

Electrogenerated Chemiluminescence 60. Spectroscopic Properties and Electrogenerated Chemiluminescence of Decaphenylanthracene and Octaphenylnaphthalene

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Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday

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The spectroscopic properties and electrogenerated chemiluminescence (ECL) of octaphenylnaphthalene (OPN) and decaphenylanthracene (DecPA) have been investigated. OPN displays a featureless fluorescence band at 424 nm and a fluorescence quantum yield of 0.06, while DecPA exhibits a structured fluorescence emission at 486 nm and a quantum yield of 0.10. Cyclic voltammetric measurements reveal the formation of radical cations and radical anions for both compounds, all of which appear relatively stable, although OPN^{•+} decomposes at scan rates below 200 mV s⁻¹.

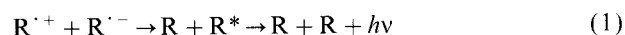
The ECL spectrum of OPN, generated by sequential production of the radical cation and radical anion of the compound at an electrode surface, is broad and red-shifted by about 100 nm from the compound's fluorescence maximum. This indicates that the emission is not that of OPN, but of a decomposition product, presumably derived from the unstable radical cation. DecPA, however, displays very stable green ECL similar in energy to its fluorescence spectrum.

Ebersson has worked in the area of the production of radical cations and their electron-transfer reactions.^{1–3} Among the interesting reactions of radical cations are those with strong reductants which can produce excited states. The recent surge of interest in polycyclic aromatic hydrocarbons (PAHs) can be attributed to the unique and potentially useful properties common to this diverse class of compounds. PAHs are particularly suited for spectroscopic and electrochemical studies, since the π orbital energies, which are needed to explain their properties, can be easily obtained from molecular orbital calculations.

The study of electrogenerated chemiluminescence (ECL) has employed PAHs in both fundamental and application-oriented research.^{4,5} In fact, the first studies in this area described the ECL of many of these compounds in non-aqueous solvents.^{6,7} Since then, numerous reports on the ECL of PAHs have been published, in which 9,10-diphenylanthracene^{8–11} (DPA) and 5,6,11,12-

tetraphenylnaphthalene^{12–14} (rubrene) have been studied extensively.

Prolonged production of ECL requires that both the radical cation and radical anion of a species be relatively stable, since it is the annihilation reaction between these two ions that produce excited states capable of luminescence [eqn. (1)].^{4,5}

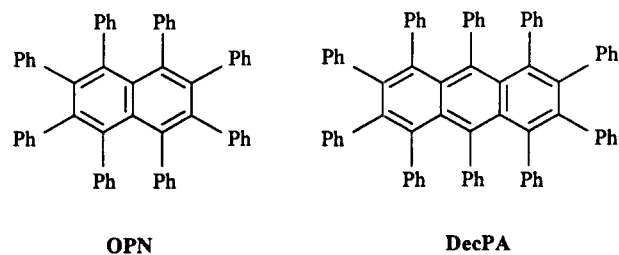


DPA and rubrene fulfill this criterion and also possess the high fluorescence quantum yields (≈ 1.0) desired to make the process efficient. However, attempts to produce solution ECL cells capable of extended light emission have often been disappointing, with light production lasting only minutes to a few hours.^{12,13} Proposed explanations for the decrease or cessation of light from these systems illustrate the difficulties involved. For example, the radical cation of DPA is unstable in many solvents over prolonged times, leading to loss of compound available for ECL and filming of the electrodes. Both DPA and rubrene radical ions are also extremely

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sensitive to impurities, in particular to sources of protons that can attack the radical anions and nucleophiles that react with the radical cations to form products that are incapable of ECL.

