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Contrasting Electrogenerated Chemiluminescence for a Dissolved and Surface-Attached Carbazole Thiophene Cyanoacrylate Dye

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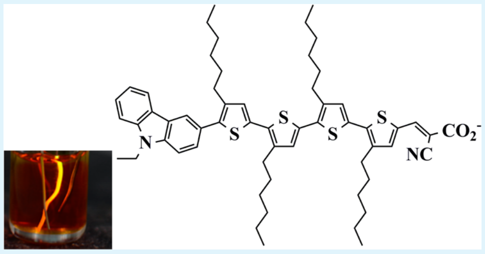
ABSTRACT: The electrogenerated chemiluminescence (ECL) of a carbazole thiophene cyanoacrylate dye ((2-cyano-3-[5‴-(9-ethyl-9H-carbazol-3-yl)-3′,3″,3‴,4-tetra-*n*-hexyl-[2,2′,5′,2″,5″,2‴]-quarter-thiophenyl-5yl]acrylate) = MK-2) has been investigated in solution, where the maximum ECL wavelength occurs at 640 nm, and in a thin film on an ITO surface, where the ECL is substantially red-shifted to 730 nm. The ECL intensity for the solution annihilation reaction is relatively weak, whereas a much higher ECL intensity is measured with oxalate as a co-reactant. This result is attributed to the two Nernstian reversible oxidation waves of the thiophene moiety of MK-2, whereas the reduction is stabilized by the unblocked carbazole and cyanoacrylate groups.

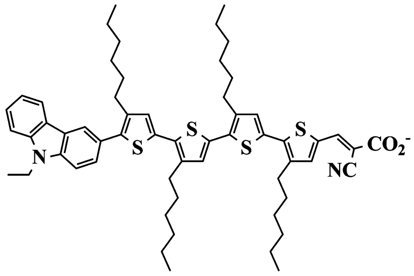


KEYWORDS: *aggregation, ECL shift, oligothiophenes, carboxylate binding, thin film emission*

1. INTRODUCTION

Electrogenerated chemiluminescence (ECL) is a phenomenon where high-energy reactive species are electrochemically produced that subsequently react with another electrogenerated species or a coreactant to produce an emissive excited state.[1−5] Often, the light is generated through the diffusion of a dissolved species to an electrode surface or through electron transfer to a surface film.[1] In all known cases, the maximum ECL wavelength of the surface film has only a small shift of ∼20−30 nm, compared to the solution ECL.[6−8] Herein, we report that the ECL wavelength of the carbazole thiophene cyanoacrylate dye, (2-cyano-3-[5‴-(9-ethyl-9H-carbazol-3-yl)-3′,3″,3‴,4-tetra-*n*-hexyl-[2,2′,5′,2″,5″,2‴]-quaterthiophenyl-5yl]acrylate (MK-2, see Scheme 1), is significantly different in solution than in a thin film on an indium tin oxide (ITO) electrode.[9,10]

Scheme 1. Chemical Structure of MK-2 Dye



ECL is a process with broad range of applications in various areas such as bioassays, light-emitting devices, and lasing technologies.[1,11−13] There are several different mechanisms to produce ECL. The most common mechanism is an annihilation that involves simultaneous electrochemical reduction and oxidation of one or a mixture of compounds resulting in the formation of stable radical cations and radical anions. The produced radical ions can react with each other to produce a species in an excited state, as shown in Scheme 2:[14]

Scheme 2

$$A + e \rightarrow A^{\bullet -} \tag{1}$$

$$A - e \rightarrow A^{\bullet +} \tag{2}$$

$$A^{\bullet +} + A^{\bullet -} \rightarrow {}^{1}A^{*} + A \tag{3}$$

$${}^{1}A^{*} \rightarrow A + h\nu \tag{4}$$

Another mechanism for efficient light generation uses a so-called co-reactant that, upon oxidation or reduction, can produce a highly reduced or oxidized species, capable of generating an emissive excited state. This mechanism allows practical applications of ECL in aqueous solutions without deaerating the solvent[1] and is widely used in commercial labeling applications. The most commonly used reducing co-reactants are oxalate and tripropylamine and the common oxidizing co-reactants are benzoyl peroxide and persulfates. An example of a co-reactant mechanism using oxalate is presented in Scheme 3. An oxidizing potential is applied to the electrode

