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Electrogenerated Chemiluminescence of 9,10-Diphenylanthracene, Rubrene, and Anthracene in Fluorinated Aromatic Solvents

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The electrogenerated chemiluminescence (ECL) of 9,10-diphenylanthracene (DPA), rubrene, and anthracene has been studied in fluorinated aromatic solvents. Mixed annihilation ECL between aromatic luminophores and quinones was observed in solvent systems containing acetonitrile and either benzene, benzotrifluoride, 3-fluorobenzotrifluoride, or 1,3-bis(trifluoromethyl)benzene. Increases in ECL efficiency (φ_{ecl}, photons generated per redox event) correlated with decreasing solvent polarity when 1,4-benzoquinone was used as a nonemitting ECL partner. However, opposite results were observed using 1,4-naphthaoquinone (NQ) as a nonemitting partner. φ_{ecl} also correlated with radical anion stability of NQ in these solvent systems, as indicated by reverse/forward current ratios (I_r/I_f), suggesting noncovalent interactions between the solvent and the nonemitting ECL partner. Specifically, the reaction of an aromatic luminophore with 1,4-naphthoquinone in acetonitrile/benzotrifluoride showed a 1.03−1.63-fold increases in ECL efficiency over that of acetonitrile/benzene. Slight blue shifts (~3 nm) in photoluminescence and ECL emissions were seen as solvent polarity increased. Reaction enthalpies of each system were estimated using half-wave potentials of oxidation and reduction and were found to correlate well with emission energy.

Introduction

The investigation of new systems and environments in electrogenerated chemiluminescence (ECL) produces a deeper mechanistic understanding of this phenomenon. In annihilation ECL, light is produced from organic and organometallic species through the electrochemical formation of radical cations and anions at the surface of an electrode. These ions then recombine to form excited states thus capable of light emission.[1−5]

$$A + e^- \rightarrow A^{-\bullet} \quad (1)$$

$$D - e^- \rightarrow D^{+\bullet} \quad (2)$$

$$A^{-\bullet} + D^{+\bullet} \rightarrow {}^1A^* + D \quad (3)$$

$${}^1A^* \rightarrow A + h\nu \quad (4)$$

In classic examples, A and D are the same species, but ECL from mixed systems involving nonemitting species have also been investigated.[6,7] When the combination of the two species is not sufficiently energetic to directly produce an excited state, a triplet−triplet annihilation (TTA) mechanism leads to light emission.[8−13]

$$A^{-\bullet} + D^{+\bullet} \rightarrow {}^3A^* + D \quad (5)$$

$${}^3A^* + {}^3A^* \rightarrow {}^1A^* + A \quad (6)$$

$${}^1A^* \rightarrow A + h\nu \quad (7)$$

The mechanisms and energetics[14,15] of 9,10-diphenylanthracene,[16−18] rubrene,[19−21] and anthracene[22−24] ECL are well understood. Therefore, they were chosen for an investigation of the effects of fluorinated aromatic solvent systems on ECL. Most organic ECL experiments are carried out in acetonitrile, tetrahydrofuran, dimethylformamide, benzonitrile, or benzene or their mixtures.[4]

Fluorinated and fluorous solvents have attracted much attention for organic syntheses,[25] phase transfers, and radical reactions.[26,27] However, ECL in these systems is relatively unexplored. Recently, the enhanced ECL of the tris(2,2′-bipyridyl)ruthenium(II) [$Ru(bpy)_3^{2+}$]/tri-*n*-propylamine coreactant system in the presence of fluorinated alcohols was reported.[28] Given the significant increases in emission seen in these systems (≥270-fold), the effects of fluorinated aromatic solvents on the ECL of 9,10-diphenylanthracene (DPA), rubrene, and anthracene are also of interest. For example, solvent effects have been investigated for DPA[6,29] and rubrene.[30−32] Although studies so far have been limited to nonfluorinated solvents, significant effects on ECL were observed as solvent parameters (e.g., solvent polarity, dielectric constant) were altered. It has also been suggested that the viscosity and polarity of the solvent system in ECL can affect electrode surface dynamics, ion-pair stabilization, and ion solubility.[6,21,33]

Benzotrifluoride (BTF, Figure 1) has been shown to be an effective and relatively safe solvent for many laboratory uses.[26] Therefore, in this study, BTF and two analogues were compared to benzene in mixed aromatic/acetonitrile solutions to investigate their impact on polyaromatic hydrocarbon ECL.

