

# Electrogenerated Chemiluminescence. 70. The Application of ECL to Determine Electrode Potentials of Tri-*n*-propylamine, Its Radical Cation, and Intermediate Free Radical in MeCN/Benzene Solutions<sup>†</sup>

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We report here electrogenerated chemiluminescence (ECL) observed upon oxidation of aromatic hydrocarbons with different potentials for oxidation to the radical cations ( $D^{+\bullet}$ ) and tri-*n*-propylamine (TPrA) in MeCN/benzene solutions. In this system, with TPrA as a coreactant, ECL is generated by reaction of  $D^{+\bullet}$  with the free radical intermediate produced upon oxidation of TPrA. ECL was observed from three out of the eight compounds studied. On the basis of the energetic criterion for ECL, the potential for oxidation of the intermediate free radical,  $\text{Pr}_2\text{N}(\text{CH}^\bullet)\text{Et}$ , was found to be about  $-1.7$  V vs SCE. By studying the fluorescence quenching of several polycyclic aromatic hydrocarbons (PAHs) by TPrA, the standard potential for oxidation of TPrA to  $\text{TPrA}^{+\bullet}$  was estimated as  $0.9$  V vs SCE.

## Introduction

We show in this paper how ECL measurements can be used to gain thermodynamic information about unstable intermediates, like radical cations and free radicals in solution. An important advance in ECL was the discovery of reaction schemes for generating light in aqueous media by means of coreactants such as  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{S}_2\text{O}_8^{2-}$ , and tri-*n*-propylamine (TPrA).<sup>1,2</sup> Thus, even with a rather small potential window available in water, ECL reactions could be observed based on the ability to generate energetic precursors without potential cycling and at less extreme potentials upon bond cleavage of a coreactant. Among most currently used ECL coreactants, TPrA appears to be the most efficient in generating light. However, most studies with TPrA were conducted in aqueous media and we thought it was of interest to understand the behavior of TPrA in the presence of ECL emitting PAHs in nonaqueous solvents to see if ECL production is possible. Through such studies, the thermodynamic potentials for TPrA oxidation to its cation radical, as well as that for oxidation of the highly reducing free radical intermediate, can be estimated.

The classic form of ECL involves electron transfer between electrochemically generated radical ions resulting in an excited species that emits light. The simplest ECL process is the radical ion annihilation reaction sequence represented as:

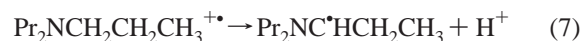
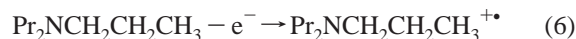


where A and D are frequently PAHs.<sup>3</sup> Many ECL reactions of this type have been investigated and their mechanisms are well

understood. However, these kinds of reactions generally involve the use of anhydrous and deoxygenated nonaqueous solvents to accommodate the large potential range required to generate these energetic precursors,  $A^{-\bullet}$  and  $D^{+\bullet}$ , to produce an excited state in the visible region (1.8–3.0 eV).

In recent years, systems using TPrA as a coreactant have been utilized in highly sensitive and selective analytical methods for immunoassay and DNA determinations and several investigations have focused on understanding the mechanisms leading to light generation in these systems. Three different mechanisms for the generation of ECL have been proposed and are shown in reaction sequences 1–3.<sup>4–7</sup>

reaction sequence 1



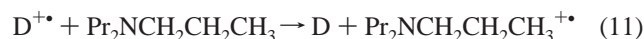
Reactions 5–7 are then followed by

reaction sequence 2



The same occurs for reaction sequence 3 as that in reaction sequence 1, except that oxidation of TPrA occurs by reaction with  $D^{+\bullet}$  rather than at the electrode:

reaction sequence 3



followed by reactions 7 and 8. Note that in the discussion that follows, the cation radical of TPrA ( $\text{Pr}_2\text{NCH}_2\text{CH}_2\text{CH}_3^{+\bullet}$ ) will

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be indicated as  $\text{TPrA}^{+\bullet}$  and the intermediate free radical ( $\text{Pr}_2\text{-NC}^{\bullet}\text{HCH}_2\text{CH}_3$ ) as  $\text{TPrA}^{\bullet}$ .