Scheme 3

$$C_2O_4^{2-} - e \rightarrow C_2O_4^{-} \rightarrow CO_2^{\bullet -} + CO_2 \tag{5}$$

$${}^{1}A^{\bullet +} + CO_2^{\bullet -} \rightarrow {}^{1}A^{*} + CO_2 \tag{6}$$

$${}^{1}A^{*} \rightarrow A + h\nu \tag{7}$$

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surface that is sufficient to simultaneously generate both stable radical cation $A^{\bullet +}$ and produce highly reducing $CO_2^{\bullet -}$ radical as in Scheme 3:

Most ECL processes go through a singlet excited state (S-route), although ECL emission through the formation of a triplet state is also possible. The formation of the triplet excited state is usually lower in energy compared to the energy needed to produce singlet−singlet annihilation and a fluorescent singlet state can then be produced through triplet−triplet annihilation (T-route), as shown in Scheme 4.

Scheme 4

$$A^{\bullet +} + A^{\bullet -} \rightarrow {}^3A^* + A \quad (8)$$

$$^3A^* + {}^3A^* \rightarrow {}^1A^* + h\nu \quad (9)$$

ECL from the films on electrodes should be similar to that in solution; however, the ECL intensity is not controlled by diffusion as in solution.[1]

2. EXPERIMENTAL SECTION

Chemicals. The solvents acetonitrile, benzene, and tetrahydrofuran (THF) were obtained from Sigma−Aldrich (Milwaukee, WI) and used as received. MK-2 (95%) was also obtained from Sigma−Aldrich and further purified by recrystallization from $CHCl_3$−ethanol.[9] $Ru(bpy)_3(ClO_4)_2$ was obtained from Sigma−Aldrich and recrystallized from ethanol. Tetrabutylammonium oxalate ($TBAC_2O_4$) was prepared by mixing tetra-*n*-butylammonium hydroxide (TBAOH) and oxalic acid (both from Sigma−Aldrich) in a molar ratio of 2:1 and drying under vacuum.[15]

Experimental Procedures. Absorbance and fluorescence spectra for MK-2 in 50%−50% benzene:acetonitrile mixtures and in a film state were measured using a Lambda 950 spectrophotometer (Perkin−Elmer, Waltham, MA) and a Cary Eclipse Varian (Agilent, Santa Clara, CA) fluorescence spectrometer. A quartz cell with a path length of 1 cm (Spectrocell, Oreland, PA) was used in both analyses. The fluorescence spectra were excited at the absorbance maximum. Cyclic voltammetry measurements were done using an Ivium Compact Stat potentiostat (Eindhoven, The Netherlands) and a three-electrode setup with an 0.0314 cm^2 platinum working electrode and platinum and silver wires as counter and reference electrodes (Alfa Aesar, Ward Hill, MA). The platinum working electrode was polished with 0.3 μM size alumina and sonicated in water for 10 min prior to every electrochemical measurement. The presence of a clean electrode surface was confirmed using an optical microscope (Olympus, Center Valley, PA). The geometric area of the electrode was obtained using chronoamperometric analysis, and the Cottrel equation, assuming a diffusion coefficient for ferrocene in acetonitrile of 1.2×10^{-5} cm^2/s.[16] The electrode potential was calibrated using ferrocene as a standard with a potential of +0.342 V vs SCE.[17] A glass vial containing the electrolyte served as an electrochemical cell and was sealed by using a Teflon cap. Solutions were prepared in an anhydrous oxygen-free glovebox (Vacuum Atmospheres, Hawthorne, CA) with feedthroughs for electrical connections. Surface films of the MK-2 were prepared by depositing 0.05 mL of 0.5 mM 50%−50% benzene:acetonitrile MK-2 solution dropwise onto an 0.5 cm^2 indium tin oxide (ITO) electrode (Sigma−Aldrich) with an active area of 0.03 cm^2 MK-2. Digital simulations of the cyclic voltammograms were carried out using DigiElch Electrochemical Software (Gamry Instruments, Warminister, PA). Electrogenerated chemiluminescence (ECL) spectra were measured by alternating potential steps to 80 mV past the dyes reduction and oxidation potentials (1.0 V and −1.5 V vs SCE) with a frequency of 10 Hz for annihilation experiments and holding the potential at 1.0 V for 2 min in the case of using oxalate as a co-reactant. A platinum wire was used as a working electrode in ECL experiments, and the spectra were recorded using a Cary Eclipse Varian fluorescence spectrometer.