Experimental Section

Materials. DPA (98%), rubrene (sublimed grade), anthracene (99%), benzene (PhH, 99.9%, HPLC grade), and BTF (99%) were obtained from Sigma-Aldrich (St. Louis, MO) and used as supplied. 3-Fluorobenzotrifluoride (FBTF, 99%) and 1,3-bis(trifluoromethyl)benzene (BTB, 99%) were obtained from SynQuest Laboratories (Alachua, FL) and used without further purification. 1,4-Benzoquinone (BQ, 99.5%, Aldrich) and 1,4-naphthoquinone (NQ, 99%, Acros Organics) were used in respective mixed ECL systems. Acetonitrile (ACN, 99.9%,

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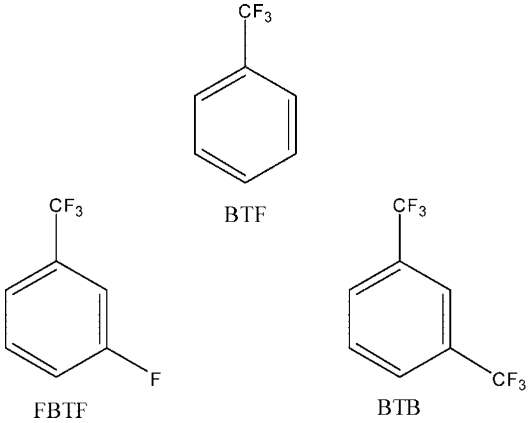

Figure 1. Structures of benzotrifluoride (BTF), 3-fluorobenzotrifluoride (FBTF), and 1,3-bis(trifluoromethyl)benzene (BTB).

Aldrich) was dried over size 3A molecular sieves and promptly used. Tetrabutylammonium hexafluorophosphate (TBAH, Aldrich) was used as a supporting electrolyte in all systems. Deionized water that had been passed through a Barnstead/Thermolyne filtration system was used throughout.

Methods. Cyclic voltammetry without photon detection was performed using a CH Instruments electrochemical analyzer (Austin, TX) with a platinum disk working electrode. The platinum electrode was cleaned after each run by polishing successively with 1.0-, 0.3-, and 0.05-μm alumina, followed by rinsing with water, sonication in dilute nitric acid solution, rinsing with water a second time, and finally rinsing with the working solvent system. All solutions were degassed by sonication and then placed over molecular sieves and kept in a desiccated N_2 atmosphere until ready for use. Purity of the solvents and electrolyte was tested by cyclic voltammetry with an observed current of less than 1.0 μA.

ECL instrumentation and experimental methods have been previously described[34] and incorporated a conventional three-electrode system using a CH Instruments electrochemical analyzer and a Hamamatsu HC 135 photomultiplier tube contained in a "light-tight" box. Luminophore and nonemitting species concentrations were between 0.1 and 1 mM, and sample solutions contained 0.1 M TBAH in 40% (v/v) ACN and 60% (v/v) aromatic solvent. All electrochemical and ECL experiments were referenced with respect to a Ag quasireference electrode (QRE) standardized to ferrocene (0.31 V vs SCE, 0.2 M $LiClO_4$ in ACN).[35] The Pt working electrode was cleaned before each run by rinsing with ACN, repeated cycling (+2.0 to −2.0 V) in BioVeris Cell Cleaner containing KOH and detergents, rinsing with deionized water, and a final rinse with ACN. ECL was obtained by repeatedly cycling the potential between potentials 0.1 V more extreme than the predetermined oxidations and reductions for a given system at a rate of 0.5 V/s while simultaneously detecting light with the photomultiplier tube.