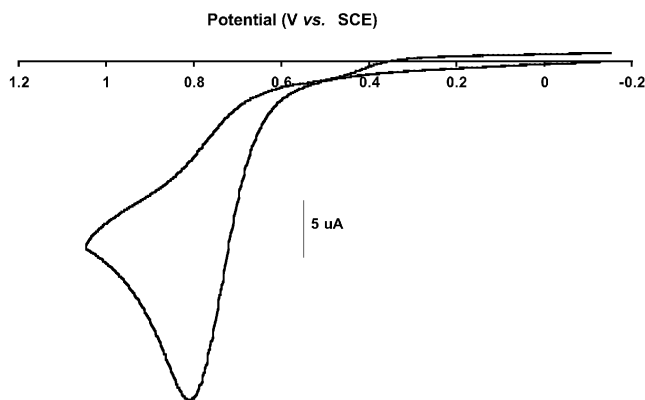
The mechanisms shown in reaction sequences 1 through 3 have been proposed for systems such as the  $\text{TPrA-Ru}(\text{bpy})_3^{2+}$  ( $\text{bpy} = 2,2'$ -bipyridine) system, but may not apply to all PAH-TPrA systems in this study. Recent studies from this laboratory have also found a new mechanism for this reaction where  $\text{TPrA}^{+\bullet}$  can react with  $\text{D}^{\bullet}$  to produce  $\text{D}^*$ . However, this route is only important in systems involving very low concentrations of D and a high concentration of the coreactant, so that its contribution is not as significant as the other three mechanisms in the current study where a high concentration of D is used.<sup>6</sup>

As observed, all three mechanisms involve the generation of  $\text{TPrA}^{\bullet}$  and  $\text{TPrA}^{+\bullet}$ , the two key intermediates in ECL generation. Although studies of alkylamine oxidation have been published,<sup>8,9</sup> it was not possible to extract thermodynamic potentials for oxidation of amines directly from cyclic voltammetric analysis or other electrochemical methods because of the electrochemical irreversibility of amine oxidations. Like any irreversible cyclic voltammetric peak, the observed oxidation peak potential of TPrA shifts with the scan rate and concentration so that peak potentials obtained from voltammetry could not be viewed as the standard potential for oxidation of TPrA to  $\text{TPrA}^{+\bullet}$ . A recent study estimated the standard potentials for oxidation of TPrA and triethylamine (TEA) using Marcus theory to correlate the experimental rate constants of electron transfer to the driving force of the reaction. In this study the potential for TPrA oxidation was estimated to be about 0.88 V (vs SCE) for aqueous solutions.<sup>5</sup> However, the thermodynamic potential of TPrA in a nonaqueous medium has not been determined. As shown in the mechanistic schemes,  $\text{TPrA}^{\bullet}$  is a major participant in the generation of ECL, but the potential for oxidation of this highly reducing radical has not been determined. In this paper, we have undertaken an electrochemical and photochemical study of the reactions of TPrA and several ECL emitting PAHs capable of radical ion annihilation. Our aim is at finding new ways to generate ECL in nonaqueous solvents in addition to determining the standard potentials of  $\text{TPrA}^{+\bullet}$  and  $\text{TPrA}^{\bullet}$ .

## Experimental Section

Rubrene, naphthol[2,3-*a*]pyrene, perylene, 1,3,6,8-tetraphenylpyrene, 9,10-diphenylanthracene (DPA), and pyrene were obtained from Aldrich (St. Louis, MO), Chem Service (West Chester, PA), or Kodak (Rochester, NY). Chemical dimers of 7,12-diphenylbenzo[*k*]fluoranthene and 9,10-dimethyl-7,12-diphenylbenzo[*k*]fluoranthene were available from a previous study.<sup>10</sup> Tri-*n*-propylamine (TPrA) was obtained from Aldrich and used without further purification. Tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was recrystallized twice and dried in a vacuum oven at 100 °C prior to transferring directly into an inert atmosphere drybox (Vacuum Atmospheres Corp., Hawthorne, CA). Anhydrous benzene (Aldrich, ACS spectro-photometric grade) and MeCN (Aldrich, ACS spectro-photometric grade) were also used as received. All solutions were prepared in a drybox with fresh anhydrous solvents and sealed in airtight vessels for measurements completed outside the drybox.

