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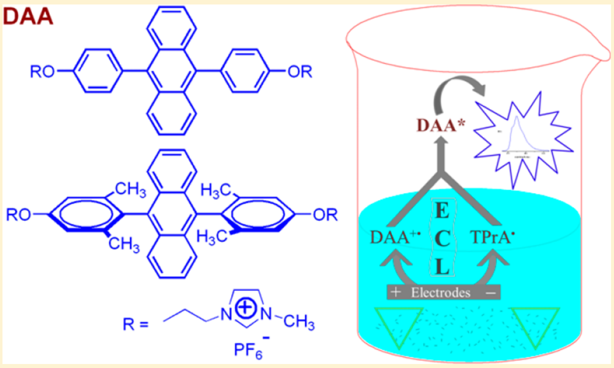
9,10-Diarylanthracenes as Stable Electrochemiluminescent Emitters in Water

Palani Natarajan* and Michael Schmittel*

Center of Micro- and Nanochemistry and Engineering, Organische Chemie I, Universität Siegen, Adolf-Reichwein-Straße 2, D-57068 Siegen, Germany

Supporting Information

ABSTRACT: Two hydrophilic diarylanthracenes, explicitly 9,10-bis(*N*-methylimidazolium-3-propoxyphenyl)anthracene (**DAA1**) and 9,10-bis(*N*-methylimidazolium-3-propoxy-2,6-dimethylphenyl)anthracene (**DAA2**), are synthesized and fully characterized. Both are found to be soluble in aqueous medium and to exhibit optical properties similar to those of the parent 9,10-diphenylanthracene, whose solubility is virtually negligible in water. The detailed analysis of their photochemical stability as well as electrochemical and electrochemiluminescent properties reveals that the sterically highly shielded anthracene **DAA2** shows inertness toward reactions with singlet oxygen and OH^- ions during photo- and electrochemical initiation and stable ECL emission in aqueous medium.



INTRODUCTION

Among the large number of organic emitters studied in electrochemiluminescence (ECL), 9,10-diphenylanthracene (**DPA**) and its derivatives exhibit remarkable luminescence properties in organic media.[1] In co-reactant ECL, **DPA** yields a bright blue emission with an ECL efficiency of 25%, which represents the theoretical maximum for ECL from **DPA** singlets.[1b] As a result, **DPA** has been used as an ECL standard in aprotic media.[1,2] However, neither **DPA** nor its derivatives have been used in biological fluids. This area is dominated so far by well-known inorganic ECL emitters, such as the tris(2,2′-bipyridyl)ruthenium(II), $[Ru(bpy)_3]^{2+}$.[1b,c] Typical diarylanthracenes are characterized by a (i) lack of any solubility in aqueous solutions, (ii) high reactivity of the radical cation state toward water, and (iii) lack of photostability due to facile oxygenation at the *meso*-positions.[3] Therefore, several attempts have been made to initiate ECL emission from **DPA** and its derivatives in aqueous solutions.[4] For example, Bard et al.[5] have introduced hydrophilic **DPA** derivatives, such as sodium 9,10-diphenylanthracene-2-sulfonate (**DPAS**), that show a good solubility in aqueous solutions. However, **DPAS** and its radical ion lack chemical stability during electrolysis, thus yielding unstable ECL signals. In addition, Bard et al.[1j,6] produced dispersed nanoparticles (also known as quantum dots) of **DPA**, but their ECL emission intensity in aqueous media was rather weak. The failure was assigned to the small diffusion coefficient of **DPA**-infused nanoparticles in aqueous solutions. Recently, Chen et al.[7] reported on **DPA**-doped polystyrene beads that were soluble in water up to a concentration of 10^{-3} M while showing reasonable ECL emission. Nonetheless, their ECL intensity rapidly decreased due to nucleophilic OH^-/water attack in aqueous phosphate buffer. Thus, the design and development of stable ECL emissive diarylanthracenes exhibiting both water solubility and high stability against nucleophilic attack on the radical cation stage has been an ongoing challenge for many years.[3−8]

