J. Am. Chem. Soc. **2000,** *122,* 4972−4979

Electrogenerated Chemiluminescence from Derivatives of Aluminum Quinolate and Quinacridones: Cross-Reactions with Triarylamines Lead to Singlet Emission through Triplet−Triplet Annihilation Pathways

E. M. Gross,† J. D. Anderson,‡ A. F. Slaterbeck,† S. Thayumanavan,‡ S. Barlow,‡ Y. Zhang,‡ S. R. Marder,‡ H. K. Hall,‡ M. Flore Nabor,‡ J.-F. Wang,‡ E. A. Mash,‡ N. R. Armstrong,‡ and R. M. Wightman*,†

Contribution from the Departments of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, and University of Arizona, Tucson, Arizona 85721

Received February 18, 2000. Revised Manuscript Received March 29, 2000

Abstract: Solution electrogenerated chemiluminescence (ECL) was evaluated for molecules of interest for organic light-emitting diodes (OLEDs), using high-frequency voltage pulses at a microelectrode. Radical cations of different energies were electrogenerated from a series of triarylamine hole-transport materials (*x*-TPD), in the presence of radical anions of a high electron affinity sulfonamide derivative of tris(8-hydroxyquinoline)-aluminum (Al(qs)$_3$), or a bis(isoamyl) derivative of quinacridone (DIQA). The resultant emission was from the excited singlet states ^{1}Al(qs)$_3$* or ^{1}DIQA*, the same excited state produced in OLEDs based on these molecules. In solution, the majority of the reaction pairs had insufficient energy to populate ^{1}Al(qs)$_3$* or ^{1}DIQA* directly, but could form the triplet states ^{3}Al(qs)$_3$* or ^{3}DIQA*. The reaction order and the temporal response of the emission were consistent with subsequent formation of the excited singlet states via triplet−triplet annihilation (TTA). For reactions with a low excess Gibbs free energy to form the triplet state ($\Delta^{T}G$), the efficiency increased exponentially with an increase in driving force (increase in oxidation potential of *x*-TPD), then reached a plateau. At the maximum, the efficiencies for formation of ^{1}Al(qs)$_3$* or ^{1}DIQA* via the TTA route reach as high as a few percent. The computed energetics of these reactions suggest that similar light-producing electroluminescent reactions, proceeding via triplet formation, could also occur in condensed phase organic thin films.

Introduction

Light emitting polymers and organic light-emitting diodes (OLEDs) represent attractive new light sources for a variety of display applications.[1−3] Among the most successful of the OLEDs created to date are those based on tris(8-hydroxyquinoline)aluminum (Alq$_3$) and a triarylamine such as 4,4′-bis(*m*-tolylphenylamino)biphenyl (TPD),[3−5] with a device geometry such as ITO/TPD (30−60 nm)/Alq$_3$ (30−60 nm)/Al (or some suitably modified Al-cathode).[5] Certain aspects of the mechanism of light production are still unclear, and several possibilities have been considered. For example, under the high fields of OLED operation (ca. 10^6 V/cm), holes could inject from the TPD layer into the Alq$_3$ layer (i.e., oxidation of Alq$_3$ occurs). Here, the electron-rich (radical anion) form of Alq$_3$ could react with the electron-deficient form (cation radical) of Alq$_3$ to create either the singlet state, ^{1}Alq$_3$*, or the triplet state ^{3}Alq$_3$*.[3a,5,6] It has been recently shown, however, that the injection of holes into the Alq$_3$ layer may limit device lifetime through decomposition of this lumophore.[7] It would clearly be advantageous to find efficient routes to emissive states not involving direct injection of holes into the Alq$_3$ layer.

Dopants are often added to the lumophore layer in OLEDs to tune the emission response, and to enhance the stability of the device. Common dopant molecules include quinacridone derivatives, which have been shown to be good electron acceptors with respect to the radical anion form of Alq$_3$, and good electron donors with respect to the cation radical form of Alq$_3$.[4,8] The anion and cation radical forms of these molecules

---

* To whom correspondence should be addressed.

† University of North Carolina at Chapel Hill.

‡ University of Arizona.

(1) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628−630.

(2) (a) Rothberg, L. J.; Lovinger, A. J. *J. Mater. Res.* **1996**, *11*, 3174 and references therein. (b) Sheats, J. R.; Antoniadis, H.; Hueschen, M.; Leonard, W.; Miller, J.; Moon, R.; Roitman, D.; Stocking, A. *Science* **1996**, *273*, 884−888. (c) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121−128.

(3) (a) Tang, C. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913−915. (b) Hamada, Y.; Sano, T.; Fujita, M.; Fuji, T.; Nishio, Y.; Shibata, K. *Jpn. J. Appl. Phys.* **1993**, *32*, 514−515.

(4) (a) Tang, C. W.; Van Slyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610−3616. (b) Hosokawa, C.; Higashi, H.; Nakamura, H.; Kusumoto, T. *Appl. Phys. Lett.* **1995**, *67*, 3853−3855. (c) Shi, J.; Tang, C. W. *Appl. Phys. Lett.* **1995**, *70*, 1665−1667. (d) Sakamoto, G.; Adachi, C.; Koyama, T.; Taniguchi, Y.; Merritt, C. D.; Murata, H.; Kafafi, Z. H. *Appl. Phys. Lett.* **1999**, *75*, 766−768.

(5) Jabbour, G. E.; Kawabe, Y.; Shaheen, S. E.; Wang, J. F.; Morrell, M. M.; Kippelen, B.; Peyghambarian, N. *Appl. Phys. Lett.*, **1997**, *71*, 1762−64.

(6) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals*; Oxford University Press: New York, 1973; pp 508−509.

(7) Aziz, H.; Popovic, Z. D.; Hu, N.; Hor, A.; Xu, G. *Science* **1999**, *283*, 1900−1902.

(8) (a) Shaheen, S. E.; Kippelen, B.; Mash, A.; Lee, P. A.; Armstrong, N. R.; Kawabe, Y. *J. Appl. Phys.* **1999**, *85*, 7939−7945. (b) Saito, S.; Tsutsui, T.; Era, M.; Takada, N.; Adachi, C.; Hamada, Y.; Wakimoto, T. *SPIE* **1993**, *1910*, 212.

10.1021/ja0005993 CCC: $19.00

are also more stable than those for Alq_3.[8] Addition of these dopants into the Alq_3 layer at 0.5 to 2.0 wt % both significantly enhances the emission efficiency of the OLED and improves its lifetime.[4c]

Light can also be generated in solution by electrogenerated chemiluminescence (ECL).[9] Emissive states typically arise from the recombination reactions of electrogenerated radical cations and radical anions. The most relevant of these processes for OLED technologies are "cross reactions" involving cation radicals of one molecule type ($D^{+\bullet}$) and anion radicals of another molecule type ($A^{-\bullet}$).[10−15] We recently established that ECL cross-reactions between radical cations (triarylamines) and radical anions of small molecule OLED materials (derivatives of Alq_3 and quinacridones) create the same emissive state in solution as in the solid state.[16] Thus, solution-phase ECL provides a convenient method to rapidly screen candidates for OLED's, and to establish the recombination mechanisms of specific reaction pairs.

