt(TPP) in methylene chloride at a Pt electrode with 0.1 M TBAP supporting electrolyte. Scan rate = 200 mV/sec.

and  $-1$  species, produced by cycling between waves II and IV is 2.49 eV and so is sufficient to produce either excited state in the electron transfer reaction

$\text{Pd(TPP)}^+ + \text{Pd(TPP)}^- \rightarrow \text{Pd(TPP)}^* + \text{Pd(TPP)}$ .  
 Emission from the triplet state is also observed in the ECL of  $\text{Ru(bipy)}_3^{2+}$  [2]. The ECL emission observed

Table I  
Electrochemical data of Pt(II) TPP and Pd(II) TPP complexes a)

		Oxidation waves			Reduction waves			
		I	II	III	IV	V	VI	VII
Pt(TPP)	$E_{pc}$	+1.27	+0.97	+0.79	-1.50	-1.60	-1.82	d)
	$E_{pa}$	+1.39	+1.10	+0.86	-1.42	c)	-1.72	-1.92
	$n^b$	1	1	1	1	e)	f)	1
Pd(TPP)	$E_{pc}$	+1.36	+0.97		-1.50			
	$E_{pa}$	+1.45	+1.05		-1.40			
	$n$	1	1		1			
TPP [3]	$E_{pc}$	+1.24	+0.98		-1.26	-1.66		
	$E_{pa}$	+1.30	+1.05		-1.19	-1.56		

a) The solutions contained either 2.0 mM Pt(TPP) or 1.7 mM Pd(TPP) in  $\text{CH}_2\text{Cl}_2$ -0.1 M TBAP. Potentials are in volt versus Ag wire reference electrode;  $E_{pc}$  and  $E_{pa}$  are the cathodic and anodic peak potentials.

b) Number of electrons involved in electron transfer step.

c) The  $E_{pa}$  for this process cannot be determined, as  $E_{pa}$  (V) is close to  $E_{pa}$  (IV).

d)  $E_{pc}$  cannot be determined accurately because of the proximity of the solvent background.

e) Number of electrons involved in process V cannot be determined due to mixing with process IV.

f) The peak current is somewhat smaller than for a one-electron event.

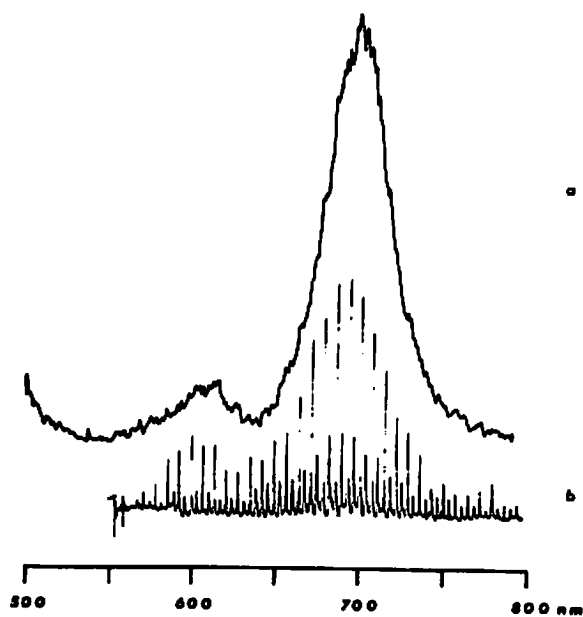


Fig. 2. Luminescence and ECL spectra of 1 mM Pd(TPP) solution in methylene chloride-0.1 M TBAP: (a) luminescence for frozen sample at liquid nitrogen temperature with excitation at 472 nm; (b) ECL emission at Pt electrode pulsing between waves II and IV. (Spectra taken with Aminco-Bowman spectrophotofluorometer and are uncorrected for detector sensitivity.)

for the TPP complexes, however, is much less intense than that of  $\text{Ru}(\text{bipy})_3^{2+}$ , although these complexes show quite high luminescence quantum efficiencies [3]. The ECL intensity may be low because of initial formation of the singlet excited state on electron transfer with inefficient crossing to the emitting triplet as compared with radiationless quenching to the ground state.

Another possible factor in the relatively low ECL intensity is quenching of the triplet state by the ground state species via formation of a triplet excimer. Such species have been found for similar molecules (e.g., Pt Etio) [4], as well as aromatic hydrocarbons [5]. This type of quenching would be especially important in ECL where the triplet and ground state species are formed within the same solvent cage or in close proximity. A similar effect may be contributing to the low efficiency of the ECL of TPP itself [2]. The existence of dimeric species of the radical ions is also possible (e.g., dimers of  $\text{ZnP}^+$  have recently been observed [6] and low ECL efficiencies have been attributed to production of species such as  $\text{R}_2^+$  [7]. The  $\text{Ru}(\text{bipy})_3^{2+}$  would probably have much less of a tendency to form dimeric species in either its excited or oxidized states.

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