UV-visible spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer. Fluorescence spectra were recorded on a Fluorolog-3 spectrofluorimeter (ISA-Jobin Yvon Hariba, Edison, NJ) using a slit width of 0.5 nm and a resolution of 1 nm. Time-resolved fluorescence decays were obtained by time-correlated single photon counting (TCSPC) exciting at 380 to 420-nm with vertically polarized excitation pulses ( $\Delta t \sim 200$



**Figure 1.** Cyclic voltammogram of a 2.5 mM solution of TPrA in MeCN at a platinum electrode (0.1 M TBAPF<sub>6</sub>; scan rate 200 mV/s).

fs, repetition rate 3.8 MHz) from a modelocked Ti:sapphire laser system (Coherent Mira 900, Coherent Pulse Picker Model 9200, Inrad SHG/THG model 5-050). Detection electronics included a microchannel plate detector (Hamamatsu R3809U-50), constant fraction discriminators (Tennelec TC454), time-to-amplitude converter (Tennelec TC864), and multichannel analyzer (Ortec TRUMP MCB). The emission decay curves were evaluated by an iterative nonlinear least-squares fitting procedure. All absorbance and fluorescence spectra of the compounds were obtained with a 20  $\mu\text{M}$  solution in MeCN or MeCN:benzene mixed solvent. The ratio of benzene and MeCN used were not exactly the same for each compound to accommodate solubility. In all steady-state fluorescence quenching experiments, the TPrA concentrations used were 21, 42, 60, and 80 mM.

Cyclic voltammograms were recorded on a CH Instruments Electrochemical Work Station (Austin, TX). The working electrode in all cases consisted of an inlaid platinum disk (2.0 mm diameter) that was polished on a felt pad with 0.05  $\mu\text{m}$  alumina (Buehler, Ltd, Lake Bluff, IL) and sonicated in water and absolute ethanol for 3 min and then dried in a oven at 100 °C before transferring into the inert atmosphere drybox. A platinum wire served as a counter electrode and a silver wire was utilized as a quasi reference electrode. The concentrations used to obtain each voltammogram are given in the corresponding figure caption. All potentials were calibrated against an aqueous SCE by the addition of ferrocene as an internal standard taking  $E^\circ(\text{Fc}/\text{Fc}^+) = 0.424\text{V vs SCE}$ .<sup>9</sup>

All ECL measurements were performed as previously reported.<sup>11</sup> Measurements were obtained with solution concentrations of 1 mM of the compound and 100 mM of TPrA in 0.1 M TBAPF<sub>6</sub> in the respective solvent. To generate the reaction, the working electrode was pulsed between 0 V and the first oxidation potential of each compound with a pulse width of 0.1 s. The resulting emission spectra were obtained with a charged coupled device (CCD) camera (Photometrics CH260, Photometrics-Roper Scientific, Tuscon, AZ) that was cooled to -100 °C. Integration times were 2 min. The CCD camera and grating system were calibrated with a mercury lamp before each measurement.

## Results and Discussion

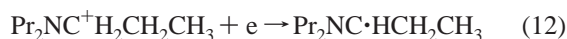
**Electrochemistry and ECL with TPrA in MeCN and MeCN:Benzen.** A cyclic voltammogram of TPrA obtained in MeCN at a platinum electrode is shown in Figure 1. Upon scanning the potential positive, an irreversible oxidation wave was observed at a peak potential of +0.81 V vs SCE at a scan rate of 200 mV/s (eq 6). This wave corresponds to the formation

**TABLE 1: Photophysical, Electrochemical, and ECL Data of the Various Systems in Relation to the Oxidation Potential of the TPr Radical**

chemical	V vs SCE		$E_S$ (eV)	ECL <sub>w/TPrA</sub>	$E_{TPrA}$ (calculated)	solvent (PhH:MeCN)
	$E_{1/2,(R/R^+)}$	$E_{1/2,(R/R^-)}$				
7,12-diphenylbenzo[k]fluoranthene (dimer)	0.95 V	-1.22 V	2.06 eV	650 nm	-1.21 V	9:1
9,10-dimethyl-7,12-diphenylbenzo[k]fluoranthene (dimer)	0.94 V	-1.26 V	2.07 eV	650 nm	-1.23 V	9:1
rubrene	0.82 V	-1.56 V	2.32 eV	563 nm	-1.60 V	1:1
naphthol[2,3- <i>a</i> ]pyrene	0.94 V	-1.70 V	2.67 eV	not observed	-1.83 V	2:1
DPA	1.29 V	-1.96 V	3.08 eV	not observed	-1.89 V	MeCN
perylene	1.02 V	-1.77 V	2.82 eV	not observed	-1.90 V	1:1
1,3,6,8 tetraphenylpyrene	1.11 V	-1.81 V	3.10 eV	not observed	-2.09 V	4:1
Pyrene	1.28 V ( $E_p$ )	-2.16 V	3.51 eV	not observed	-2.33 V	1:1

of the  $TPrA^{+\bullet}$  which then rapidly deprotonates to generate  $TPrA^\bullet$ , a highly reducing species that is involved in reactions forming the excited state (eq 8). No reverse oxidation wave was found for scan rates up to 200 V/s, demonstrating instability of  $TPrA^{+\bullet}$  due to a fast deprotonation process (eq 7). Since a reversible  $E_{1/2}$  for the one-electron step could not be obtained, the peak potential only serves as an indication of the location of the oxidation wave of TPrA in this medium. An irreversible following reaction causes an oxidation wave to shift to less positive potentials.<sup>12</sup>