In ECL cross-reactions, light production is controlled primarily by the energetics of the specific reactions. Electron-transfer reactions between the electrogenerated radical anion and cation, to reform the ground-state species, exhibit large excess free energies, placing them in the Marcus inverted region, and thus they have low rates of reaction.[10,12−14] It is more favorable for the excess energy resulting from the cross-reaction to promote one of the species to an electronically excited state. These light-producing reactions typically occur by two mechanisms. The most direct route, termed the S-route, dominates when the singlet emitting state is energetically accessible as a result of the electron-transfer reaction.[9] Such a situation is termed *energy-sufficient*. When the electron-transfer step is *energy-deficient* to reach the singlet state directly, recombination reactions may still form triplet excited states. Singlet excited states can subsequently be created as a result of triplet−triplet annihilation. This pathway, referred to as the T-route, is remarkably efficient and always competes with the S-route.[11,12] Mechanistically these pathways can be distinguished by the time course and reaction order of the light-producing reactions.[12] For example, using 9,10-diphenylanthracene (DPA) as the limiting reagent, cross-reactions producing ECL via the S-route have been shown to exhibit first-order kinetics with respect to DPA concentration, while those utilizing the T-route are second order in DPA concentration.[12]

Our initial solution studies of reactions involving $Al(qs)_3^{-\bullet}$ and *x*-$TPD^{+\bullet}$ and a quinacridone derivative, diisoamylquinacridone (DIQA), showed stable radical anions and radical cations from these molecules, and demonstrated high efficiencies of excited-state production from cross-reactions involving $DIQA^{-\bullet}$/*x*-$TPD^{+\bullet}$, $DIQA^{+\bullet}/Al(qs)_3^{-\bullet}$, and $DIQA^{-\bullet}/DIQA^{+\bullet}$.[16] We have recently created a series of alkoxy- or fluoro-substituted TPDs, which allow for tuning of the first oxidation potential of this molecule by up to 0.5 V, such that the energy of reaction couples such as $Al(qs)_3^{-\bullet}$/*x*-$TPD^{+\bullet}$ or $DIQA^{-\bullet}$/*x*-$TPD^{+\bullet}$can be systematically varied, and the resulting ECL efficiency studied as a function of reaction energy.[17a] As in the case for diphenylanthracene ECL processes,[12] we find that the T-route is a relatively efficient route to light production. It is also clear that the excess free energies in these processes is likely to increase in condensed phase media, with low dielectric constants and no supporting electrolyte. These reactions may therefore be viable routes to emissive state production in condensed phase organic thin films.

Experimental Section

Apparatus. ECL was characterized in a flow injection analysis system.[13] This system consisted of a stainless steel syringe pump, loop injector, and a channel-type electrochemical cell with a channel height of 150 μm. The floor of the channel was fabricated from epoxy into which was embedded a band or disk-shaped microelectrode. Also embedded in the epoxy was a silver band that served as a pseudoreference electrode. The ceiling of the channel contained an optical window. A Hamamatsu (R5600P, Bridgewater, NJ) photon-counting photomultiplier tube (PMT) operated at −800 V (Bertan model 230, Hicksville, NY) was placed adjacent to this window. The output of the PMT was amplified (EG&G Ortec VT120A, Oak Ridge, TN) and directed to a multichannel scalar (EG&G Ortec T-914). The working electrode was connected to a fast current to voltage converter built in-house, and the electrochemical signals were recorded with a digital oscilloscope (Tektronix TDS 380, Wilsonville, OR). The cell potential was controlled with an arbitrary waveform generator (Hewlett-Packard 33120A, Englewood, CO). To measure the ECL spectral response, an Ocean Optics spectrometer (S2000FL, Dunedin, FL) with a UV collimating lens was used.

Methods. Solvents were delivered from the pump to the electrochemical cell at a flow rate of 200 μL/min, and the solutions for ECL or cyclic voltammetric examination were introduced to the cell with a loop injector. For ECL generation, the potential waveform was a continuous, 1 or 5 kHz square wave. The potential limits of the square wave were at least 200 mV beyond the $E_{1/2}$ values of each of the redox couples using the values determined from cyclic voltammograms. In this way, the production of ECL was diffusion-limited. PMT counts were binned at 100 or 500 kHz for each cycle of the square wave and the sum of 1000 or 5000 responses was collected (1 s total acquisition time). For ECL systems following the S-route, ECL efficiencies (ϕ_{ECL}) were calculated relative to the $DPA^{+\bullet}/DPA^{-\bullet}$ system which has an efficiency of 6.4% in the solutions employed.[14] For systems following the T-route, the $TMPD^{+\bullet}/DPA^{-\bullet}$ system was used as a reference.[15] In this case only relative ECL efficiencies were obtained. Efficiencies for these reactions were compared to the emission from the TMPD-DPA system, correcting for differences in mass transport:

$$\frac{(\phi_{ECL})_{unk}}{(\phi_{ECL})_{TMPD-DPA}} = \left(\frac{I_{unk}}{I_{DPA}}\right)\left(\frac{D_{DPA}}{D_{unk}}\right)^{1/2}\left[\frac{(\phi_{fl})_{DPA}}{(\phi_{fl})_{unk}}\right] \quad (1)$$

in which ϕ_{ECL} is the ECL quantum efficiency, I is the integrated light intensity corrected for the spectral response of the PMT, D is the diffusion coefficient in the solvent system used, and ϕ_{fl} is the fluorescence quantum efficiency.[18] Each solution was prepared under the same conditions with equal concentrations of each reagent, and photons were collected for the same amount of time.

---

(9) (a) Weller, A.; Zachariasse, K. In *Chemiluminescence and Bioluminescence*; Cormier, Hercules, Lee, Eds.; Plenum Publishing Corp.: New York, London, 1973; pp 169−191. (b) Faulkne, L. R.; Bard, A. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1977; Vol. 10, pp 1−95.

(10) (a) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 2654−2657. (b) Marcus, R. A. *J. Chem. Phys.* **1970**, *52*, 2803−2804. (c) Sutin, N. *Acc. Chem. Res.* **1982**, *15*, 275−282. (d) Tachikawa, H.; Bard, A. J. *Chem. Phys. Lett.* **1974**, *26*, 246−251. (e) Kapturkiewicz, A. *Chem. Phys.* **1992**, *166*, 259−273. (f) Wallace, W. L.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 1350−1357.

(11) (a) Visco, R. E.; Chandross, E. A. *Electrochim. Acta* **1968**, *13*, 1187−1196. (b) Feldberg, S. W. *J. Phys. Chem.* **1966**, *70*, 3928−3930.

(12) Ritchie, E. L.; Pastore, P.; Wightman, R. M. *J. Am. Chem. Soc.* **1997**, *119*, 11920−11925.

(13) Collinson, M. M.; Wightman, R. M. *Anal. Chem.* **1993**, *65*, 2576−2582.

(14) Maness, K. M.; Bartelt, J. E.; Wightman R. M. *J. Phys. Chem.* **1994**, *98*, 3993−3998.

(15) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 623.

(16) Anderson, J. D.; McDonald, E. M.; Lee, P. A.; Anderson, M. L.; Ritchie, E. L.; Hall, H. K.; Hopkins, T.; Mash, E. A.; Wang, J.; Padias, A.; Thayumanavan, S.; Barlow, S.; Marder, S. R.; Jabbour, G. E.; Shaheen, S.; Kippelen, B.; Peyghambarian, N.; Wightman, R. M.; Armstrong, N. R. *J. Am. Chem. Soc.* **1998**, *120*, 9646−9655.

(17) (a) Thayumanavan, S.; Barlow, S.; Marder, S. *Chem. Mater.* **1997**, *9*, 3231−3235. (b) Anderson, J. D.; Thayumanavan, S.; Barlow, S.; Lee, P. A.; Gruhn, N.; Carter, C.; Dodelet, J. P.; Marcler, S.; Armstrong, N. R. Manuscript in preparation.

(18) $(\phi_f)_{DPA}$ was assumed to be 1 (ref 19).