9,9′-Bianthryls[3,9] and trianthryls exhibit a much better photostability against singlet oxygen $(^1O_2)$ than simple aryl- or diarylanthracenes,[8] a finding that suggests that steric bulk may equally prevent anthracenes from undergoing photo-oxidation. In our laboratories, we established that copper(I) ions are much more inert toward oxidation when they are coordinated to bulky 2,9-bis(2,6-dimethylphenyl)-1,10-phenanthroline ligands,[10] as the *ortho*-methyl groups in the 2,6-dimethylaryl unit provide good steric protection against oxygen/water attack. On the basis of these observations and our experience in ECL,[11] we herein introduce the water-soluble and sterically hindered anthracene **DAA2**, 9,10-bis(*N*-methylimidazolium-3-propoxy-2,6-dimethylphenyl)anthracene (Chart 1), as a useful water-stable ECL emitter. For comparison, **DAA1** will be prepared and its photochemical and electrochemical stability as well as its luminescence activity in organic and aqueous solvents shall be evaluated. Our design considerations were based on the observation that the electron-deficient imidazolium groups should not affect luminescence quantum yields and radical cation stability as manifested from other anthracene derivatives decorated by imidazolium groups.[12]

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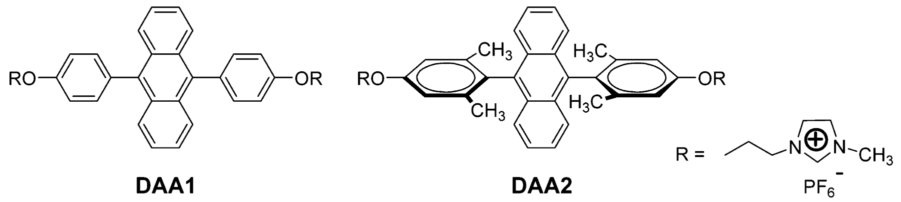
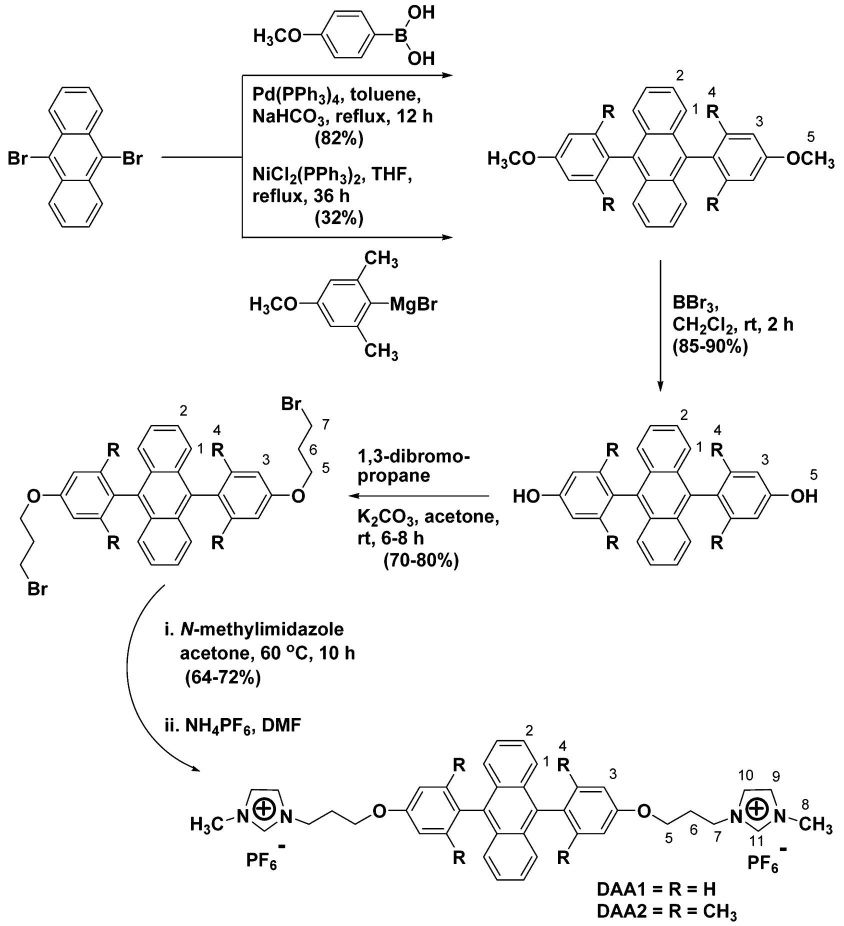
Chart 1. Molecular Structure of Aqueous Soluble 9,10-Diarylanthracenes DAA1 and DAA2



Scheme 1. Synthetic Route for 9,10-Diarylanthracenes DAA1 and DAA2[a]



[a]The numbering in the structures is only used for the ^{1}H NMR assignments, which are not necessarily in accordance with the IUPAC nomenclature pattern.