To estimate the potential for the half reaction



we apply the ECL energetic criterion equation<sup>13</sup>

$$E^\circ(D^+/D) - E^\circ(A/A^-) - 0.1 \geq E_S(\text{eV}) \quad (13)$$

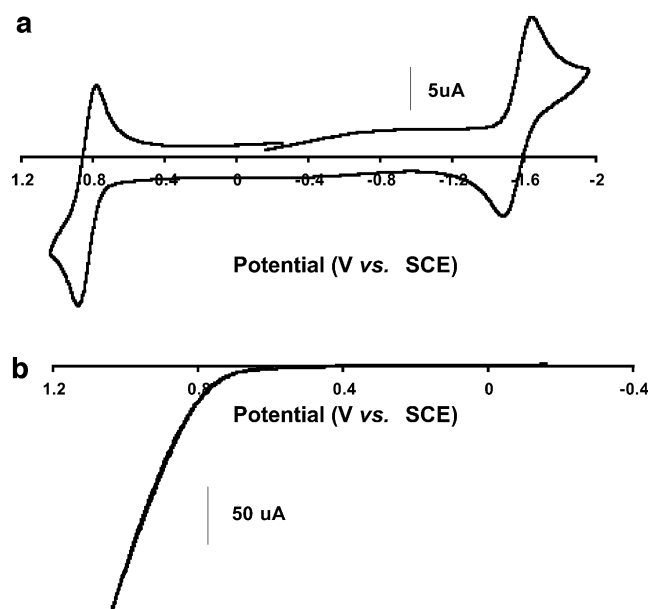
which is simply based on the free energy of the annihilation reaction, eq 3, with an approximate correction for entropy, being larger than the singlet state energy of the emitter (e.g.,  $D^*$ ). Thus, by choosing a series of PAHs with different  $E^\circ$  and  $E_S$  values and noting which produce ECL emission with TPrA, the potential of reaction 12 can be estimated. Eight PAHs that produce ECL via the radical ion annihilation route were chosen for this study based on their redox potentials and their singlet state energies. These are listed in Table 1. The compounds chosen range from high energy blue emitters, such as pyrene and DPA, to low energy red emitters. All of the PAHs, except pyrene and naphthol[2,3-*a*]pyrene, demonstrated electrochemical reversibility for both oxidation and reduction in their respective solvents. A quasi-reversible oxidation wave was observed for pyrene even at scan rates up to 50 V/s. An adsorption peak was observed in the reverse scan of the oxidation of naphthol[2,3-*a*]pyrene in the solvent system used (2:1 MeCN:benzene). Since the PAHs used in this study are known ECL emitters and have been widely studied,<sup>3</sup> only the cyclic voltammogram (CV) of rubrene is shown here (Figure 2a). CVs of the other species are given in the Supporting Information. Details of the electrochemical, fluorescence, and ECL measurements are summarized in Table 1.

The electrochemical behavior of all of the PAHs in the presence of TPrA was generally the same. The peak potentials of the compounds did not change upon addition of TPrA. However, the oxidation peak of most of the PAHs was not observed because of the much larger current from the oxidation of TPrA at a concentration 100 times higher than that of the PAH. As observed in Figure 2b, in the presence of TPrA, the defined oxidation peak of rubrene was replaced by the TPrA oxidation current.

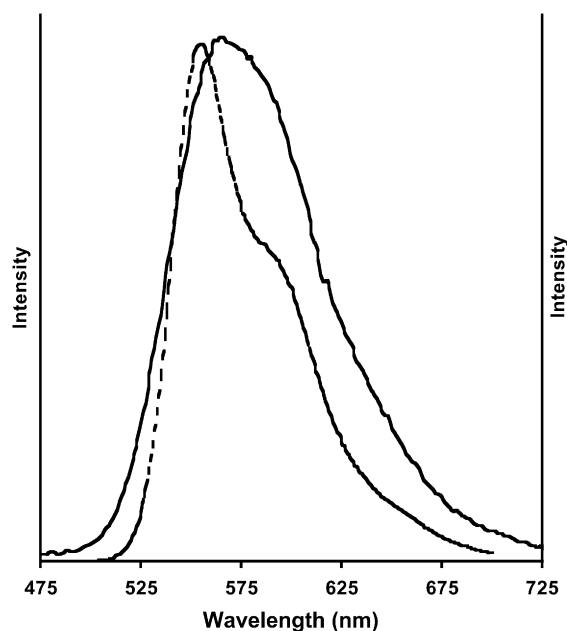
To generate ECL, excess TPrA was added to each compound and pulsed between 0.0 V and the first oxidation potential of the compound. Among the eight PAHs, ECL was observed from