We report here an investigation of the properties of two recently reported compounds, octaphenylnaphthalene (OPN) and decaphenylanthracene (DecPA).¹⁵ The fluorescence and electrochemical properties of these compounds were determined to locate energies and evaluate their potential for ECL. The high degree of substitution on these compounds should block possible decomposition pathways of the radical ions and thus lead to more stable ECL. The results of ECL studies of OPN and DecPA are compared with those of their less substituted derivatives in an attempt to understand the influence of high phenyl-substitution on the properties of PAHs.



Experimental

OPN and DecPA were available from a previous study.¹⁵ Tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆, SACHEM, Inc., Austin, TX) was recrystallized from EtOH-H₂O (4:1) three times and dried at 100 °C before use. Benzene (Aldrich, ACS grade), CH₃CN (Burdick and Jackson, UV grade), and cyclohexane (Sigma, spectroscopic grade) were used as received after being transported unopened into an inert atmosphere drybox (Vacuum Atmospheres Corp., Los Angeles, CA). UV, fluorescence, electrochemical, and ECL solutions were prepared in a drybox and sealed in air-tight cells for measurements completed outside the drybox.

Relative fluorescence efficiencies were measured¹⁶ by using 5 μM solutions in benzene using DPA as a standard [$\Phi_{\text{DPA}} = 0.96$ in benzene using wide slit widths (4 mm)];¹⁷ $\lambda_{\text{ex}} = 364$ nm for DecPA and 334 nm for OPN]. Fluorescence spectra were recorded on an SLM Aminco SPF-500 spectrofluorometer, and UV spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer.

Cyclic voltammograms were recorded on a Bioanalytical Systems 100A electrochemical analyzer. The working electrode in all cases consisted of an inlaid platinum disk (1.3 mm diameter) that was polished on a felt pad with 0.05 μm alumina (Bueler, Ltd.) and sonicated in absolute EtOH for 1 min before each experiment. A platinum gauze served as a counter electrode. A silver wire served as a quasi-reference electrode, and

potentials were calibrated versus SCE by the addition of ferrocene as an internal standard using $E^\circ(\text{Fc}/\text{Fc}^+) = 0.424$ V vs. SCE.

ECL procedures were performed as described elsewhere,¹⁸ utilizing a charge-coupled device (CCD) camera (Photometrics CH260) cooled to -135 °C to measure emission. Solutions used for ECL production were similar in composition to those used for electrochemical measurements.

Results and discussion

Absorption spectra. Absorption and emission spectra for OPN and DecPA in cyclohexane are shown in Fig. 1. OPN exhibits an absorption band centered around 329 nm corresponding to excitation into the lowest singlet state ($^1A \rightarrow ^1L_a$ in Platt's notation¹⁹). The band is red-shifted from that of naphthalene, which displays a very structured absorption centered around 280 nm.²⁰ Examination of the less-substituted derivatives of naphthalene indicate that increased phenyl substitution leads to an increased red shift, as exemplified by 1-phenylnaphthalene ($\lambda_{\text{max}} = 290$ nm), diphenylnaphthalenes ($\lambda_{\text{max}} = 300$ nm) and 1,4,5,8-tetraphenylnaphthalene ($\lambda_{\text{max}} = 335$ nm).²⁰ The increasing substitution also has the effect of broadening the vibrational fine structure of the absorption band, a result of the decreased planarity