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical Investigations. The electrochemical behavior of a dye can provide information about the relative and absolute energy positions of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels that are relevant to both dye sensitization and ECL. MK-2 has been shown to be an effective sensitizer in dye-sensitized solar cells by injecting photoexcited electrons into nanocrystalline TiO_2. The light-to-electricity conversion efficiency for this cell is ∼8.0%.[9−18] Cyclic voltammograms of MK-2 at a platinum electrode are shown in Figure 1.

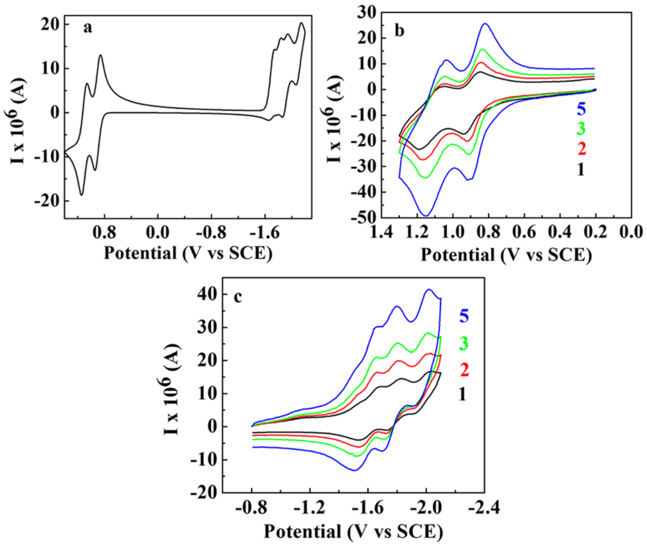

Figure 1. Cyclic voltammograms of 0.5 mM solution of MK-2 dye: (a) full scan and (b, c) scan rate (V/s) dependence for 0.28 mM dye in solution of a 50%−50% benzene:acetonitrile mixture with 0.1 M $TBAPF_6$ used as a solvent and supporting electrolyte. A platinum electrode with an area of 0.0314 cm^2 was used as a working electrode.

MK-2 demonstrates electrochemical behavior typical of an oligomeric thiophene dye with two reversible oxidation waves (Figures 1a and 1b).[19−21] Sterically blocked oligothiophenes with small polymerization chain lengths also have two characteristic reversible reduction waves.[19,20] The reversibility of MK-2 reduction is perturbed by the presence of additional electrochemically active substituents. Carbazole moieties with no alkyl protecting groups usually show irreversible reductions due to following chemical reactions involving the accessible carbon atoms of the reduced species (Figure 1c).[22,23] Reduction of an ethyl acrylate group at −2.1 V vs SCE has also been previously reported and could also contribute to the electrochemical reduction of MK-2.[24]

Digital simulations of cyclic voltammograms for the oxidation of MK-2 provide estimates of the oxidation and reduction standard potentials and also diffusion coefficients and kinetic parameters (see Figure 2).