Table 1. Optical Absorption, PL, PL Quantum Yields, Redox Potential, ECL, and Relative ECL Quantum Yield of DAA1 and DAA2

	λ_{max}^{abs} (nm)^a	band gap λ (eV)^b	λ_{max}^{fl} (nm)^a	Φ_{fl}^c	oxid. E°_{ox} (V)^d	λ_{max}^{ecl} (nm)^e	$\Phi_{rel,ECL}^{f,g}$
DAA1	372^{sm}	412 (3.01)^{sm}	427^{sm}	0.78^{sm}	0.78, 1.02^{sd}	431^{sd}	7.72 ± 0.3^{sd}
	374^{sw}	417 (2.97)^{sw}	433^{sw}	0.77^{sw}	0.94^{sw}	435^{sw}	7.73 ± 0.7^{sw}
DAA2	366^{sm}	407 (3.05)^{sm}	421^{sm}	0.61^{sm}	0.71, 0.99^{sd}	423^{sd}	6.84 ± 0.1^{sd}
	367^{sw}	409 (3.05)^{sw}	424^{sw}	0.60^{sw}	0.86, 1.07^{sw}	425^{sw}	6.83 ± 0.1^{sw}

[a]Absorption and emission spectra are recorded for dilute solutions (10 μM). [b]Optical band gap values are calculated from the tail end absorption. [c]Quantum yields are calculated using 9,10-diphenylanthracene as a standard with λ_{exc} = 365 nm. [d]All potentials are obtained from cyclic voltammetry and referenced versus Fc/Fc$^+$ at a scan rate of 100 mV s^{-1}. [e]Electrochemiluminescence is measured using tris-*n*-propylamine as a co-reactant (50 mM). [f]$\Phi_{rel,ECL}$ is the relative ECL compared to [Ru(bpy)$_3$]$^{2+}$, which is taken as unity. [g]Values are the average of at least 5−6 independent experiments: sm, experiment performed in methanol; sw, experiment performed in aqueous buffer; sd, experiment performed in DMF.

■ RESULTS

Synthesis and Characterization. The 9,10-diarylanthracenes **DAA1** and **DAA2** (Chart 1) were readily synthesized according to the routes presented in Scheme 1. A Pd(PPh$_3$)$_4$-mediated Suzuki coupling reaction between 9,10-dibromoanthracene and 4-methoxyphenylboronic acid afforded 9,10-bis(4-methoxyphenyl)anthracene, which was demethylated with BBr$_3$, furnishing the 9,10-bis(4-hydroxyphenyl)anthracene. Ether-