only three compounds, 7,12-diphenylbenzo[k]fluoranthene and 9,10-dimethyl-7,12-diphenylbenzo[k]fluoranthene and rubrene. Figure 3 shows the ECL spectrum of 1 mM rubrene in the presence of 100 mM TPrA and the fluorescence spectrum of 20  $\mu$ M rubrene in the same solvent. When compared to the fluorescence spectra, the ECL spectrum appears slightly broader in shape and is shifted slightly to lower energy. This is probably due to an inner filter effect as a result of the high concentrations of rubrene needed to obtain measurable ECL in addition to the difference in resolution between the two instruments where the spectra were collected. Overall, the ECL signals observed for the three compounds were quite weak when compared to the signals obtained via radical ion annihilation under the same conditions. However, when pulsed at a potential slightly more positive than the first oxidation peak potential of the compound, a larger ECL signal was observed. For some PAHs, an extra 0.3 V was applied to maximize the amount of light collected. To prevent possible interference from oxidation of the solvent in situations where the anodic peak potential of the compound was fairly close to the oxidation of the solvent, this was not done. For those PAHs where no ECL was observed when pulsed between 0.0 V and their first anodic peak potential, no ECL emission was observed even when higher potentials were applied.

As shown in Table 1, the three PAHs producing ECL with TPrA as the coreactant are of lower singlet energies, ranging from 2.06 to 2.32 eV. This clearly indicates that  $TPrA^\bullet$  does not have a sufficiently negative potential to generate the excited



**Figure 2.** Cyclic voltammograms of a 1 mM solution of rubrene in MeCN/benzene at a platinum electrode (0.1 M TBAPF<sub>6</sub>; scan rate 200 mV/s) (a) without TPrA, (b) with 100 mM TPrA.



**Figure 3.** ECL spectra of 1 mM rubrene and 100 mM TPrA in 0.1 M TBAPF<sub>6</sub> in MeCN/benzene with pulsing (0.1 s) between 0.0 V and +1.44 V (vs SCE).

states that lead to ECL emission for the higher energy compounds. As observed, TPrA<sup>•</sup> is a good reductant, but it is not as good as the perylene or DPA anion radicals. The thermodynamic potential of the TPrA<sup>•</sup> ( $E^{\circ}_{\text{TPrA}^{\bullet}}$ ), eq 12, was determined from an equation derived from eq 13:

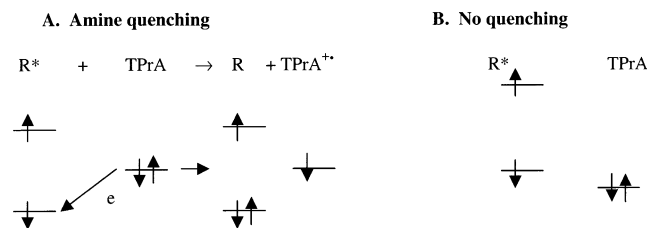
$$E^{\circ}_{\text{TPrA}^{\bullet}} = -(E_s - E_{1/2,(\text{R/R}^+)}) + 0.1 \text{ V} \quad (14)$$

where  $E_s$  is the singlet excited state of the compound, and  $E_{1/2,(\text{R/R}^+)}$  is the half wave potential of the first oxidation of the compound. Values calculated from each set of data are shown in Table 1. Since ECL was observed in the rubrene–TPrA system, the potential of TPrA<sup>•</sup> is sufficient to produce the singlet state of the rubrene (2.32 eV), yet not as reducing as the radical anion of naphthol[2,3-*a*]pyrene (−1.70 V). Thus, the potential for TPrA<sup>•</sup> oxidation should lie between the value for rubrene (−1.60 V) and naphthol[2,3-*a*]pyrene (−1.83 V), so  $E^{\circ}_{\text{TPrA}^{\bullet}} = -1.7 \pm 0.1$  V vs SCE. Note that the value obtained for the CO<sub>2</sub><sup>•−</sup>, generated as an intermediate upon oxidation of oxalate, is about −2.14 V vs SCE in aqueous solvents.<sup>14</sup> Because CO<sub>2</sub><sup>•−</sup> is more reducing than TPrA<sup>•</sup>, it can generate the singlet excited state of DPA in nonaqueous media, like MeCN, while TPrA<sup>•</sup> cannot.