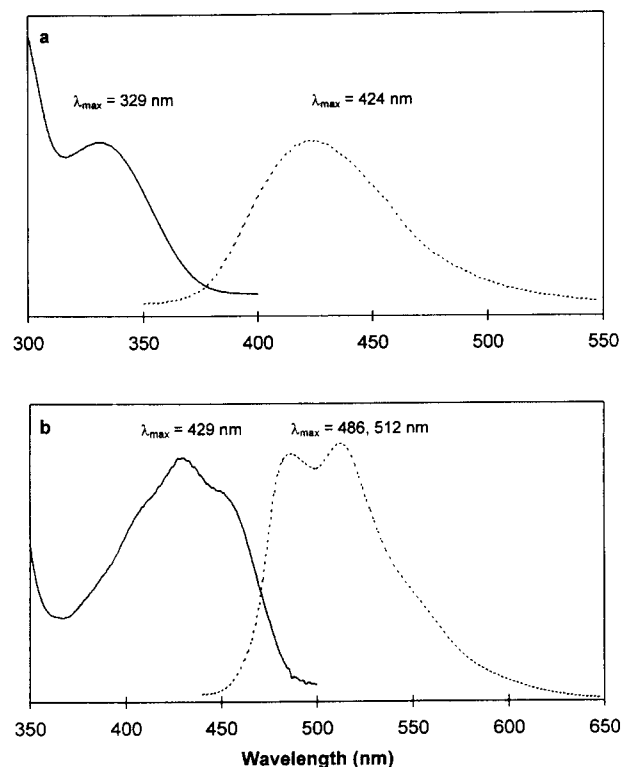


Fig. 1. Absorption and emission spectra of (a) OPN ($\lambda_{\text{ex}} = 330$ nm) and (b) DecPA ($\lambda_{\text{ex}} = 430$ nm) in cyclohexane.

of the naphthalene chromophore and the increase in rotational and conformational structure of the molecule. The intensity of the OPN absorption band also attests to a loss of symmetry in the molecule upon substitution: OPN ($\epsilon = 14\,200$) has a much stronger molar absorptivity than naphthalene ($\epsilon = 6000$) since the formally forbidden transition is more allowed in the non-symmetric molecule.²⁰

DecPA displays a broad absorption band centered around 429 nm ($^1A \rightarrow ^1L_b$). Some structure is evident in this band, although it is much less defined than for unsubstituted anthracene or 1,4- and 9,10-diphenylanthracene.²⁰ When *peri* substitutions are present as in 1,4,9,10-tetraphenylanthracene²¹ and in DecPA, broader absorption bands are observed, which can be attributed to the decreased planarity of the molecules due to the large steric interactions of neighboring phenyls. The fine structure evident in the DecPA absorption band is typical for anthracene, indicating that the π system of the anthracene core is not disrupted to any great extent, despite the 63° end-to-end twist in the crystalline molecule as shown by X-ray crystallography.¹⁵

The red shift of the DecPA absorption as compared to anthracene (longest wavelength absorption at 375 nm) is large, but consistent with the addition of multiple phenyl groups. Other examples of phenyl-substituted anthracenes include 9-phenyl- ($\lambda_{\max} = 383$ nm), 9,10- and 1,4-diphenyl- ($\lambda_{\max} = 393$ nm),²⁰ and 1,4,9,10- and 1,4,5,8-tetraphenylanthracenes ($\lambda_{\max} = 405$ nm and 415 nm, respectively).²¹ The crystal structure of DecPA reveals that in the solid state, the phenyl groups are twisted 60° to 80° with respect to the anthracene core, indicating that very little delocalization into their π systems is possible.¹⁵ Even in solution the high steric congestion will prevent the phenyls from attaining a near-planar alignment with respect to the anthracene. It has been noted that a slight interaction of the π systems of adjacent phenyl groups on PAHs causes a greater red absorption shift than would be expected from inductive effects alone, even though the π systems cannot attain a planar configuration.²² However, the reported absorption for decamethylanthracene ($\lambda_{\max} = 427, 405$ nm)²³ is very similar in shape and energy to that of DecPA, suggesting that the number of substitutions may have more of an effect on the absorption energy than the type of substituent.

Fluorescence spectra. Fluorescence spectra for both OPN and DecPA in cyclohexane are shown in Fig. 1. OPN exhibits a broad, structureless blue fluorescence centered around 424 nm, and a low fluorescence efficiency, $\phi_f = 0.06$. This can be compared with naphthalene, which has a very structured emission beginning at 320 nm, and a fluorescence quantum yield of 0.23.