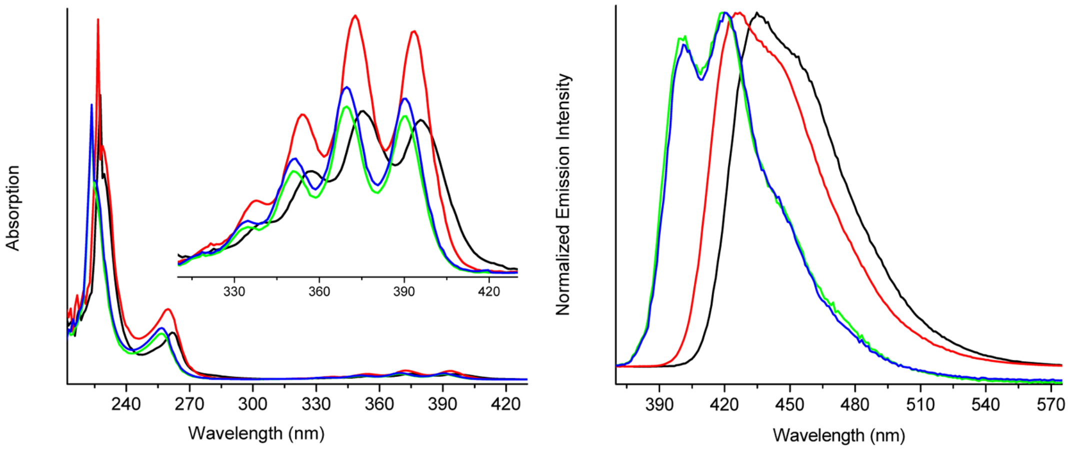


Figure 1. Absorption (left) and fluorescence (right, λ_{exc} = 365 nm) spectra of **DAA1** and **DAA2** in methanol and aqueous buffer solutions. Inset on the left shows the expanded visible portion of **DAA1** and **DAA2**. Color codes: In aqueous solution: **DAA1**, black; **DAA2**, green. In methanol; **DAA1**, red; **DAA2**, blue.

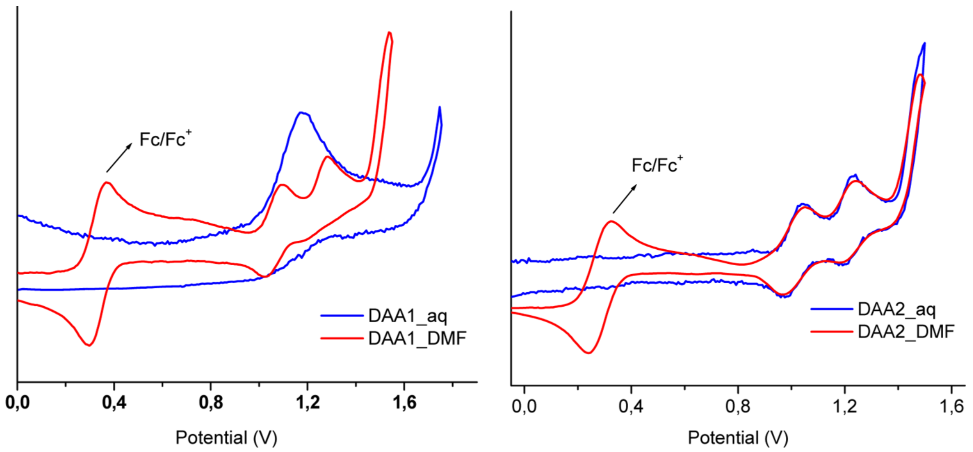


Figure 2. Cyclic voltammograms of 0.5 mM **DAA1** (left) and **DAA2** (right) in aqueous (blue) and DMF (red) solutions at 100 mV s^{-1} scan rate.

ification of the latter bisphenol with excess of 1,3-dibromopropane was followed by reaction with *N*-methylimidazole to deliver **DAA1** in 64−66% yield (Scheme 1). A similar protocol starting from 9,10-bis(4-methoxy-2,6-dimethylphenyl)anthracene led to **DAA2** (Scheme 1); the 9,10-bis(4-methoxy-2,6-dimethylphenyl)anthracene precursor was, in turn, prepared by a $NiCl_2(PPh_3)_2$-mediated coupling reaction between 9,10-dibromoanthracene and 4-methoxy-2,6-dimethylphenylmagnesium bromide.[13] All of the compounds were purified by column chromatography. All intermediate compounds and **DAA1** and **DAA2** were characterized by the usual spectroscopy techniques (Supporting Information).

DAA1 and **DAA2** are both readily soluble in aqueous (2−2.5 mM) as well as in alcoholic solutions, whereas they lack solubility in common organic solvents, such as hexane, dichloromethane, chloroform, ethyl acetate, toluene, etc. Therefore, the following experiments were performed either in dimethylformamide (DMF), methanol, or aqueous phosphate buffer solutions (pH = 7.0 at 20 °C) as needed.