We note that an additional route to ECL emission is the T-route, where triplet states of the PAH are generated in the electron-transfer reaction followed by triplet–triplet annihilation (TTA) to produce the emitting singlet excited state.<sup>13</sup> Clearly, TPrA<sup>•</sup> is sufficiently energetic to generate the triplets of these PAHs. For example,  $E_T$  for DPA is 1.8 eV.<sup>13</sup> The absence of emission by this route must then be ascribed to the rather low overall efficiency of this coreactant pathway because of instability of the intermediates, the second order nature of TTA, and the quenching of triplets by radical ions so that ECL emission via the T-route is simply too low to detect.

We can compare our estimated  $E^{\circ}_{\text{TPrA}^{\bullet}}$  with previously measured values for the related triethylamine (TEA). A measurement employing modulated photolysis to generate the free radical and voltammetry at a gold electrode to measure its potential in MeCN containing 0.1 M tetra-*n*-butylammonium perchlorate, reported a value of −1.12 V vs SCE,<sup>15</sup> significantly less negative than our value. An earlier study, based on

## SCHEME 1



quenching of triplet benzophenone by TEA in 1:9 H<sub>2</sub>O:MeCN containing 0.02 M NaOH, reported a value of −1.70 V vs SCE,<sup>16</sup> which given the expected similarity between the free radicals derived from TPrA and TEA, is in good agreement with our estimate.

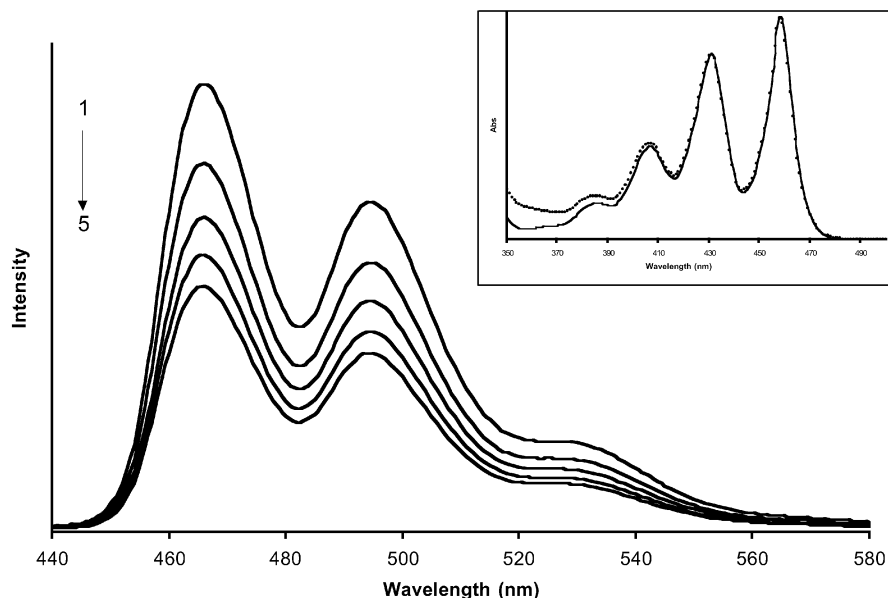
**Fluorescence Quenching Studies of TPrA.** The potential for the oxidation of TPrA to TPrA<sup>•+</sup> in benzene:MeCN was obtained by fluorescence measurements of the electron-transfer quenching of several PAHs. Fluorescence quenching via the formation of exciplexes or solvated radical ion pairs between aromatic hydrocarbons (acceptors) and aliphatic amines (donors) has been widely studied.<sup>17–21</sup> In general, the amine's quenching ability is inversely proportional to its ionization potential. As shown in the simplified schematic below, the potential to oxidize the PAH must be more positive than that of TPrA for quenching to occur. The first step involves the electron transfer from TPrA to the excited PAH to form TPrA<sup>•+</sup> while the following step involves the back electron transfer from the PAH radical anion to TPrA<sup>•+</sup> to regenerate the ground state.