Photoluminescence (PL) and ECL spectra were obtained with a Shimadzu RF-5301 spectrofluorophotomer (Shimadzu Corp.) with detection between 375 and 600 nm. Slit widths were 3 nm for PL spectroscopy and 20 nm for ECL spectroscopy. Excitation for photoluminescence was at the lowest-energy absorption wavelength maximum (Supporting Information, Table 1). Photoluminescence efficiencies (φ_{em}, photons emitted per photons absorbed) were obtained relative to DPA in benzene at 25 °C ($\varphi_{em} = 0.91$),[36] and ECL efficiencies (φ_{ecl}, photons generated per redox event) were obtained by literature methods,[37,38] using DPA in ACN as the standard (DPA^+/DPA^- $\varphi_{ecl} = 0.08$)[18,39] and correcting for photomultiplier tube counting efficiency per manufacturer's instructions. Observed photoluminescence and ECL efficiencies were corrected for varying refractive indexes as shown in the eq 8, where n is the refractive index of the solvent system and n_o is the refractive index of the reference solvent (either ACN or PhH).[40]

TABLE 1: Spectroscopic Data of DPA, Rubrene, and Anthracene in Mixed Solvent Systems

	PhH/ACN		BTF/ACN		FBTF/ACN		BTB/ACN	
	λ_{em}[a] (nm)	φ_{em}[b]	λ_{em}[a] (nm)	φ_{em}[b]	λ_{em}[a] (nm)	φ_{em}[b]	λ_{em}[a] (nm)	φ_{em}[b]
DPA	431	0.804	429	0.683	429	0.625	429	0.611
rubrene	554	0.411	553	0.325	552	0.321	551	0.301
anthracene	402	0.238	401	0.196	400	0.169	400	0.159

[a] Excited at respective lowest-energy absorption. [b] φ_{em} relative to DPA in benzene at 25 °C ($\varphi_{em} = 0.91$) and corrected for refractive index.

$$\varphi_r = \varphi_r^{obs}\left(\frac{n^2}{n_o^2}\right) \tag{8}$$

Refractive indexes of solvent systems were tested using a Bausch and Lomb refractometer, and viscosities were measured with a Cannon-Fenske viscometer (size 150). Both employed an attached water circulation system to maintain a constant temperature of 25 °C. Values of pure solvents were compared to literature values,[41] with errors of less than 0.11% for refractive indexes and less than 5.0% for viscosities.

Solvent systems were chosen based on luminophore solubility and previous studies using PhH/ACN systems.[42] A ratio of 1.5:1 (aromatic/ACN) was found to be optimal and was used throughout.

Dipole moments were calculated using density functional theory (DFT) via the Gaussian 03[43]-supported computational method B3LYP with a 6-31G(d,p) basis set. Values were referenced to literature[41] with less than 10% error. Dielectric constants (ε) were calculated by literature methods[44] using dipole moments, molecular weights, densities, and refractive indexes. Calculated values for ε gave <5% error compared to tabulated experimental values.[41]

Reported values for ECL intensity are based on the average of at least three scans with a relative standard deviation of less than ±8%. Values for photoluminescence efficiencies and electrochemical oxidations and reductions are based on the average of at least three scans with a relative standard deviation of less than ±4%.

Results and Discussion

UV−Vis Spectroscopy and Photoluminescence. UV−vis data are presented in the Supporting Information. Photoluminescence (PL) data for DPA, rubrene, and anthracene are presented in Table 1. Absorption bands are assigned to $\pi \rightarrow \pi^*$ transitions. As expected, increases in aromaticity (e.g., DPA is a larger conjugated system than anthracene) result in bathochromic absorbance shifts.[45] Excitation wavelengths for the respective luminophores were based on the lowest-energy absorbance for each in mixed benzene (PhH), BTF, 3-fluorobenzotrifluoride (FBTF), or bis(1,3-trifluoromethyl)benzene (BTB) with acetonitrile. At room temperature, slight shifts were seen in PL emission based on the polarity of the solvent system. As solvent polarity increased (as indicated by lower refractive indexes, Table 2), emissions increased in energy by 2−3 nm. However, PL efficiencies (φ_{em}) decreased with increasing polarity for all systems (Table 1). Similar results have also been

TABLE 2: Refractive Indexes and Viscosities of Selected Solvent Systems

solvent	n^a	η^a (cP)
ACN	1.3428	0.369
PhH	1.5001	0.638
BTF	1.4130	0.623
FBTF	1.3999	0.667
BTB	1.3930	0.731
PhH/ACN	1.4344	0.421
BTF/ACN	1.3861	0.391
FBTF/ACN	1.3780	0.437
BTB/ACN	1.3728	0.503

[a] Measured at 25 °C without luminophore or electrolyte.