Photophysical Data. The UV−vis absorption and photoluminescence (PL) of **DAA1** and **DAA2** are studied in methanol and aqueous buffer solutions (for a summary of the results, see Table 1). The UV−vis spectra of **DAA1** and **DAA2** (Figure 1) exhibit similar absorption peaks between 315 and 420 nm that are assigned to $\pi-\pi^*$ transitions of the central anthracene core by analogy.[3,14] The two absorption bands in the 210−270 nm region are attributed to the substituted aryl groups. The optical band gap energy, as calculated from the tail end of the absorption, varies from 2.97 to 3.05 eV (Table 1). A PL study of **DAA1** and **DAA2** shows a strong emission in the 390−520 nm range (blue emission, Figure 1) that is independent of the excitation wavelength. Notably, no aggregation induced red shift emission is observed neither from **DAA1** nor from **DAA2**, even at high concentration (1×10^{-4} M, cf. Supporting Information).[11] As expected, **DAA2** exhibits blue-shifted absorption and emission maxima due to the reduced conjugation as compared to **DAA1**. PL quantum yields (Φ_{fl}) are determined using 9,10-diphenylanthracene (**DPA**, Φ = 0.9 in cyclohexane) as a standard.[15] They amount to 0.77−0.78 and 0.60−0.61 for **DAA1** and **DAA2**, respectively (Table 1).

Photostability. In order to establish the photostability of **DAA1** and **DAA2**, photo-oxygenation reactions are conducted separately in oxygen-saturated aqueous and methanol solutions in the presence of catalytic methylene blue as photosensitizer. After 4−5 h, **DAA1** affords the corresponding 9,10-endoperoxide as a main product, which is isolated and characterized by NMR analysis. The photo-oxidation is readily monitored by absorption and PL because their peak intensities decreased gradually with time as a result of the breakdown of the anthracene core (Supporting Information). In contrast, **DAA2** is found to be inert

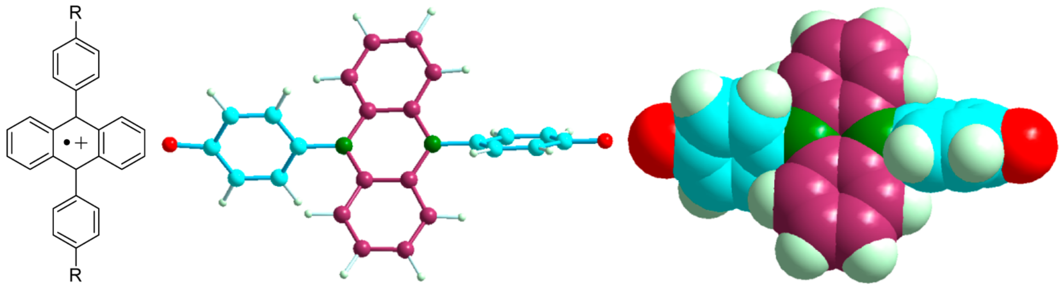


Figure 3. DFT (6-311G*) optimized structure of **DAA1**$^{+\bullet}$ (the imidazolium substituents are omitted in the above drawing). Notice that the C9 and C10 atoms (green) are readily accessible without steric crowding.

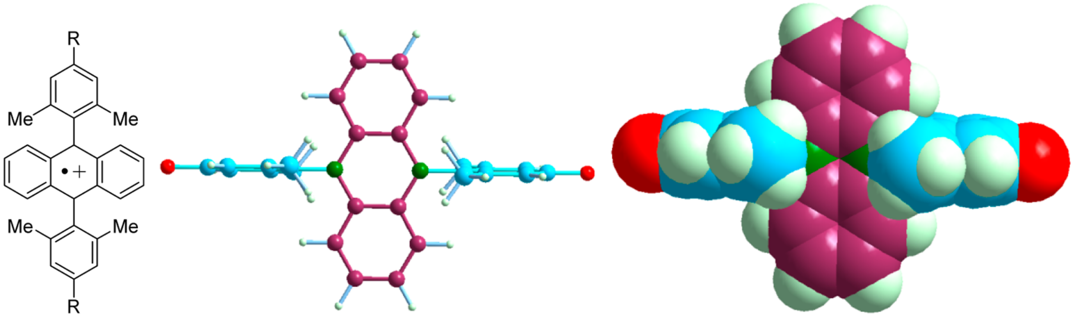


Figure 4. DFT (6-311G*) optimized structure of **DAA2**$^{+\bullet}$ (the imidazolium substituents are omitted in the above drawing). Notice that the C9 and C10 atoms (green) are shielded by the *ortho*-methyl groups of the phenyl substituents.

under photo-oxidation conditions, even after 20 h of irradiation, as confirmed by NMR and PL analysis.