The best achieved fit is for consecutive one-electron transfers with standard oxidation potentials of 0.87 and 1.10 V vs SCE, a diffusion coefficient of 3.1×10^{-5} cm^2/s, and a fast heterogeneous rate constant of >1 cm/s. The thiophene center of the molecule is not blocked by bulky substituents, which allows for fast heterogeneous kinetics. Slower heterogeneous rate constants of ∼0.02 cm/s have been recorded for rigid

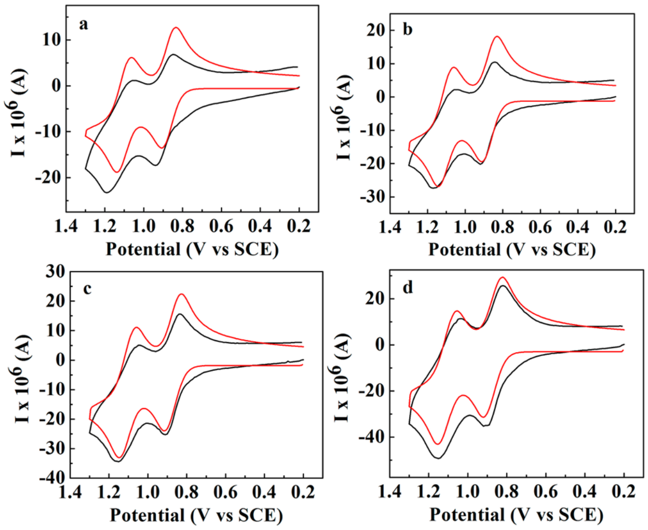

Figure 2. Experimental and digital simulations of cyclic voltammograms at various scan rates: (a) 1 V/s, (b) 2 V/s, (c) 3 V/s, and (d) 5 V/s. A resistance of 500 Ω and a capacitance of 6×10^{-7} F were used in the simulations.

bulky organic fluorophores.[25] Some deviation of the simulations, compared to the experiments at slow scan rates, can be attributed to the instability of doubly charged radical cations.[16]

Evaporation of a drop of 0.5 mM 50%−50% benzene:acetonitrile MK-2 solution onto an ITO electrode should result in the formation of strong bonds between the carboxylate groups of the dye and ITO.[18,26−28] Characteristic surface waves are recorded near the potentials of the solution waves after the evaporation step (see Figures 3a and 3b).

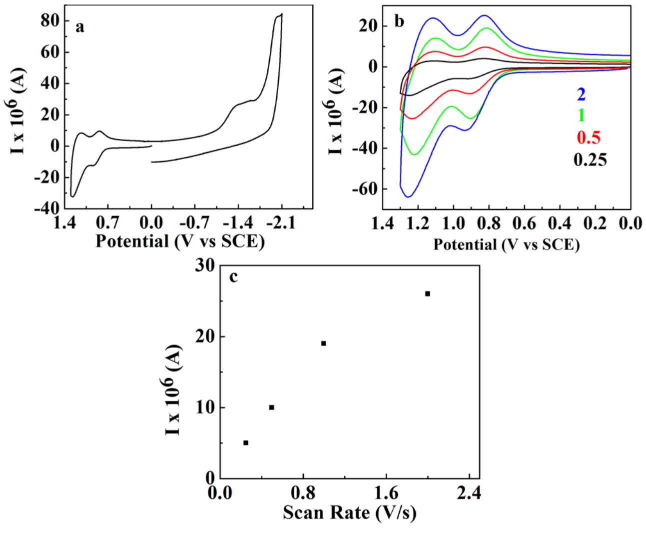

Figure 3. Cyclic voltammograms for MK-2 films deposited from a solution of 0.5 mM onto ITO: (a) full scan and (b) scan rate dependence (V/s); (c) current vs scan rate dependence for data from panel (b). A 50%−50% benzene:acetonitrile mixture with 0.1 M $TBAPF_6$ was used as a solvent and supporting electrolyte. An ITO electrode with an area of 0.5 cm^2 (active area with 0.03 cm^2 MK-2) was used for the surface film measurements. The electrode with MK-2 solution was submerged in solution with the electrolyte prior the electrochemical measurements for 1 h.

The magnitude of the current has a nearly linear scan rate dependence, providing further confirmation of the surface attachment (Figure 3c). Deviation from the linearity at faster scan rates might be due to desorption of the surface-bound radical anions. The surface coverage of the MK-2 on ITO, obtained from the peak current values at slow scan rates, is $\sim 5 \times 10^{-11}$ mol/cm^2, whereas the deposition amount calculated from the initial concentration and volume of solution used corresponds to $\sim 3 \times 10^{-10}$ mol/cm^2.[16] This difference could be due to either the dissolution of noncovalently attached MK-2 from the electrode surface or the fact that some of the MK-2 in a thicker layer is electrochemically inaccessible.