TABLE 3: Electrochemical and ECL Data

solvent	$E_{ox}{}^a$ (V)	$E_{red}{}^a$ (V)	ΔH (eV)	λ_{ecl} (nm)	$\varphi_{ecl}{}^b$
		DPA^+/BQ^-			
PhH/ACN	1.332	−0.556	1.73	430	0.0108
BTF/ACN	1.260	−0.616	1.72	429	0.0059
FBTF/ACN	1.245	−0.607	1.69	429	0.0056
BTB/ACN	1.236	−0.622	1.70	428	0.0052
		DPA^+/NQ^-			
PhH/ACN	1.332	−0.868	2.04	430	0.0602
BTF/ACN	1.260	−0.901	2.00	429	0.0619
FBTF/ACN	1.245	−0.918	2.00	429	0.0593
BTB/ACN	1.236	−0.936	2.01	428	0.0053
		$rubrene^+/BQ^-$			
PhH/ACN	0.888	−0.556	1.28	552	0.0027
BTF/ACN	0.843	−0.616	1.30	550	0.0021
FBTF/ACN	0.772	−0.607	1.22	549	0.0021
BTB/ACN	0.752	−0.622	1.21	549	0.0021
		$rubrene^+/NQ^-$			
PhH/ACN	0.888	−0.868	1.60	552	0.0123
BTF/ACN	0.843	−0.901	1.58	550	0.0020
FBTF/ACN	0.772	−0.918	1.53	549	0.0139
BTB/ACN	0.752	−0.936	1.53	549	0.0168
		$anthracene^+/BQ^-$			
PhH/ACN	1.367	−0.556	1.76	–	0.0018
BTF/ACN	1.362	−0.616	1.82	–	0.0014
FBTF/ACN	1.359	−0.607	1.81	–	–
BTB/ACN	1.318	−0.622	1.78	–	–
		$anthracene^+/NQ^-$			
PhH/ACN	1.367	−0.868	2.08	400	0.0050
BTF/ACN	1.362	−0.901	2.10	400	0.0056
FBTF/ACN	1.359	−0.918	2.12	–	0.0052
BTB/ACN	1.318	−0.936	2.09	–	0.0055

[a] Half-potential vs Ag QRE with 0.1 M TBAH. [b] φ_{ecl} relative to DPA in ACN (DPA^+/DPA^- $\varphi_{ecl} = 0.08$) and corrected for refractive index and photomultiplier tube response.

seen with $Ru(bpy)_3{}^{2+}$ and were attributed to increases in nonradiative decay as solvent polarity increased.[46]

Electrochemical Properties. The electrochemical windows of each solvent system were determined using cyclic voltammetry. Because PhH, BTF, FBTF, and BTB reduce starting at −1.1 V, the working electrochemical window is confined to a point lower than the electrochemical reductions of DPA, rubrene, and anthracene (−1.75, −1.37, and −1.96 V, respectively).[17,20,22]

To overcome these limitations, the nonemitting radical anions of 1,4-benzoquinone and 1,4-naphthoquinone were used to generate ECL. Reduction values for each anion in various solvent systems are listed in Table 3. A representative cyclic voltammogram for the DPA^+/BQ^- system is shown in Figure 2.

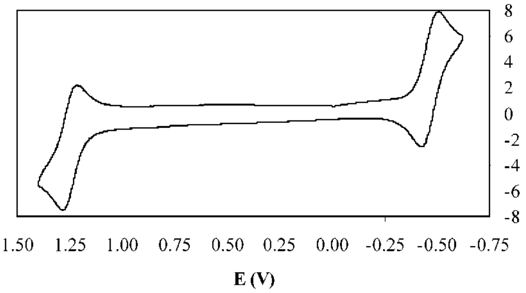

Figure 2. Cyclic voltammogram of 0.1 mM DPA and BQ in BTF/ACN (1.5:1) (0.1 M TBAH). Scan rate = 100 mV/s at glassy carbon working electrode vs Ag QRE.