Electrochemical Data. Oxidation potentials of **DAA1** and **DAA2** are determined by cyclic voltammetry (CV) in DMF and in aqueous buffer solution (Figure 2), and the results are summarized in Table 1. Reduction potentials could unfortunately not be determined due to structureless waves at negative potential. **DAA1** in aqueous buffer solution shows a quasi-reversible oxidation wave at 0.94 V, whereas **DAA2** exhibits two reversible oxidation waves, the first at 0.86 V and the second at 1.07 V (scan rate = 100 mV s^{-1}). Clearly, the cation radical of **DAA1** is unstable, as evidenced by the lack of chemical reversibility. A similar behavior is observed at a scan rate of 1000 mV s^{-1} (Supporting Information). It is possibly due to the reaction of the radical cation of **DAA1** with water, vide infra. In contrast, experiments with **DAA1** and **DAA2** in non-aqueous DMF show two oxidation waves. The first wave is found to be reversible for both **DAA1** and **DAA2**, whereas the second oxidation wave is reversible for **DAA2** only (Figure 2). The irreversible second oxidation of **DAA1** in DMF indicates that the dication (**DAA1**$^{2+}$) is unstable under the conditions used in this study.

DFT Computations. DFT computational studies are performed using the 6-311G* basis set in order to establish the dihedral angles and the influence of steric hindrance on photochemical and electrochemical properties of neutral and radical cations of **DAA1** and **DAA2** (atomic coordinates and absolute energies of all structures presented in the Supporting Information, cf. Tables S1−S4).[16] The calculated dihedral angles between the aryl group and the central anthracene unit are 67 and 89° for **DAA1** and **DAA2**, respectively (Supporting Information). They are in good agreement with the value reported in the literature for other diarylanthracenes as received from single-crystal X-ray structures.[17] As shown in Figures 3 and 4, the one-electron oxidation of **DAA1** and **DAA2** to their corresponding radical cation (**DAA1**$^{+\bullet}$ and **DAA2**$^{+\bullet}$) affects, in particular, the orientation of aryl units in **DAA1**, as its dihedral angle changes from 67 to 53°. In contrast, the dihedral angle remains unaltered for **DAA2** (89°) and its radical cation **DAA2**$^{+\bullet}$ (88°) (Figure 4). The calculated value of the dihedral angle for **DAA1**$^{+\bullet}$ is rather similar to the value of 57° reported for **DPA**$^{+\bullet}$ (produced by dissolving **DPA** in hexane and treated with concentrated sulfuric acid), determined by electron spin resonance spectroscopy (ESR) and molecular model estimation.[18] This suggests that the level of theory used here is suitable for the system studied.

Electrochemiluminescence. ECL emission of **DAA1** and **DAA2** in presence of tris-*n*-propylamine (TPrA, 50 mM) as co-reactant is measured by reversibly scanning across the first oxidation potential (0.15−0.95 V with respect to a silver wire as a quasi-reference electrode, Table 1) in aqueous buffer as well as in non-aqueous DMF solution.[19] As shown in Figure 5, both **DAA1** and **DAA2** provide noticeable ECL emission even at low concentrations ($1{-}5 \times 10^{-4}$ M), while no emission is observed in the absence of either TPrA or luminophore. In line with their different PL quantum yields, the ECL emission intensity of **DAA1** is 20% more than that observed from **DAA2**. The emission maxima in ECL and PL of **DAA1** and **DAA2** are found to be similar, indicating that the emission occurs from the same excited states (Table 1). In aqueous buffer solution, the ECL signal is generated by reversibly sweeping the electrode potential in the range of 0.15 to 0.95 V in the presence of 50 mM TPrA as a co-reactant at a scan rate of 100 mV s^{-1}. However, ECL emission intensity diminishes with each subsequent scan due to electrode passivation as a consequence of irreversible oxidation of co-reactant and luminophore. Therefore, for each resultant experiment conducted in aqueous buffer solution, the electrode surface was mechanically polished using an alumina slurry. After polishing, **DAA2** shows an ECL signal without any significant drop of the emission intensity, at least for 100 repeated potentials scans (Figure 6). On the other hand, the ECL emission intensity