Optical Measurements. Fluorescence quantum efficiencies were estimated relative to a DPA standard using the following equation,

$$(\phi_{\mathrm{fl}})_1 = (\phi_{\mathrm{fl}})_2\left(\frac{I_1}{I_2}\right)\left(\frac{A_2}{A_1}\right) \tag{2}$$

in which $(\phi_{\mathrm{fl}})_1$ is the unknown quantum efficiency, $(\phi_{\mathrm{fl}})_2$ is the quantum efficiency of the standard, I is the integrated fluorescence intensity, and A is the absorbance at the excitation wavelength. Fluorescence measurements were taken on an ISA Fluorolog FL3-21 fluorimeter (Edison, NJ). Absorbance was measured on a Perkin-Elmer Lambda 40 (Norwalk, CT) spectrophotometer.

Determination of D and $\Delta E_{1/2}$. Steady-state cyclic voltammograms (CV) at a Au disk microelectrode with a radius of 2.5 μm were used to determine both the diffusion coefficients (D) and peak separations ($\Delta E_{1/2}$) of the compounds in the different solutions employed. The radius (r_o) of the microelectrode was calculated from the limiting current (i_{lim}) obtained in a 1 mM ferrocene solution in acetonitrile,

$$i_{\mathrm{lim}} = 4r_o nFDC^* \tag{3}$$

where n is the number of electrons per mole, F is Faraday's constant, D is the diffusion coefficient, and C^* is the bulk concentration. This electrode was then used to determine the unknown diffusion coefficients. All solutions contained 0.1 M electrolyte. A BAS-100 (Bioanalytical Systems, West Lafayette, IN) was used to obtain all steady-state CV data.

Calculation of Work Terms and Radii. It was necessary to calculate $w_{a,\mu}$, the work required to bring the two different reactants (A and D) to within a likely separation distance (a), to determine ΔG. It was calculated using Debye−Hückel theory[10c,20]

$$w_{a,\mu} = \frac{z_A z_D e^2 f}{\epsilon a} \tag{4}$$

where f is an ionic strength factor equal to:

$$f = \frac{1}{2}\left[\left\{\frac{\exp(\beta r_A \mu^{1/2})}{1+\beta r_A \mu^{1/2}}\right\} + \left\{\frac{\exp(\beta r_D \mu^{1/2})}{1+\beta r_D \mu^{1/2}}\right\}\right]\exp(-\beta a \mu^{1/2}) \tag{5}$$

and

$$\beta = \left(\frac{8\pi N e^2}{1000 k_B T}\right)^{1/2} \tag{6}$$

and z is the charge on reactants, e is electron charge in esu, ϵ is static dielectric constant, r is the radius of the reactant plus counterion, μ is ionic strength, N is Avogadro's number, and k_B is Boltzmann's constant (in erg/Kelvin). This was calculated in erg/molecule and converted to eV. The values of r_A and r_D were determined using the Stokes−Einstein relation:

$$D = \frac{k_B T}{6\pi r \eta} \tag{7}$$

where D is the diffusion coefficient, T is temperature, and η is the solution viscosity. Viscosity measurements of the mixed solvent systems containing electrolyte were made on a Cannon−Fenske viscometer.

Chemicals. Acetonitrile (UV grade, Burdick and Jackson, Muskegon, MI) and benzene (HPLC grade, Aldrich,) were dried on an activated alumina column. Ferrocene and *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine (TMPD) (Aldrich) were purified by vacuum sublimation. 9,10-Diphenylanthracene (DPA, Aldrich) was recrystallized twice from absolute ethanol. 4,4′-Bis(*m*-tolylphenylamino)biphenyl (TPD) was purified by gradient sublimation. Preparation of 8-hydroxy-5-piperdinylquinolinesulfonamide ($Al(qs)_3$) has been published elsewhere.[21] The synthesis of *N*,*N*′-diisoamylquinacridone (DIQA) has also been described.[8a] Preparation of the TPD derivatives, 4,4′-bis(*m*-fluorophenyl-*m*′-tolylamino)biphenyl (*m*-FTPD), 4,4′-bis(*p*-methoxyphenyl-*m*′-tolylamino)biphenyl (*p*-MeOTPD), 4,4′-bis(*m*,*m*-difluorophenyl-*m*-tolylamino)biphenyl (*m*-DFTPD), has been published.[17a] The synthesis of 4,4′-bis(4,4′-t-butoxyphenylamino)biphenyl (*p*-tetraBuOTPD) will be published shortly.[17b] N-Ethyl-3,6-di-tert-butylcarbazole (ETBC) synthesis has also been published.[22] Tetrabutylammonium hexafluorophosphate (TBAH, Fluka) was used as received. All chemicals were dried overnight in a vacuum oven at 60 °C. All solutions were deoxygenated with solvent saturated nitrogen before use.

Results

The Gibbs free energy (ΔG) of reaction of the electrogenerated radical ions depends on the separation of the standard reduction potentials of the donor and acceptor participants in the light-producing reaction. The free energy determines the efficiency of light production because it dictates the mechanism by which emissive states are formed. In practice, this value is estimated from the potential difference between the cyclic voltammetric waves ($\Delta E_{1/2}$) of the oxidation and reduction processes, respectively.[9b] Specifically, the Gibbs free energy for the reaction of $D^{+\bullet}$ and $A^{-\bullet}$ is:

$$\Delta G = \Delta E_{1/2} - w_{a,\mu} + E_{0,0} \tag{8}$$

in which $\Delta E_{1/2}$ is $(E^\circ_{A,A^-} - E^\circ_{D,D^+})$, $w_{a,\mu}$ is the work required to bring together the ion reactants,[10c,20] and $E_{0,0}$ is the energy necessary to populate the excited singlet state (E_S), the excited triplet state (E_T), or the ground state (E_G) as determined from the (0−0) energy level transition. Because high ionic strength was used in all of the present experiments, $w_{a,\mu}$ was always $<$15 meV. By appropriate selection of conditions, precise control over the energetics of the ECL reactions can be achieved.[14,23,24] For example, the specific solvent employed affects the $\Delta E_{1/2}$[14,23b−d] as does altering the ionic strength of the solution.[14,23a,e] However, the most apparent route to controlling this value is by appropriate choice of precursor compounds.[12,24] This is the approach used in the following sections.

DIQA ECL with Energy-Sufficient Reactions. In previous work we demonstrated that the DIQA radical cation/radical anion system is an efficient ECL emitter.[16] In an OLED, such substituted quinacridones function as dopants which increase both the quantum efficiency (photons out/electrons in) and lifetime of the device.[8] They are, however, inappropriate as pure OLED luminescent layers due to their small Stokes shift, leading to significant self-absorption of the emitted light.[8] A dopant is either imbedded into a bulk polymer or used as a thin layer of its own. Typically, because the energy gap of the dopant is smaller, the light emission is red shifted from the luminescent material in the device. Dopants have been thought to emit primarily as a result of energy transfer; however, recent evidence

---

(19) Heinrich, G.; Schoof, S.; Gusten, H. *J. Photochem.* **1974/75**, *3*, 315−320.

(20) Debye, P. *Trans. Electrochem. Soc.* **1942**, *82*, 265.

(21) Hopkins, T. A.; Meerholz, K.; Shaheen, S.; Anderson, M. L.; Schmidt, A.; Kippelen, B.; Padias, A. B.; Hall, H. K., Jr.; Peyghambarian, N.; Armstrong, N. R. *Chem. Mater.* **1994**, *8*, 344−351.

(22) Ambrose, J. F.; Nelson, R. F. *J. Electrochem. Soc.* **1968**, *115*, 1159.