Similarly, if the potential of the quencher is not sufficient to electron transfer to the excited state, no fluorescence quenching is observed. (Scheme 1B)

Different amounts of TPrA, in excess to the PAH, was successively added to each solution of the same eight PAHs used in the above ECL studies. From the steady state fluorescence quenching measurements, the fluorescence of naphthol[2,3-*a*]pyrene, perylene, DPA, 1,3,6,8 tetraphenylpyrene, and pyrene in MeCN or MeCN/benzene solutions were effectively quenched by TPrA. The compounds in which no significant quenching was observed within statistical error were 7,12-diphenylbenzo[*k*]fluoranthene and 9,10-dimethyl-7,12-diphenylbenzo[*k*]fluoranthene, and rubrene. Among the five PAHs quenched by TPrA, no obvious changes were observed in either the fluorescence or absorption spectra in the presence of TPrA. This is clearly shown in Figure 4 where the fluorescence and absorption spectra of naphthol [2,3-*a*]pyrene are shown both in the absence and presence of excess TPrA. As observed, the fluorescence intensity  $I$  was lowered by the successive additions of the amine, but no new longer wavelength emission was detected. The lack of change in the shape of the observed fluorescence spectra indicates that no emissive exciplex intermediate was formed during the interaction of the excited species with TPrA at these concentrations, probably because of competition between solvated radical ion pair formation and exciplex formation from the encounter complex.<sup>22</sup> Additionally, no longer wavelength absorption in the presence of TPrA suggests lack of ground-state complex formation. Thus, at the concentrations used, the steady-state fluorescence quenching should follow the Stern–Volmer (SV) relation.<sup>23</sup>

$$I_0/I = 1 + K_{\text{sv}}[\text{Q}] = 1 + k_q\tau_0[\text{Q}] \quad (15)$$

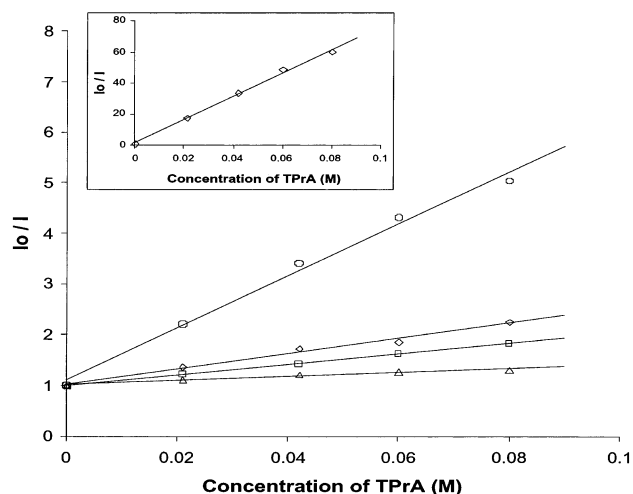
where  $I$  and  $I_0$  are the relative fluorescence intensities in the absence and presence of the quencher (TPrA),  $\tau_0$  is the fluorescence lifetime of the fluorophore in the absence of the



**Figure 4.** Steady-state fluorescence quenching of a 20  $\mu\text{M}$  naphthol[2.3-*a*]pyrene solution by TPrA. The TPrA concentrations are (1) 0.0 M, (2) 0.021 M, (3) 0.042 M, (4) 0.060 M, and (5) 0.080 M. (excitation wavelength, 458 nm) Inset: Optical absorption (20  $\mu\text{M}$ ) of naphthol[2.3-*a*]pyrene in MeCN/benzene in absence (solid line) and in the presence (dotted line) of 0.080 M of TPrA.

**TABLE 2: Photophysical, Electrochemical, and Fluorescence Quenching Data of the Various Systems in Relation to the Potential of TPrA Oxidation**

chemical	V vs SCE			$\tau$ (ns)	$k_q$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$E_{\text{TPrA oxidation}}$ (calculated)
	$E_{1/2,(\text{R/R}^+)}$	$E_{1/2,(\text{R/R}^-)}$	$E_s$ (eV)			
rubrene	0.82 V	-1.56 V	2.32 eV		not quenched	0.82 V
9,10-dimethyl-7,12-diphenylbenzo[ <i>k</i> ]fluoranthene (dimer)	0.94 V	-1.26 V	2.07 eV		not quenched	0.82 V
7,12-diphenylbenzo[ <i>k</i> ]fluoranthene (dimer)	0.95 V	-1.22 V	2.06 eV		not quenched	+0.84 V
naphthol[2.3- <i>a</i> ]pyrene	0.94 V	-1.70 V	2.67 eV	7.8	$\sim 1.33 \times 10^9$	+0.97 V
perylene	1.02 V	-1.77 V	2.82 eV	4.9	$\sim 3.09 \times 10^9$	+1.05 V
DPA	1.29 V	-1.96 V	3.08 eV	8.1	$\sim 6.33 \times 10^9$	+1.12 V
1,3,6,8 tetraphenylpyrene	1.11 V	-1.81 V	3.10 eV	2.0	$\sim 3.26 \times 10^9$	+1.29 V
pyrene	1.28 V ( $E_p$ )	-2.16 V	3.51 eV	300	$\sim 2.52 \times 10^9$	+1.35 V