Phenyl substitution on naphthalene shifts the fluorescence of these derivatives to longer wavelengths for the same reasons that the absorption bands shift, as discussed above. For example, 1-phenylnaphthalene emits at

345 nm, and 1,4-diphenylnaphthalene at 380 nm.²⁰ The fluorescence quantum yields for these derivatives are all similar to or slightly greater than naphthalene itself, and therefore it is surprising that OPN has such a low quantum yield. Naphthalene has a low fluorescence efficiency due to a relatively long fluorescence lifetime and a forbidden transition to the ground state from the singlet. Substitution decreases the symmetry of the molecule and the transition becomes more allowed. The much lower efficiency of OPN is likely due to the presence of a greater number of non-radiative pathways available to this highly substituted, non-planar, and non-rigid molecule.

DecPA displays a broad fluorescence band with observed maxima of 486 and 512 nm and has a fluorescence efficiency of 0.10. For comparison, anthracene fluorescence begins at 390 nm and DPA at 406 nm¹⁶ and exhibit quantum yields of 0.36 and 0.90,²⁰ respectively, in cyclohexane. These latter compounds have structured emissions similar to that of DecPA, which is typically interpreted as a sign of a rigid system, specifically in the ground state. Thus DecPA, with a fuclional disposition on the NMR timescale,¹⁵ is sufficiently rigid on the nanosecond scale to show a structured fluorescence emission. The compound's quantum yield is more in line with its properties, because a molecule with a non-rigid chromophore typically displays a low fluorescence efficiency, due to efficient internal conversion through molecular vibrations, rotations, and conformational changes, of which this molecule should have many.

The fluorescence of DecPA displays a red shift from that of anthracene consistent with the compound's high substitution. Again, a comparison can be made with decamethylanthracene, which fluoresces at 480 nm,²³ indicating that it is the substitution that has more effect on the fluorescence than the nature of the substituent in these highly congested systems.

Electrochemistry. Cyclic voltammograms of OPN and DecPA obtained in acetonitrile–benzene (1 : 1) are shown in Fig. 2. The radical cation and radical anion of OPN are generated at +1.41 and –2.28 V vs. SCE, respectively. Both waves appear reversible, denoting fairly stable ions. At scan rates below 200 mV s⁻¹, however, the oxidation wave becomes less reversible, suggesting that the radical cation undergoes slow decomposition.

The addition of phenyl substituents onto a naphthalene ring tend to make the molecule easier to oxidize and reduce. For example, the first oxidation of naphthalene and 1,8-diphenylnaphthalene in DMF occur at +1.81 and +1.59 V, whereas their reductions are observed at –2.56 and –2.25 V in CH₂Cl₂, respectively.²⁴ Although it is impossible to compare accurately these potentials with the values measured for OPN because of solvent differences, the gap between the first oxidation and reduction waves can be compared. This value decreases upon increased phenyl substitution, mirroring the