(23) (a) Keszthelyi, C. P.; Tokel-Takvoryan, N. E.; Tachikawa, H.; Bard, A. J. *Chem. Phys. Lett.* **1973**, *23*, 219−222. (b) Pighin, A.; Conway, B. E. *J. Electrochem. Soc.* **1975**, *122*, 619−624. (c) Mussel, R. D.; Nocera, D. G. *J. Phys. Chem.* **1991**, *95*, 6919−6924. (d) Kapturkiewicz, A. *J. Electroanal. Chem.* **1994**, *372*, 101−106. (e) Maness, K. M.; Wightman, R. M. *J. Electroanal. Chem.* **1995**, *396*, 85−95.

(24) (a) Weller, A.; Zachariasse, K. *J. Chem. Phys.* **1967**, *46*, 4984−4985. (b) Faulkner, L. R.; Tachikawa, H.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 691−699. (c) Wallace, W. L.; Bard, A. J. *J. Electrochem. Soc.* **1978**, *125*, 1430−1435. (d) Beideman, F. E.; Hercules, D. M. *J. Phys. Chem.* **1979**, *83*, 2203−2209.

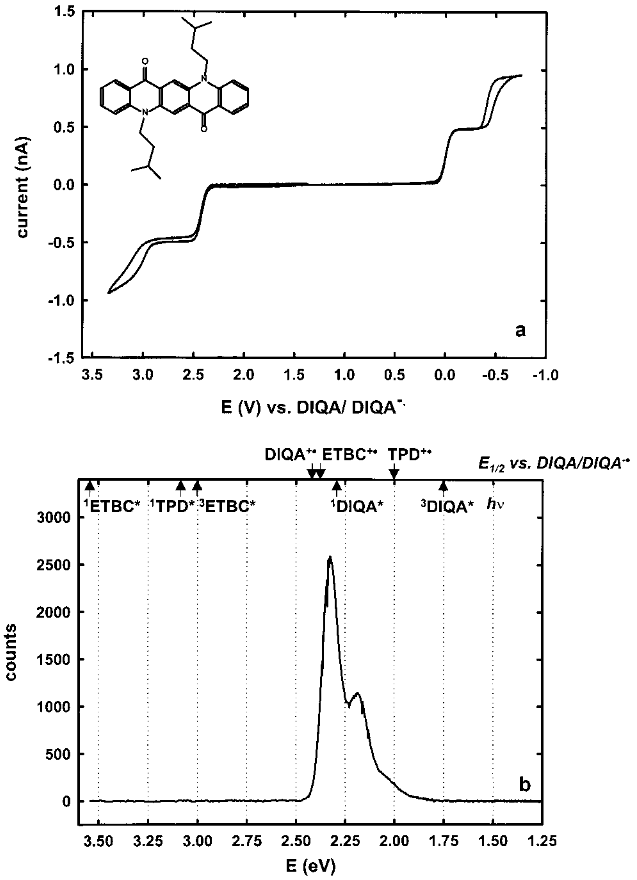

Figure 1. (a) Steady-state cyclic voltammogram of 400 μM DIQA in 70:30 ACN:BZ containing 0.1 M TBAH. Scan rate was 100 mV/s at a $r = 2.5$ μm Au disk. The structure of DIQA is shown. (b) ECL emission spectrum of 400 μM DIQA in 70:30 ACN:BZ containing 0.1 M TBAH. A square wave was applied at 500 Hz to a $r = 50$ μm Au disk. The light intensity was integrated over 60 s, and the data were digitally filtered with a first-order Chebychev filter at a sampling frequency of 2 Hz, a cutoff frequency of 0.05 Hz, and 1 dB band-pass ripples. At the top of the graph the energy levels are marked for DIQA$^{-\bullet}$ with various radical cation reaction partners. For DIQA $E_S = 2.32$ eV[16] and $E_T = 1.78$ eV.[26] The excited states of TPD ($E_S = 3.10$ eV[16]) and ETBC[27] ($E_S = 3.59$ eV and $E_T = 3.01$ eV) are inaccessible.

suggests that electron transfer also plays a part in light production in OLEDs.[8a,25]

In 70:30 ACN:BZ containing 0.1 M TBAH, DIQA exhibits reversible cyclic voltammetric waves for both its reduction and oxidation to the corresponding radical anion and cation (Figure 1a). The magnitude of $\Delta E_{1/2}$ (2.44 V) determined from this voltammogram indicates that the energetics of the combination reaction between DIQA$^{+\bullet}$/DIQA$^{-\bullet}$ are sufficient to produce directly the first excited singlet state of DIQA (2.32 eV).[16] Generation of ECL with a high-frequency square wave, with the limits set just beyond the first oxidation and reduction potentials, results in emission with a spectrum similar to the fluorescence of DIQA (Figure 1b). The efficiency of this light-producing reaction is remarkably high. When corrected for the luminescence efficiency ($\phi_{meas} = \phi_{fl}\phi_{ECL}$), the efficiency value in 70:30 ACN:BZ containing 0.1 M TBAH is 7%, higher than for DPA, one of the most efficient ECL systems.

The energetics of the DIQA system, both luminescent and electrochemical, are diagramed in Figure 1b for some of the systems investigated, and a complete list of the systems investigated in this work is given in Table 1. The donors selected for reaction with DIQA$^{-\bullet}$ are substituted triarylamines that are frequently used in the hole-transport layer of OLEDs.[28] These compounds have also been used to construct hole-transporting triphenyldiamine side-group polymers.[29] In addition, the compound ETBC, a derivative of the monomer in poly(*N*-vinylcarbazole), a common hole transporting polymer,[30] was used. As can be seen, only the reactions with ETBC$^{+\bullet}$ and DIQA$^{+\bullet}$ have sufficient energy to populate directly the excited singlet state of DIQA; the remainder only have sufficient energy to form the triplet state.

The ETBC$^{+\bullet}$/DIQA$^{-\bullet}$ cross-reaction generates bright ECL. The ECL emission spectrum of the ETBC$^{+\bullet}$/DIQA$^{-\bullet}$ system (data not shown) matches that of DIQA$^{+\bullet}$/DIQA$^{-\bullet}$ ECL (Figure 1b), indicating that the light originates from the first excited singlet state of DIQA. When the ETBC concentration is maintained in excess and ECL generated with a 1 kHz potential square wave, light emission is generated only during the negative potential step (Figure 2a) when the limiting reagent, DIQA$^{-\bullet}$, is formed. The peaked shape of this temporal profile is indicative of an S-route pathway.[12] When the ETBC concentration remains in excess and the DIQA concentration varied over a few orders of magnitude, the slope of a logarithmic plot of the light intensity versus DIQA concentration reveals the reaction order of DIQA in the rate-determining step. The best-fit line in Figure 2b (circles) determines a reaction order of approximately 1 for DIQA, establishing S-route behavior for the ETBC/DIQA system.

DIQA ECL with Energy-Insufficient Reactions. The reactions between DIQA$^{-\bullet}$ and the radical cations of the TPDs examined are expected to generate light via the T-route because of the $\Delta E_{1/2}$ and ΔG values for these reaction couples (Table 1). For example, when TPD is paired with DIQA, the magnitude of the $\Delta E_{1/2}$ for the couple (2.09 V) is energetically insufficient to produce directly ^{1}DIQA* via electron transfer. However, the ECL emission spectrum is identical with that in Figure 1b, revealing that the light arises from ^{1}DIQA*. To investigate the mechanism of first excited singlet formation, the ECL was examined during high-frequency potential steps. When the TPD concentration is in excess, ECL generated with a 1 kHz potential square wave occurs only during the negative potential step (Figure 2c) as with the ETBC/DIQA system. However, the temporal profile of the emission is quite different in that it remains more constant during the light-emitting potential step. This shape is characteristic of the T-route pathway.[12] When the TPD concentration is in excess and the DIQA concentration varied over a few orders of magnitude, the slope of a logarithmic plot of the light intensity versus DIQA concentration reveals

---

[25] (a) Wakimoto, T.; Murayama, R.; Nagayama, K.; Okuda, Y.' Nakada, H. *Appl. Surf. Sci.* **1997**, *113/114*, 698−704. (b) Uchida, M.; Adachi, C.; Koyama, T.; Taniguchi, Y. *J. Appl. Phys.* **1999**, *86*, 1680−1687.