TABLE 4: Dipole Moments, Dielectric Constants, Electrochemical Reversibility, and ECL Efficiencies for Luminophore/NQ Systems

solvent	$(I_r/I_f)_{red}$	$\mu^{a,b}$ (D)	ε^a	φ_{ecl} DPA	rubrene	anthracene
PhH/ACN	0.71	0	–	0.0482	0.0123	0.00497
FBTF/ACN	0.78	2.165	6.75	0.0528	0.0139	0.00522
BTB/ACN	0.91	2.422	6.82	0.0593	0.0168	0.00548
BTF/ACN	0.96	2.576	9.66	0.0619	0.0200	0.00561

[a] Calculated dipole moments (in Debyes) and dielectric constants of the pure aromatic compounds. [b] Compare to literature value for BTF of $\mu = 2.86$ D and $\varepsilon = 9.22$.[41]

In general, the oxidative waves of DPA, rubrene, and anthracene move to less positive potentials whereas the reductions of BQ and NQ move to more negative potentials as solvent polarity increases. E_{ox} and E_{red} for each system can be used to estimate ΔH as follows

$$\Delta H = E_{ox} - E_{red} - 0.16\ \text{eV} \tag{9}$$

where 0.16 eV corrects for both differences between oxidation and reduction values between the standard electrode potential and the factor $T\Delta S$ that accounts for temperature and change in system entropy.[21,14,47]

All three luminophores produce reverse current (I_r) to the forward current (I_f) ratios (I_r/I_f) greater than 0.9, indicating nearly complete electrochemical reversibility for the radical cations. However, in polar aprotic solvent systems such as those employed in this study, anions are generally less stable.[4] Whereas BQ showed strong reversibility ($I_r/I_f > 0.9$), the I_r/I_f ratio for NQ varied considerably depending on solvent system (Table 4). This could be due to a number of reasons, including chemical reactions of NQ following electron transfer (EC mechanism) and stabilization of the $NQ^{-\bullet}$ radical by the aromatic solvents. No evidence for an EC mechanism was seen in voltammetric experiments. However, solvent reduction does begin at approximately −1.1 V, so reaction of reduced NQ with the solvent to form a nonelectroactive species is possible. However, one would assume that, if an EC mechanism with solvent were occurring, as the potential of $NQ/NQ^{-\bullet}$ moved to more negative values, closer to those of solvent reduction, there would be a decrease in I_r/I_f values. However, no clear trend emerges. For example, half-wave potentials for the reduction of NQ are −0.868V in PhH/ACN with I_r/I_f of 0.71, −0.901V in BTF/ACN with I_r/I_f of 0.96, −0.918V in FBTF/ACN with I_r/I_f of 0.78, and −0.936V in BTB/ACN with I_r/I_f of 0.91. Likewise, the decomposition of NQ following electron transfer also seems unlikely considering the structural similarity of the solvents and the known thermodynamic reversibility of quinone complexes.

Only NQ, with its adjoining aromatic ring, exhibits changes in reversibility. This observation might indicate a quadrupole

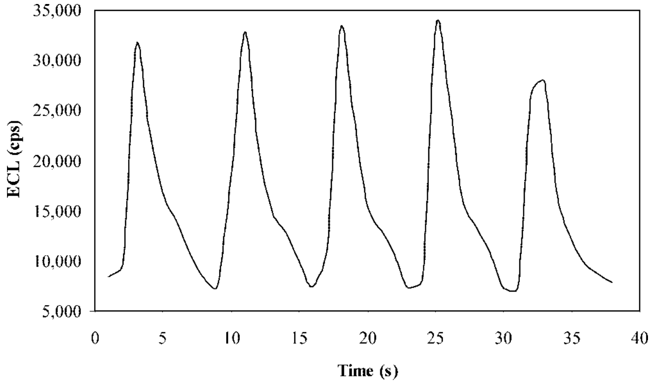

Figure 3. ECL vs time for DPA^{+}/BQ^{-} in BTF/ACN (1.5:1) (0.1 M TBAH). Potential scanned from −0.70 V to +1.35 V to −0.70 at 0.5 V/s vs Ag QRE.