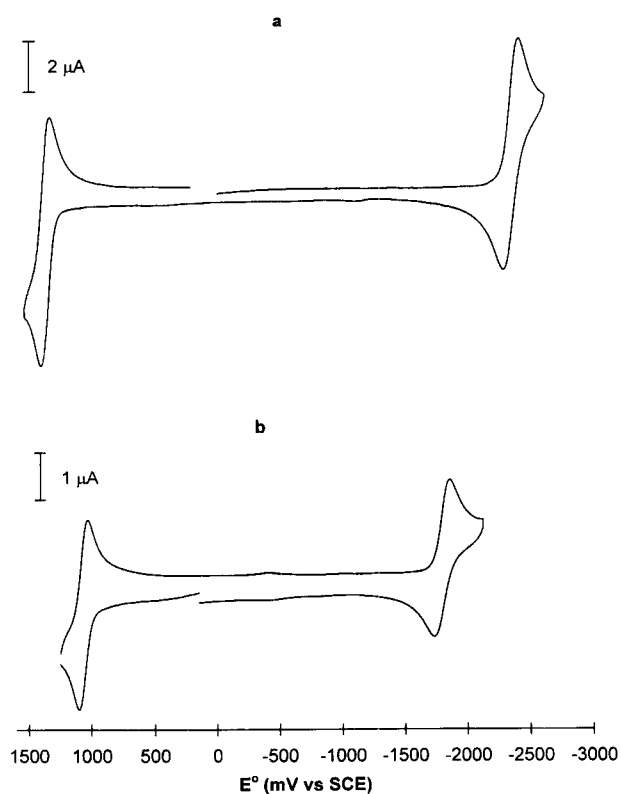


Fig. 2. Cyclic voltammograms of (a) 1.0 mM OPN and (b) 0.23 mM DecPA in acetonitrile–benzene (1:1), scan rates 500 and 200 mV s^{-1} , respectively (electrolyte: 0.1 M TBAPF₆).

decrease in absorption energy, as this potential difference is a measure of the HOMO–LUMO energy gap.

DecPA displays reversible oxidation and reduction peaks at +1.00 and -1.79 V vs. SCE, respectively, in benzene–acetonitrile (Fig. 2b). Irreversible second oxidation ($E_{\text{pa}} = +1.40$ V) and reduction peaks ($E_{\text{pc}} = -2.28$ V) can also be observed (not shown). 9,10-Diphenylanthracene under the same conditions is reduced at -1.96 V and is oxidized at $+1.23$ V, demonstrating again that increased phenyl substitution causes both redox processes to become easier. Other studies report the same trends up to tetraphenyl substituted anthracenes.^{24,25} The cyclic voltammograms cannot be used to determine the long-term stability of DecPA ions in this medium, but both radical ions are stable at scan rates as slow as 50 mV s^{-1} .

Electrogenerated chemiluminescence. When an electrode immersed in a (1.0 mM) solution of OPN is pulsed between the compound's first oxidation and reduction waves, pale blue light that is visible by eye in a darkened room is produced at the electrode surface by the annihilation reaction outlined in eqn. (1). The spectrum of this electrogenerated light is shown in Fig. 3a, and consists of a very broad peak trailing out to almost 800 nm, with a maximum at 518 nm. Typically, PAHs that possess

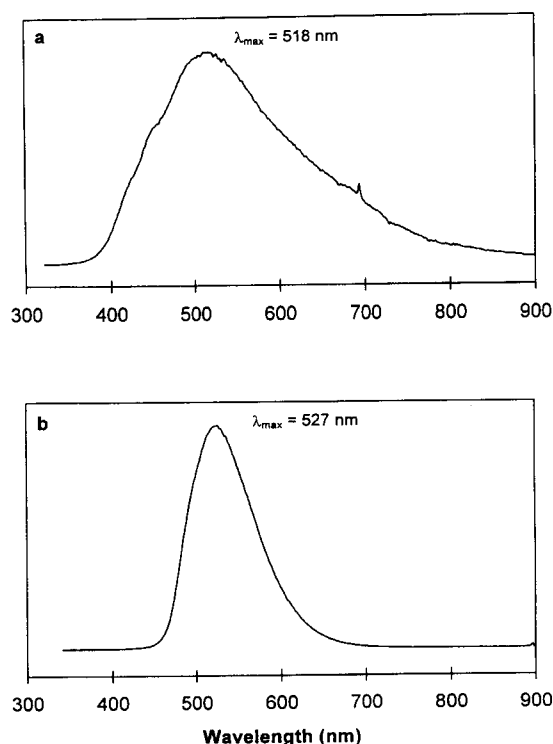


Fig. 3. ECL spectra of (a) OPN (1.0 mM) and (b) DecPA (0.23 mM) in benzene–acetonitrile (1:1), (electrolyte: 0.1 M TBAPF₆).