3.2. Electrogenerated Chemiluminescence Studies.

MK-2 is insoluble in pure acetonitrile, and so its ECL and electrochemical properties were measured in 50%−50% benzene:acetonitrile mixtures (see Scheme 5 and Figure 4a). The weak ECL signal obtained for radical anion/radical cation annihilation is a consequence of the instability of the radical anions.

Scheme 5

$$\text{MK-2} + e \rightarrow \text{MK-2}^{\bullet -} \quad (10)$$

$$\text{MK-2} - e \rightarrow \text{MK-2}^{\bullet +} \quad (11)$$

$$\text{MK-2}^{\bullet -} + \text{MK-2}^{\bullet +} \rightarrow \text{MK-2}^{*} \quad (12)$$

$$\text{MK-2}^{*} \rightarrow \text{MK-2} + h\nu \quad (13)$$

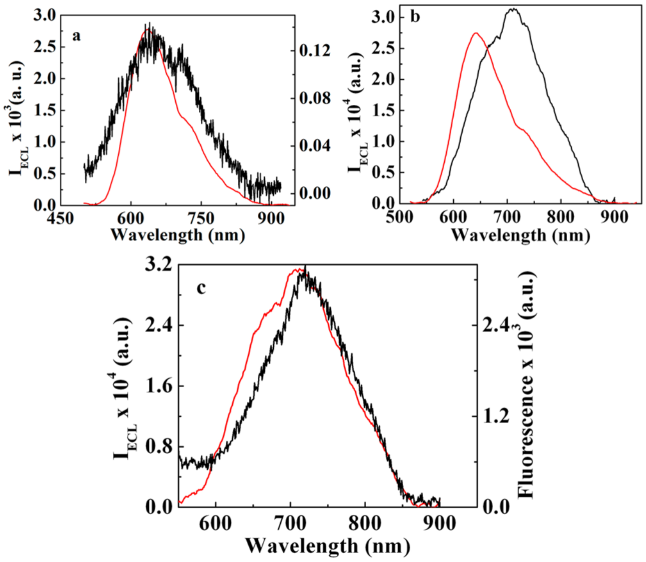

Figure 4. Electrogenerated chemiluminescence (ECL) spectra for a solution of 1 mM MK-2: (a) radical anion/radical cation annihilation (black line, right Y-axis) and with the addition of 20 mM $TBAC_2O_4$ as a co-reactant (red line, left Y-axis); (b) comparison of the ECL spectrum of MK-2 dye in solution (red line) with a film of MK-2 deposited on an ITO substrate (black line); (c) comparison of the ECL (red line) and fluorescence (black line) spectra of the MK-2 film deposited on ITO. A 50%−50% benzene:acetonitrile mixture with 0.1 M $TBAPF_6$ was used as a solvent and supporting electrolyte. A 0.0314 cm^2 platinum electrode was used for solution experiments and the ITO electrode with an area of 0.5 cm^2 (active area with 0.03 cm^2 MK-2) was used for the surface film measurements. The electrode with deposition from a 1 mM MK-2 solution was submerged for 1 h in solution with electrolyte prior to the electrochemical measurements.

The addition of tetrabutylammonium oxalate ($TBAC_2O_4$) as a co-reactant that, upon reduction, produces very strongly reducing (−2.1 V vs SCE) carbon dioxide anion radicals ($CO_2^{\bullet -}$), results in strong ECL with a quantum efficiency of ~10% that of $Ru(bpy)_3^{2+}$ (see red line in Figure 4a, as well as Scheme 6):[15,29]The ECL peak wavelength in solution is close to the fluorescence maximum.