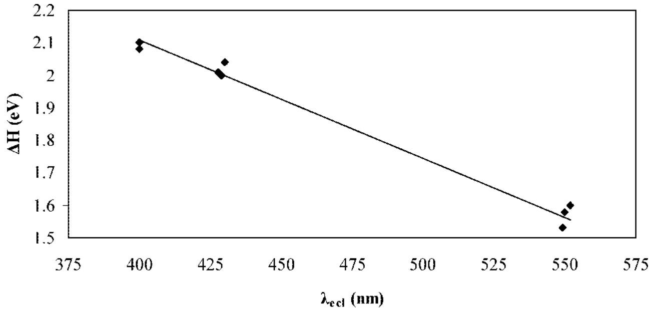

Figure 4. Estimated reaction enthalpies (see eq 9) vs ECL emission. $\Delta H = -0.0036\lambda_{\mathrm{ecl}} + 3.56$; $R^2 = 0.9867$.

interaction between the reduced species ($NQ^{-\bullet}$) and the aromatic solvent component. However, BTF, FBTF, and BTB each exhibit a significant dipole moment, which reduces the influence of an inherent quadrupole moment. Interestingly, there is a direct correlation between dipole moment and I_r/I_f.

For example, BTF has a calculated dipole moment of 2.576 D and, in mixed solution, produces an NQ I_r/I_f ratio of 0.96, whereas the corresponding values for FBTF are 2.165 D and 0.78, and those for PhH are 0 (in the gas phase) and 0.71, respectively. Although no definite conclusions can be drawn from this observation, a stronger quadrupole moment (as indicated by a lower dipole moment) in FBTF, for example, could result in solvent stabilization of the $NQ^{-\bullet}$ radical anion, making it less likely to undergo reoxidation at the electrode surface.

Electrogenerated Chemiluminescence. Mixed annihilation ECL was observed for DPA, rubrene, and anthracene using either 1,4-benzoquinone or 1,4-naphthaquinone as nonemitting partners in mixed fluorinated aromatic/acetonitrile solvent systems. Half-wave potentials, estimated reaction enthalpies, ECL emission energies, and ECL efficiencies (φ_{ecl}) are listed in Table 3.

ECL was generated at 0.5 V/s by cycling the potential 0.1 V past the peak of the oxidative or reductive wave (Table 3). A typical ECL vs time diagram for several scan cycles (from −0.7 to +1.35 to −0.7 V) is shown in Figure 3. ECL intensity was stable for four to six cycles and then decreased, presumably as a result of accumulation of reaction products on the electrode surface. After the working electrode was cleaned, peak intensity returned.

ECL emission energy correlates well with estimated reaction enthalpies (Figure 4). As ΔH increases, so does the HOMO−LUMO gap of the two reactants, thus leading to higher-energy emissions. PL and ECL spectra and emission energies were nearly identical, indicating that the same excited state was formed in both experiments. It was not possible to obtain ECL spectra for the $\mathrm{anthracene}^{+}/BQ^{-}$ system or for $\mathrm{anthracene}^{+}/NQ^{-}$ in FBTF/ACN or BTB/ACN.

Emission from the excited singlet state of a polyaromatic hydrocarbon such as DPA can be produced by one of two mechanisms. If the enthalpy of reaction for the radical ion annihilation is greater than the energy of the lowest singlet state (e.g., ∼430 nm or 2.88 eV for DPA), then the mechanism is "energy-sufficient", and direct population of the excited singlet state occurs (i.e., eqs 1−4). If the enthalpy for the radical ion annihilation reaction is less than the energy of the lowest excited singlet state but higher than the lowest triplet state (e.g., 1.8 eV for DPA), the system is "energy-deficient", and a triplet−triplet mechanism occurs (i.e, eqs 5−8). The data shown in Table 3 clearly indicate that these systems are energy-deficient and that excited states are formed via triplet−triplet annihilation.