[26] Shcherbo, S. N.; Val'kova, G. A.; Shigorin, D. N. *Russ. J. Phys. Chem.* **1981**, *55*, 452−453. The value used was for linear *N*-methylquinacridone.

[27] Hisada, K.; Tsuchida, A.; Ito, S.; Yamamoto, M. *J. Phys. Chem. B* **1998**, *102*, 2640−2645. The value used was for carbazole.

[28] (a) Kido, J.; Ohtaki, C.; Hongawa, K.; Okuyama, K.; Nagai, K. *Jpn. J. Appl. Phys*. **1993**, *32*, 917−920. (b) Tanaka, H.; Tokito, S.; Taga, Y.; Okada, A. *Chem. Commun.* **1996**, 2175−2176. (c) Giebeler, C.; Antoniadis, H.; Bradley, D. D. C.; Shirota, Y. *J. Appl. Phys.* **1999**, *85*, 608−615.

[29] (a) Bellman, E.; Shaheen, S. E.; Thayumanavan, S.; Barlow, S.; Grubbs, R. H.; Marder, S. R.; Kippelen, B.; Peyghambarian, N. *Chem. Mater*. **1998**, *10*, 1668−1676. (b) Shaheen, S. E.; Jabbour, G. E.; Kippelen, B.; Peyghambatian, N.; Anderson, J. D.; Marder, S. R.; Armstrong, N. R.; Bellman, E.; Grubbs, R. H. *Appl. Phys. Lett.* **1999**, *74*, 3212−3214. (c) Bellman, E.; Shaheen, S. E.; Grubbs, R. H.; Marder, S. R.; Kippelen, B.; Peyghambarian, N. *Chem. Mater*. **1999**, *11*, 399−407.

[30] Kido, J.; Shionoya, H.; Nagai, K. *Appl. Phys. Lett.* **1995**, *67*, 2281−2283.

Table 1. Data for the Reactions of Various Radical Cations with $Al(qs)_3^{-\bullet}$ and $DIQA^{-\bullet}$ (All ϕ_{ECL} Values Are Relative to a $TMPD^{+\bullet}/DPA^{-\bullet}$ Standard, See Text)

solvent	system	$\Delta E_{1/2}$ (V)	$\Delta^{S}G$ (eV)[a]	$\Delta^{T}G$ (eV)[b]	$\phi_{ecl}{}^{c}/\phi_{ecl,TMPD-DPA}$
70:30 ACN:BZ	$DIQA^{-\bullet}$				
	p-tetraBuOTPD$^{+\bullet}$	−1.92	0.41	−0.14	0.12 ± 0.02
	p-MeOTPD$^{+\bullet}$	−2.01	0.32	−0.22	0.99 ± 0.03
	TPD$^{+\bullet}$	−2.09	0.24	−0.30	1.69 ± 0.04
	m-FTPD$^{+\bullet}$	−2.19	0.14	−0.40	1.88 ± 0.09
	m-DFTPD$^{+\bullet}$	−2.29	0.04	−0.50	3.4 ± 0.3
	ETBC$^{+\bullet}$	−2.42	−0.10	−0.64	*d*
	DIQA$^{+\bullet}$	−2.44	−0.11	−0.65	17.6 ± 0.2
70:30 ACN:BZ	$Al(qs)_3^{-\bullet}$				
	p-tetraBuOTPD$^{+\bullet}$	−2.04	0.44	0.09	0.0028[e]
	p-MeOTPD$^{+\bullet}$	−2.14	0.34	−0.01	0.068 ± 0.008
	TPD$^{+\bullet}$	−2.23	0.25	−0.10	1.17 ± 0.06[f]
	m-FTPD$^{+\bullet}$	−2.32	0.16	−0.19	3.7 ± 0.4
	m-DFTPD$^{+\bullet}$	−2.43	0.05	−0.30	5.6 ± 0.6
	ETBC$^{+\bullet}$	−2.59	−0.11	−0.46	1.88 ± 0.08
50:50 ACN:TOL	*p*-tetraBuOTPD$^{+\bullet}$	−2.08	0.39	0.04	0.00055 ± 0.00003[f]
	p-MeOTPD$^{+\bullet}$	−2.22	0.25	−0.10	0.018 ± 0.005
	TPD$^{+\bullet}$	−2.32	0.15	−0.20	1.58 ± 0.04
	m-FTPD$^{+\bullet}$	−2.43	0.04	−0.31	5 ± 3
	m-DFTPD$^{+\bullet}$	−2.56	−0.09	−0.44	0.9 ± 0.1

[a] $\Delta^{s}G$ = free energy of excited singlet production; $^{1}Al(qs)_3^* = 2.47$ eV,[16] $^{1}DIQA^* = 2.32$ eV.[16] [b] $\Delta^{T}G$ = free energy of excited triplet production; $^{3}Al(qs)_3^* = 2.12$ eV,[31] $^{3}DIQA^* = 1.78$ eV [26]. [c] For all efficiency calculations, three measurements were made, and the mean and standard deviation were calculated unless otherwise noted. The fluorescence quantum efficiencies for DIQA and $Al(qs)_3$ versus DPA were 0.8 and 0.3. [d] Due to interference from $DIQA^{+\bullet}$ when the compounds are at equal concentrations, the efficiency could not be calculated. [e] One measurement. [f] Two measurements.

that the rate of light emission is second order in [DIQA]. The line in Figure 2b (diamonds) establishes T-route behavior for the TPD/DIQA system.

ECL of $Al(qs)_3$. $Al(qs)_3$ is a derivative of aluminum quinolate (Alq_3), a common lumophore in OLEDs. The addition of the sulfonamide groups enhances the solubility in common organic solvents, improves the electrochemical behavior,[16] and causes a blue shift in the fluorescence spectrum.[21] Reduction of $Al(qs)_3$ gives a stable radical anion; however, its oxidation is irreversible and more positive than the oxidations of the other compounds examined. When the ECL of $Al(qs)_3^{+\bullet}/Al(qs)_3^{-\bullet}$ is examined with the application of a high-frequency square wave, light is only produced during the positive potential step due to the instability of $Al(qs)_3^{+\bullet}$. The amount of light decreases quickly, and has a lower intensity than nearly all of the other ECL reactions between $Al(qs)_3$ and the hole transport materials. Comparable results have been obtained in ECL processes with the parent compound, Alq_3. Consistent with the instability of the radical cation in solution, in the solid state it is suspected to lead to deterioration of the OLEDs.[7]

The ECL of $Al(qs)_3$ was also evaluated with various TPD's and ETBC in two different solvent mixtures. These solvent mixtures were selected to have sufficiently different dielectric constants as to measurably affect the values of $\Delta E_{1/2}$. The $\Delta E_{1/2}$ values were approximately 80 mV larger in 50:50 ACN:TOL vs 70:30 ACN:BZ solvents (Table 1). ECL from the solvent/TPD mixtures without $Al(qs)_3$ precluded a detailed study of $Al(qs)_3$ excited singlet state formation as a function of concentration. However, as can be seen from the electrochemical values (Table 1), the majority of the systems are energy-insufficient with respect to the singlet state. For example, the magnitude of $\Delta E_{1/2}$ (2.23 V) between the oxidation of TPD to its radical cation and reduction of $Al(qs)_3$ to its radical anion (Figure 3a) in 70:30 ACN:BZ containing 0.1 M TBAH, is less than the 2.47 eV required to produce $^{1}Al(qs)_3^*$ via the singlet route. An ECL emission spectrum (Figure 3b), however, reveals that the emission is from $^{1}Al(qs)_3^*$. A similar spectrum was found for the TPD/$Al(qs)_3$ mixture in 50:50 ACN:TOL.[16] Additionally, the temporal profile of the emission is consistent with the T-route (Figure 2d). Thus, we conclude that the singlet is formed via triplet−triplet annihilation in all of the energy-insufficient systems in both solvents. Figure 4 shows a plot of all of the efficiency data versus $\Delta^{T}G$.