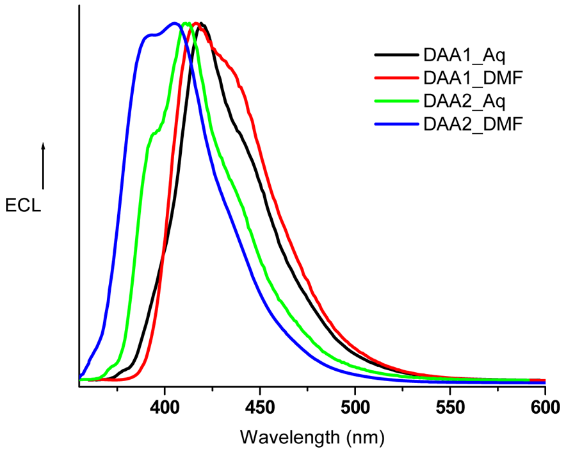


Figure 5. Normalized ECL spectra of 0.5 mM **DAA1** and **DAA2** in aqueous phosphate buffer (pH = 7 at 20 °C) as well as in DMF solutions. ECL spectra were recorded in the presence of 50 mM TPrA as co-reactant.

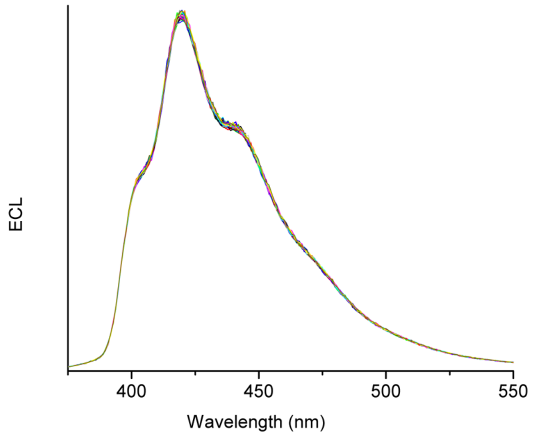


Figure 6. ECL emission spectrum of **DAA2** in aqueous phosphate buffer (pH = 7 at 20 °C) solution taken with repeated scans (100 cycles). Notice that there is no change in ECL intensity.

of **DAA1** is still diminished by about 15–25% for each following scan in aqueous buffer solution (Figure 7), most likely due to the instability of the oxidized **DAA1** against water/oxygen. The formation of byproducts, such as 9,10-bis(*N*-methylimidazolium-3-propoxyphenyl)-9,10-dihydroanthracenediol, is confirmed by NMR[20] and PL analysis. PL is monitored after each scan of **DAA1** in aqueous solution (after each scan 20 μL of sample is removed and diluted to 2.5 mL for PL measurement). The initial PL emission intensity between 350 and 500 nm drops gradually due to destruction of the anthracene core.

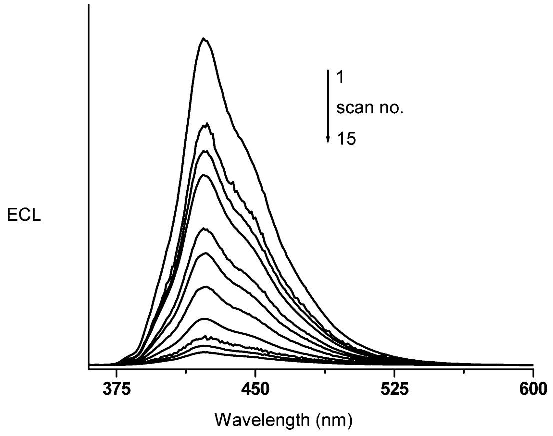


Figure 7. ECL emission spectrum of **DAA1** in aqueous phosphate buffer (pH = 7 at 20 °C) solution taken with repeated potential scans. Notice that the ECL intensity decreases with every subsequent scan.