Scheme 6

$$\text{MK-2} - e \rightarrow \text{MK-2}^{\bullet +} \tag{14}$$

$$C_2O_4^{2-} - e \rightarrow C_2O_4^{\bullet -} \tag{15}$$

$$C_2O_4^{\bullet -} \rightarrow CO_2 + CO_2^{\bullet -} \tag{16}$$

$$\text{MK-2} + CO_2^{\bullet -} \rightarrow CO_2 + \text{MK-2}^{\bullet -} \tag{17}$$

$$\text{MK-2}^{\bullet +} + \text{MK-2}^{\bullet -} \rightarrow \text{MK-2}^{*} + \text{MK-2} \tag{18}$$

$$\text{MK-2}^{*} \rightarrow \text{MK-2} + h\nu \tag{19}$$

The 730 nm ECL peak from adsorbed MK-2 is substantially red-shifted, compared to the solution value of 640 nm (Figure 4b). The fluorescence spectra and ECL spectra of the film are similar, and both are red-shifted, compared to the fluorescence and ECL spectra in solution (Figure 4c).[19,30,31] This shift with solvent polarity is attributed to aggregation induced by the substitution of hexyl groups on thiophene moiety.[32,33] Aggregation of thiophene polymers and oligomers in solution or in the solid state is well-known. There are different explanations of the nature of these aggregates, with the majority of them being related to the formation of H and/or J aggregates.[34,35] The emission maximum for the MK-2 monomer corresponds to the 0−0 transition, whereas 1−0 transitions were observed for aggregated species and thin films.[18] The change of fluorescence is correlated with the transition from a more-linear monomer conformation into a coiled aggregate.[36] A detailed description of the effect of aggregation on absorbance and fluorescence of MK-2 dye was reported in a previous work.[15] Atomic force microscopy (AFM) imaging and surface analysis confirmed the formation of different types of aggregates on a ZnO single-crystal surface. Lower dye sensitization electron injection efficiencies into the ZnO conduction band were measured from aggregated solutions, compared to dissolved monomer species, reflecting the influence of aggregation on adsorption and electron transfer.

The mechanism of MK-2 ECL emission in the film (Scheme 7), where there are only aggregates present, can be similar to that for solution species.

MK-2 ECL emission is different from that of BODIPY (boron dipyrromethene) dyes with long alkyl chains, where the formation of aggregates was present only in the excited states and was observed in ECL spectra but not in absorbance and fluorescence spectra.[37]

Scheme 7

$$\text{MK-2}_{aggr} + e \rightarrow \text{MK-2}_{aggr}{}^{\bullet -} \tag{20}$$

$$\text{MK-2}_{aggr} - e \rightarrow \text{MK-2}_{aggr}{}^{\bullet +} \tag{21}$$

$$\text{MK-2}_{aggr}{}^{\bullet -} + \text{MK-2}_{aggr}{}^{\bullet +} \rightarrow {}^{1}\text{MK-2}_{aggr}{}^{*} \tag{22}$$

$${}^{1}\text{MK-2}_{aggr}{}^{*} \rightarrow \text{MK-2}_{aggr} + h\nu \tag{23}$$

To our knowledge, this is the first report of a substantially different ECL emission between a dissolved species and a surface-attached species, whereas previous ECL investigations show that surface bound and dissolved species display similar ECL spectra.[6−8] The ECL intensity for surface-bound species was similar to that of the solution ECL but with a much higher efficiency with the oxalate co-reactant, when compared to the annihilation mechanism.

ECL and fluorescence spectra are usually comparable, since they often result from the formation of similar excited states. However, the formation of an identical excited state for ECL cannot be assumed, since not all phenomena observed in fluorescence spectra are observed in ECL and *vice versa*. For example, the presence of Förster resonance energy transfer (FRET), which is widely used in fluorescent assays, results in the absence of efficient ECL.[1] The stability and size of the emitting molecules is also much more influential in ECL, compared with fluorescence.

4. CONCLUSIONS

Our results demonstrate that electrogenerated chemiluminescence (ECL) is a viable technique to study the aggregation behavior of dyes and that surface attachment can result in ECL emission at different wavelengths, compared to that in bulk solutions. This provides a pathway to tune the ECL emission wavelength of a compound through variation of the solvent and surface environment. The current investigations could also be extended to aggregates in solution, where the different ratios of solvents can induce the formation of different aggregates, resulting in a shift of the ECL wavelength.

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Notes

The authors declare no competing financial interest.

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