Discussion

Our prior work established that small molecules used as components of OLEDs also can be used to generate light via ECL, and that the emission had quite similar characteristics to that in the solid state.[16] The object of the present work was to determine the mechanism of singlet formation during ECL, especially when the energy released in a cross reaction does not appear to be sufficient to populate the singlet state directly. A series of donors which differed in their oxidizing power were chosen to be reactants with $DIQA^{-\bullet}$ and $Al(qs)_3^{-\bullet}$ so that the effect of a systematic variation of ΔG of reaction on light intensity could be probed. While previous studies have manipulated the solution conditions, i.e., solvent and electrolyte concentration, and used different precursor compounds,[24] the range of ΔG for the ECL reaction used in this work has been manipulated over a much wider range (~0.75 eV) than in previous studies (Table 1).[14,23]

For the majority of light-emitting partners studied, the energy available for reaction (computed from the measured $\Delta E_{1/2}$ values with eq 8) predicts that the available energy is insufficient to form the singlet directly. Nevertheless, in all cases the observed emission is from the excited singlet. For reaction of $DIQA^{-\bullet}$ with $DIQA^{+\bullet}$ or $ETBC^{+\bullet}$, sufficient energy is available to directly form the singlet via electron transfer:

$$A^{-\bullet} + D^{+\bullet} \xrightarrow{k'_s} {}^{1}A^* + D \qquad (9)$$

followed by light emission. Consistent with this scheme, the reaction of $DIQA^{-\bullet}$ and $ETBC^{+\bullet}$ is first order with respect to DIQA. Most of the remaining partners, however, do not have sufficient energy to populate the singlet state directly. They do,

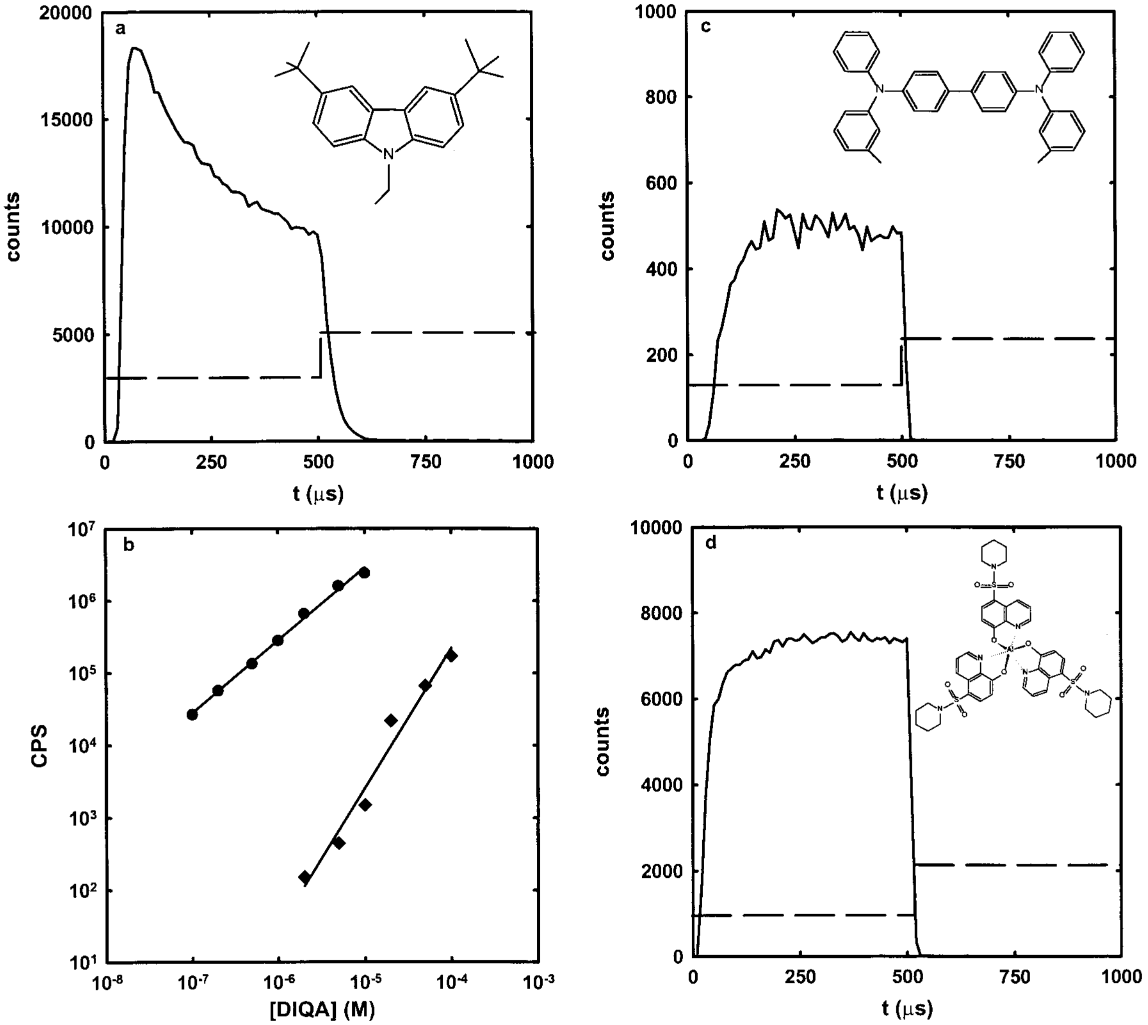

Figure 2. (a) Temporal ECL emission profile for a solution of 100 μM ETBC and 2 μM DIQA in 70:30 ACN:BZ containing 0.1 M TBAH. In parts a, b, and c, a 1 kHz square wave (dotted lines) was applied to a $r = 30$ μm Au disk, and data were collected in 10 μs bins for 1000 cycles of the square wave (1 s collection total). The structure of ETBC is shown. (b) Logarithmic plot of light intensity in cumulative counts per second (CPS) versus DIQA concentration in 70:30 ACN:BZ containing 0.1 M TBAH for (●) an ETBC concentration of 100 μM and (◆) a TPD concentration of 1 mM. The equations for the linear regressions are log(CPS) = 1.0054 log[DIQA] + 11.485 ($R^2 = 0.9959$) and log(CPS) = 1.9362 log[DIQA] + 13.091 ($R^2 = 0.9690$), respectively. (c) Temporal ECL emission profile for a solution of 1 mM TPD and 20 μM DIQA in 70:30 ACN:BZ containing 0.1 M TBAH. The structure of TPD is shown. (d) Temporal ECL emission profile for a solution of 1 mM TPD and 50 μM Al(qs)$_3$ in 50:50 ACN:TOL containing 0.1 M TBAH. A 1 kHz square wave (dotted line) was applied to a 3 μm wide Au band. Data were collected in 10 μs bins for 6000 cycles of the square wave (6 s collection total). The structure of Al(qs)$_3$ is shown.