stable ions exhibit ECL spectra resembling their fluorescence spectra, since in each case the same emitting state is produced. However, in the case of OPN, the ECL emission is shifted almost 100 nm from the fluorescence spectrum, and the band is much wider than expected. The emission is also not stable, and the light intensity from the electrode decreases fairly rapidly if the solution is not stirred. This indicates that some decomposition is occurring to decrease the concentration of the compound at the electrode surface. By observing the electrode during both cathodic and anodic pulses, it is seen that the cathodic pulse produces less light, implying that it is the radical cation that is unstable. This is true for many PAHs, where the cations undergo reactions such as deprotonation, radical–radical coupling reactions, and nucleophilic attack. OPN could undergo any one of these reactions; however, the longer-wavelength emissions can be explained by a coupling reaction to form ECL-active compounds with more extended π systems.^{26–28} In fact, electrolysis of an OPN solution at a potential capable of producing the radical cation results in decomposition of $\text{OPN}^{\cdot+}$ and formation of many unidentified products, as observed by thin-layer chromatography. Some of these products exhibit blue, yellow, or red fluorescence, and ECL from these species is likely the source of the longer wavelength emissions.

The ECL spectrum of DecPA is shown in Fig. 3b. In contrast to OPN, however, the emission from DecPA is

similar in shape and energy to the compound's fluorescence spectrum. The maximum is located at 527 nm, which is slightly red-shifted from the fluorescence due to an inner-filter effect of the ECL solution, because it is more concentrated than solutions used for fluorescence measurements. The green emission is very stable over time and for much longer periods than, for example, ECL emission from DPA, which is observed to decrease in intensity over a few minutes under the same conditions. The intensity of the ECL compared with DPA under similar conditions is 0.27. Since the fluorescence efficiency of DecPA is about one-tenth that of DPA, this suggests that DecPA has a higher ECL efficiency (number of excited states produced per annihilation) than DPA.

The stability of DecPA ECL indicates that the radical ions are fairly robust under the conditions employed. It has been observed in the past that anions of anthracene are stabilized by the addition of phenyl substituents, primarily in the 9 and 10 positions because these are the sites of highest electron density and thus of electrophilic attack (e.g., protonation).^{25,29} Cations of anthracene and its derivatives are also stabilized by blocking the 9 and 10 positions with substituents.^{25,29} The stability of DecPA ions is thus presumably due to the presence of the ten phenyl substituents that remove the possibility of anthracene deprotonation, and that also sterically protect the core against electrophilic and nucleophilic attack.

Conclusions

The spectroscopic properties of two highly substituted PAH systems, octaphenylnaphthalene and decaphenylanthracene, have been investigated. The high degree of substitution in these compounds shifts their absorption and fluorescence spectra to longer wavelengths and greatly decreases their fluorescence efficiencies as compared with naphthalene and anthracene, respectively. These effects can be explained by the twisting of the chromophores present in these compounds by the phenyl groups and also by the highly fluctuating nature of these substituents.

The electrochemistry displayed by the two compounds also shows the influence of high substitution, in that both are easier to reduce and oxidize than their parent PAHs. Their radical ions, notably the cations, are much more stable than those of anthracene and naphthalene as a result of the phenyl ligands blocking reactive sites on the PAH. All singly charged ions appear quite stable except for the radical cation of OPN, which displays slight irreversibility in its cyclic voltammogram, but only at slow scan rates.

OPN and DecPA are both capable of electrogenerated chemiluminescence. OPN is not a good candidate for applications, because decomposition of the radical cation occurs, leading to a decrease in ECL intensity and the production of longer-wavelength emitting species. DecPA on the other hand produces very stable ECL. This is due

to stabilization of the radical ions by blocking all possible reactive sites on anthracene. The emission is weaker than that of DPA, a result of the much lower fluorescence efficiency of the compound. This lower ECL efficiency may be acceptable if extended light emission is possible with this system, e.g., in ECL display applications.

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