**Figure 5.** Stern-Volmer plots for 1,3,6,8-tetraphenylpyrene ( $\Delta$ ), naphthol[2.3-*a*]pyrene ( $\square$ ), perylene ( $\diamond$ ), and DPA ( $\circ$ ) in the presence of TPrA in MeCN or MeCN/benzene solutions. Inset: Stern-Volmer plot for pyrene in MeCN/benzene solution.

quencher, and  $k_q$  is the bimolecular quenching constant which could be obtained from the slope of  $I_0/I$  vs  $[Q]$  plots.

Linear SV plots following eq 15 were obtained in all cases (Figure 5) and bimolecular quenching rate constants were calculated from these. No positive deviations were observed in the SV plots even in the presence of high amine concentrations. This, again, shows the lack of formation of a ground-state

complex between the compound and the quencher, which could cause static quenching leading to positive deviations in the kinetic plots.<sup>17</sup> Moreover, saturation effects indicated by downward curvature in the SV plots at higher amine concentrations were not observed. Saturation behavior in SV plots often suggests a quenching mechanism involving an exciplex or encounter complex in dynamic equilibrium whose decay route is intersystem crossing to the triplet state of the compound. This behavior is more pronounced in systems where the quenchers have low quenching efficiencies.<sup>24,25</sup> The lack of negative deviations in the kinetic plots agrees with our previous assumption that no emissive exciplex was formed in the PAH-TPrA systems investigated (Figure 4). The  $k_q$  values for the five compounds are listed in Table 2. Because of the differences of the ratios of MeCN to benzene used in this set of experiments, the observed  $k_q$  values could vary slightly when compared to values obtained from experiments done in the same solvent.

Since fluorescence quenching between TPrA and the hydrocarbon is an electron-transfer process between an excited acceptor and a ground state donor, the standard potential for oxidation of TPrA could be determined as follows:

$$E_{\text{TPrA}/\text{TPrA}^{+\bullet}}^{\circ} = E_{1/2,(\text{R/R}^-)} + E_s \quad (16)$$

where  $E_{1/2,(\text{R/R}^-)}$  is the half-wave potential of the first reduction of the PAH and  $E_s$  is the singlet excited state of the compound. Values calculated for the eight PAHs are listed in Table 2. From these results,  $E_{\text{TPrA}/\text{TPrA}^{+\bullet}}^{\circ}$  is between 0.84 and 0.97 V vs SCE, the values calculated for 7,12-diphenylbenzo[*k*]fluoranthene and

naphthol[2,3-a]pyrene, respectively. Thus, we take  $E^{\circ}_{\text{TPrA}/\text{TPrA}^{\bullet+}} = 0.9 \pm 0.07$  V vs SCE. This value can be compared with essentially the same value proposed in aqueous solutions, 0.88 V vs SCE, based on kinetic measurements.<sup>5</sup>

### Conclusions

Generation of ECL with several PAHs with TPrA as the coreactant in MeCN:benzene solutions was investigated. ECL was observed from three compounds, but the reducing power of TPrA was not sufficient to generate light emitting excited states for the remaining five with higher energy singlet states. These studies allowed one to estimate the standard potential of the intermediate free radical in TPrA oxidation,  $\text{TPrA}^{\bullet}$ , as  $E^{\circ}_{\text{TPrA}^{\bullet}} = -1.7 \pm 0.1$  V vs SCE. Additionally, steady-state fluorescence quenching of the PAHs by TPrA yielded the standard potential for  $\text{TPrA}/\text{TPrA}^{\bullet+}$  as  $E^{\circ}_{\text{TPrA}/\text{TPrA}^{\bullet+}} = 0.9 \pm 0.07$  V vs SCE.

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**Supporting Information Available:** Cyclic voltammograms of 7,12-diphenylbenzo[*k*]fluoranthene (dimer), 9,10-dimethyl-7,12-diphenylbenzo[*k*]fluoranthene (dimer), naphthol[2,3-a]pyrene, perylene, DPA, 1,3,6,8-tetraphenylpyrene, and pyrene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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