however, have sufficient energy to form excited triplet states via electron exchange:

$$A^{-\bullet} + D^{+\bullet} \xrightarrow{k'_t} {}^3A^* + D \qquad (10)$$

Triplet–triplet annihilation can then result in a singlet state:

$${}^3A^* + {}^3A^* \xrightarrow{k_{tta}} {}^1A^* + A \qquad (11)$$

with subsequent emission of a photon. Consistent with this mechanism, the reaction of DIQA$^{-\bullet}$ and TPD$^{+\bullet}$ is second order with respect to DIQA. For the other energy-insufficient systems, the temporal behavior of the emission curves with the donor in excess provided evidence of the triplet route to emission from a singlet state. The characteristic shape of emission for T-route mechanisms arises because the rate of reaction 11 is slow relative to the rate of electron transfer.[12]

For both mechanisms, the efficiency of light production is directly related to the velocity of the rate determining step of the light-forming reactions relative to those with which it competes. Reactions 9 and 10 are electron-transfer reactions in which the excited state is formed as a consequence of formation of an encounter complex of the radical ions:

$$A^{-\bullet} + D^{+\bullet} \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} [A^{-\bullet}\text{—}D^{+\bullet}] \xrightarrow{k_{et}} {}^3A^* + D \qquad (12)$$

Thus, the bimolecular rate constant (k' in reactions 9 and 10) is actually a composite of the microscopic rate constants $(k_{et}k_d)/(k_{et} + k_{-d})$, where k_d and k_{-d} are the diffusion-controlled rate constants for formation and dissociation of the encounter complex, and k_{et} is the unimolecular electron-transfer rate constant.[32] The unimolecular rate coefficient for electron transfer (k_{et}) for each annihilation reaction can be related to ΔG through

---

(31) Fernandez de la Campa, M. R.; Liu, Y. M.; Díaz García, M. E.; Sanz-Medel, A. *Anal. Chim. Acta* **1990**, *238*, 297–305. This value is for an aluminum–ferron chelate which is similar in structure to Al(qs)$_3$.

(32) (a) Chiorboli, C.; Indelli, M. T.; Scandola, M. A. R.; Scandola, F. *J. Phys. Chem.* **1988**, *92*, 156–163. (b) Collinson, M. M.; Pastore, P.; Wightman, R. M. *J. Phys. Chem.* **1994**, *98*, 11942–11947.

(33) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271.

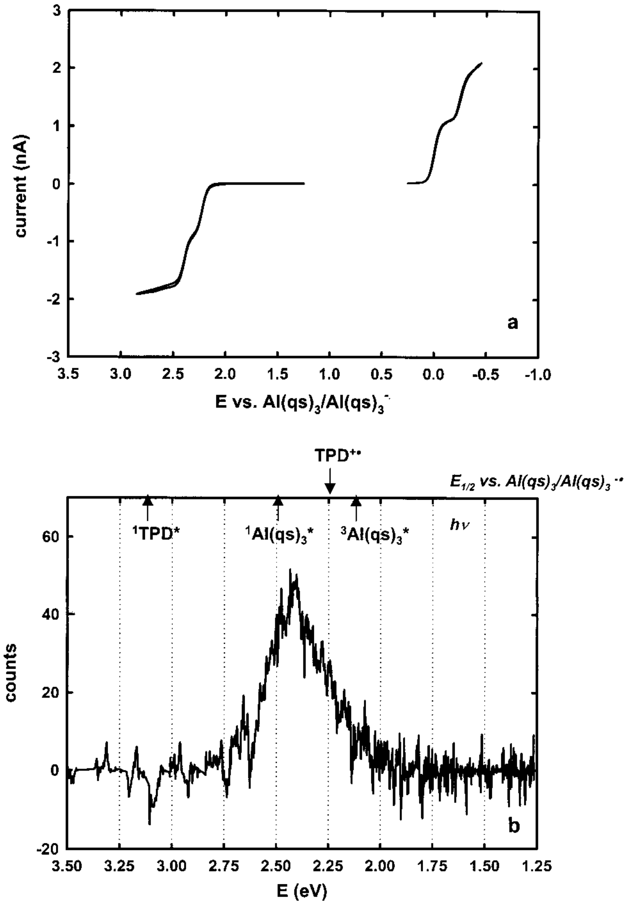

Figure 3. (a) Steady-state cyclic voltammogram of 1 mMAl(qs)$_3$ and 1 mM TPD in 70:30 ACN:BZ containing 0.1 M TBAH. Scan rate was 50 mV/s at a $r = 2.5$ μm Au disk. (b) ECL emission spectrum of 1 mM Al(qs)$_3$ and 1 mM TPD in 70:30 ACN:BZ containing 0.1 M TBAH. A square wave was applied at 500 Hz to a $r = 50$ μm Au disk. The light intensity was integrated over 60 s, and the data were digitally filtered with a first-order Chebychev filter at a sampling frequency of 2 Hz, a cutoff frequency of 0.05 Hz, and 1 dB band-pass ripples. At the top of the graph the energy levels are marked for Al(qs)$_3^{-\bullet}$ with TPD$^{+\bullet}$. For Al(qs)$_3$ $E_S = 2.47$[16] eV and $E_T = 2.12$ eV.[31] The excited states of TPD are inaccessible.

classical electron transfer theory[10a−c] by

$$k_{et} \propto \exp\left[\frac{-(\Delta G - \lambda)^2}{4\lambda k_B T}\right] \tag{13}$$

in which k_B is Boltzmann's constant, T is temperature, and λ is the sum of the inner-sphere and the outer-sphere reorganizational energies. Thus, as ΔG becomes more negative, k_{et} increases until the magnitude of ΔG becomes equal to λ, then decreases as ΔG becomes greater in magnitude than λ. Usually for bimolecular reactions, this predicted decrease in rate is not observed experimentally because the overall rate of reaction becomes limited either by k_d or the production of low-lying electronic excited states of the radical ions.[33] Alternately, in the case of the T-route, the decrease in rate is not seen because the reaction in eq 11 becomes rate-limiting. The changes in ECL efficiency with ΔG of other S-route ECL systems are consistent with a rate-limiting electron transfer for the singlet formation, and diffusion control for the competing reactions.[32b]

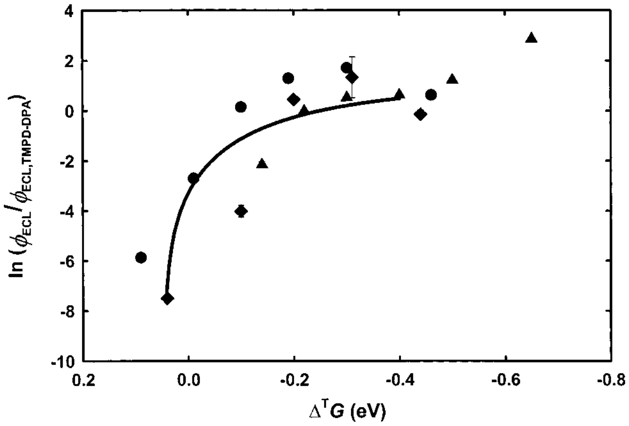

Figure 4. Plot of log of ECL quantum efficiency as a function of $\Delta^T G$. ECL values have been corrected for differences in fluorescence quantum efficiencies and normalized to the ECL from the TMPD-DPA system (eq 1). Al(qs)$_3$ systems in 1:1 ACN:TOL (◆); Al(qs)$_3$ systems in 70:30 ACN:BZ (●); DIQA systems in 70:30 ACN:BZ (▲). All solutions contain 0.1 M TBAH. The regression curve is a plot of a rate expression with consecutive second-order reactions in which only the first reaction depends on ΔG. The four points with the greatest $\Delta^T G$ were not included in the regression because they are predicted to produce light via the S-route. In the plot, some of the error bars are hidden by the symbols.