As the solvents are changed from PhH/ACN to BTB/ACN, the viscosities, polarities, and dielectric constants also change (Tables 2−4). All of these properties might affect ECL intensities and efficiencies. No correlation between solution viscosity and ECL efficiency was seen, indicating that possible changes in diffusion characteristics and annihilation rates do not alter ECL behavior to any great extent. This was also observed for DPA in a variety of nonfluorinated solvents.[6,30]

The addition of fluorinated solvents to benzene results in dramatic increases to solvent polarity and dielectric constants (Table 4). In general, the ECL efficiencies (φ_{ecl}) of systems with BQ decreased as the solvent polarity and dielectric constants increased (Table 3). Such trends have been observed before for DPA in nonfluorinated systems[6,21,48](i.e., dimethylformamide, ACN, benzonitrile, tetrahydrofuran) and attributed to increased singlet−singlet emission in solvents with low dielectric constants, with triplet−triplet emission being less efficient. In the present study, however, the change in enthalpy associated with changes in solvent properties is not sufficient to result in the direct formation of excited singlet states. Although the exact reasons for the greater ECL efficiency is unknown, considerable evidence exists that the mechanistic steps outlined in eqs 1−8 are oversimplifications and that several pathways exist for the formation of triplet and singlet excited states.[4,5] Therefore, as in the DPA and DPA/thianthrene system, in ACN/PhH/benzonitrile systems,[18] the greater efficiency is probably due to changes in electron-transfer and excited-state dynamics as the solvent systems vary.

When NQ was used as the nonemitting species, the ECL efficiencies (φ_{ecl}) increased as the solvent polarity and dielectric constants increased, opposite to the behavior observed with the BQ systems (Table 4). φ_{ecl} values for all three luminophores also increased with increasing electrochemical reversibility of the $NQ/NQ^{-\bullet}$ couple (Figure 5). This is not surprising, given that the intensity and stability of DPA ECL generated via mixed annihilation has been shown to depend on the stability of the radical anion.[6] One factor that might be responsible for the observed behavior is increased ion pairing between radical ions and supporting electrolyte ions with decreasing solvent polarity and dielectric constants, resulting in fewer $NQ^{-\bullet}$ radicals available to react either electrochemically or in ECL. Ion pairing has been used to explain the effects of the supporting electrolyte in DPA systems using tri-*p*-tolylamine as the radical cation.[48]

Conclusions

This study illustrates the use of fluorinated aromatic solvents for ECL studies of organic luminophores such as DPA, rubrene,

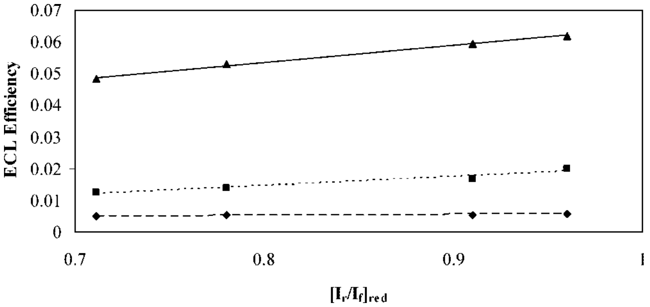

Figure 5. ECL efficiencies (φ_{ecl}) vs NQ reversibility for DPA (▲, —), rubrene (■, - - -), and anthracene (◆, — — —) in respective solvent systems. DPA: $\varphi_{ecl} = 0.0541(I_r/I_f) + 0.0101$; $R^2 = 0.9965$. Rubrene: $\varphi_{ecl} = 0.0299(I_r/I_f) + 0.0085$; $R^2 = 0.9522$. Anthracene: $\varphi_{ecl} = 0.0025(I_r/I_f) + 0.0033$; $R^2 = 0.9855$.

and anthracene. Although these solvents have a limited potential window and thus require a mixed annihilation ECL approach, they have led to a 1.03−1.63-fold increase in ECL of organic luminophores with NQ in BTF/ACN over that of traditional PhH/ACN systems.

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Supporting Information Available: UV−vis aborption data of DPA, rubrene (RUB), and anthracene (ANT). This material is available free of charge via the Internet at http://pubs.acs.org.

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