Figure 4 shows the efficiency of light production for all of the systems studied as a function of ΔG for formation of the triplet state ($\Delta^T G$) from the electron transfer between the radical ions. First, at low values of $\Delta^T G$, the efficiency exponentially increases as the free energy becomes more exothermic. While, in the case of rubrene ECL, this type of behavior has previously been suggested to be indicative of a combined S and T-route,[10d,23a,34] it seems more likely in this case that it simply reflects rate-limiting control by the electron-transfer reaction that forms the triplet (predicted by eq 13). At intermediate values of $\Delta^T G$, the efficiencies reach a plateau, the behavior predicted when reaction 11 is rate-limiting. Because this reaction does not depend on the energetics of the radical ions, the efficiency shows no dependence on $\Delta^T G$. Finally, at the most negative $\Delta^T G$ values, ϕ_{ECL} appears to increase again. However, in these cases most reactants have sufficient energy to form the singlet directly. From the plot, it is apparent that when the T-route is rate-limiting, it can become almost as efficient as the S-route, especially at high reagent concentrations.

Thus, the experimental data from ECL experiments clearly show that excited singlet states from lumophores similar to those used in OLEDs can be formed from precursor radical ions by both the S- and T-route. Furthermore, the data demonstrate that both the pathway and relative efficiency of light production can be predicted from the energy available for reaction. Previous studies have proposed or positively identified radical cations and radical anions (polarons) as the charge-transporting species in condensed phase organic materials such as those in use for OLEDs, and we would predict that their relative energies of formation would control the energetics for recombination and the pathway that is taken to production of emissive states.[6,25,35] While the S-route formation of singlets has been proposed in the solid state,[16] the T-route to singlet formation has been less often invoked.[6] The presence of high concentrations of triplet states, even in materials where recombination is energetic enough to occur via the S-route, is clear, as seen from recent

---

[34] (a) Glass, R.; Faulkner, L. R. *J. Phys. Chem.* **1982**, *86*, 1652−1658. (b) Kim, J.; Faulkner, L. R. *J. Am. Chem. Soc.* **1988**, *110*, 112−119.

[35] (a) Ziemelis, K. E.; Hussain, A. T.; Bradley, D. D. C.; Friend, R. H.; Rühe, J.; Wegner, G. *Phys. Rev. Lett.* **1991**, *66*, 2231−2234. (b) Charra, F.; Lavie, M.; Lorin, A.; Fichou, D. *Synth. Met.* **1994**, *65*, 13−17. (c) Redecker, M.; Bässler, H. *Appl. Phys. Lett.* **1996**, *69*, 70−72. (d) Redecker, M.; Bässler, H.; Hörhold, H. H. *J. Phys. Chem. B* **1997**, *101*, 7398−7403.

studies where dopants are added to the lumophore layer to efficiently harvest those excited states.[36]

We can estimate the viability of light production via a T-route mechanism by consideration of the changes expected in the energetics of the redox processes studied here, extrapolated to condensed phase, nonpolar environments. The central intermediate that must be formed either in solution or in the solid state is the encounter complex that precedes electron transfer. In solution, the free energy of this state relative to the ground state is computed as a function of the $\Delta E_{1/2}$ values to form the radical anion and cation corrected by the work required to bring the reactants together (eq 8). For the solution conditions used in these experiments the dielectric constant ($\epsilon = 21$ for 70:30 ACN:BZ)[37] and ionic strength ($\mu = 0.1$ M) were sufficiently high that the work function was negligible and for ground-state production $\Delta G \approx \Delta E_{1/2}$. Following Weller[38] and the relationship between the oxidation and reduction potentials to ionization potential (IP) and electron affinity (EA),[23e,39] the free energy of the encounter complex relative to the ground state is given by:

$$\Delta G = -IP_{\mathrm{D}} + EA_{\mathrm{A}} - \Delta G^{\circ}_{\mathrm{solv,D^+}} - \Delta G^{\circ}_{\mathrm{solv,A^-}} - w_{\mathrm{a},\mu} \qquad (14)$$

where $\Delta G^{\circ}_{\mathrm{solv}}$ is the Born solvation energy of the charged species (the solvation energy of the neutral species is negligible), expressed as

$$\Delta G^{\circ}_{\mathrm{solv,A^-,D^+}} = -\frac{e^2}{2}\left(\frac{1}{r_{\mathrm{A}}} + \frac{1}{r_{\mathrm{D}}}\right)\left(1 - \frac{f}{\epsilon}\right) \qquad (15)$$

where r is the radius, ϵ is the dielectric constant of the medium, and f (eq 5) is an ionic strength factor ($f = 1$ for an ionic strength of 0). These equations allow for the calculation of the free energy available for reaction in a medium of any dielectric or ionic strength. Because EA values have been measured for only a limited number of organic molecules,[40] we must estimate it in this case. The EA of a compound can be computed from the measured $\Delta E_{1/2}$ and the reported IP:[16]

$$\Delta E_{1/2} = -\mathrm{IP}_{\mathrm{D}} + EA_{\mathrm{A}} - \Delta G^{\circ}_{\mathrm{solv,D^+}} - \Delta G^{\circ}_{\mathrm{solv,A^-}} \qquad (16)$$

For the $\Delta E_{1/2}$ values for TPD and *m*-FTPD with $\mathrm{Al(qs)_3}$ and DIQA (Table 1), EA values were estimated to be 1.35 and 1.26 ± 0.05 eV, respectively. Using these values for electron affinity, the ΔG available for the reaction of TPD or *m*-FTPD with $\mathrm{Al(qs)_3}$ in thin film with a dielectric constant of 5 and ionic strength of 0 were determined to be 2.44 and 2.46 eV, respectively. These are just below the amount of energy required to produce $^1\mathrm{Al(qs)_3}^*$ (2.47 eV). Under the same conditions, the ΔG values available for the reaction of TPD or *m*-FTPD with DIQA were calculated to be 2.33 and 2.34 eV, respectively. These values are just higher than the energy of $^1\mathrm{DIQA}^*$ (2.32 eV). These values are summarized in the upper axes of Figures 1b and 3b. These calculations suggest that, for the molecules studied here, taken to condensed phase environments, ECL-like “cross-reactions” will be marginal for light production via the S-route, suggesting that light will arise from a “mixed” S and T-route. Studies are underway to characterize such processes.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE-9800560 to R.M.W.) and by the ONR-MURI Center for Multifunctional Polymers and Molecular Assemblies (CAMP to N.R.A.). The assistance of M. E. Williams and A. C. Templeton in flourescence experiments and S. M. Gross in absorbance measurements is gratefully acknowledged.

JA0005993

---

(36) (a) Baldo, M. A.; O’Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151−154. (b) Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *75*, 4−6.

(37) Kolling, O. W. *Anal. Chem.* **1985**, *57*, 1721−1725.

(38) (a) Weller, A. *Pure Appl. Chem.* **1968**, *16*, 115−123. (b) Weller, A. *Z. Phys. Chem.* **1982**, *133*, 93−98.

(39) Peover, M. E. In *Electroanalytical Chemistry: A Series of Advances*; Bard, A. J., Ed.; Dekker: New York, 1967; Vol. 2, p 40.

(40) Lias, S. G.; Bartness, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data*, **1988**, *17* (Suppl. 1).