Both **DAA1** and **DAA2** first undergo a reversible one-electron oxidation in non-aqueous DMF as apparent from CV analysis. Indeed, ECL behavior in DMF is markedly different from that observed in aqueous solution of **DAA1** and **DAA2**, vide infra. The slightly blue-shifted ECL emission of **DAA1** and **DAA2** in DMF as compared to that in aqueous solution (Figure 5 and Table 1) is a result of a solvent effect that is equally manifested in PL. Although the radical cations of **DAA1** and **DAA2** in DMF show good stability during a single CV trace, the ECL intensity of **DAA1** decreases gradually with repeated scans. However, intensity loss for every subsequent scan is much smaller (3–5%) than that for **DAA1** in aqueous solution (15–25%). ECL emission of **DAA1** in DMF reaches a somewhat constant value after several repeated scans, which is maintained only for 3–4 further repeated pulses (Supporting Information). Afterward, the intensity drops again for the subsequent scan. A similar behavior has been observed with other diarylanthracene derivatives as reported in the literature.[1,2] In contrast, the ECL emission intensity of **DAA2** in DMF is found to be invariable for each repeated scan, which is similar to the behavior observed in aqueous solution. In other words, the ECL intensity of **DAA2** is very stable and independent of the medium as well as of repeated oxidative scans (Figure 6). For the quantification of the ECL emission of **DAA1** and **DAA2**, relative ECL efficiency ($\Phi_{\mathrm{rel,ECL}}$, integrated light intensity under an emission curve) was measured using $[\mathrm{Ru(bpy)_3}]^{2+}$ as a standard; the results are summarized in Table 1. The values of $\Phi_{\mathrm{rel,ECL}}$ of **DAA1** and **DAA2** are found to be ca. 7-fold higher than the standard Ru complex.

■ DISCUSSION

The high luminescence quantum yield and facile oxidation and reduction behavior of diarylanthracenes applies to applications in diverse areas including optoelectronic materials, sensors, electroluminescence, solar cells, etc.[1,21] The UV–vis absorption and PL spectra of **DAA1** and **DAA2** are measured in aqueous and methanol solutions; they both resemble closely that of the parent **DPA**.[3,14] The $\lambda_{\max}$ absorption and emission values are slightly increased with solvent polarity in regard to the solvent effect on photophysical properties of diarylanthracenes.[1] A blue-shifted absorption and emission maximum is observed for **DAA2** ($\lambda_{\max}^{\mathrm{abs}}$ 366 nm, $\lambda_{\max}^{\mathrm{em}}$ 422 nm) as compared to those of **DAA1** ($\lambda_{\max}^{\mathrm{abs}}$ 373 nm, $\lambda_{\max}^{\mathrm{em}}$ 430 nm) as a result of the reduced conjugation between the dimethylphenyl substituents and the anthracene core in the former system. The dimethylphenyl groups in **DAA2** twist out of the plane of the anthracene core by 89°, which is 22° higher than the torsional angle between phenyl and anthracene in **DAA1** (67°), owing to higher steric interaction between the $-\mathrm{CH_3}$ with the nearest hydrogens of the anthracene ring in **DAA2**. Hence, the dimethylphenyl groups have weak communication with the anthracene when compared to **DAA1**. The lack of planarity between phenyl rings and anthracene inhibits excimer formation of **DAA1** and **DAA2** in solution (Supporting Information). The fluorescence quantum yields of **DAA1** and **DAA2** vary from 0.60 to 0.78 in aqueous and organic solutions. One may notice that the imidazolium residues in **DAA1** and **DAA2** do not affect the electronic and optical properties of the diarylanthracene core,[12] which is apparent from similar spectral features with those of the parent **DPA** (Figure 1). The marginal differences in PL quantum yields of **DAA1** and **DAA2** as compared to **DPA** may be due to the greater internal conversion of the *n*-propyl substituents in the former chromophores. Thus, **DAA1** and **DAA2** conserve the electronic and photophysical properties of **DPA**.

One of the frequent drawbacks of diarylanthracenes is their lack of photostability due to facile oxygenation at the *meso*-positions of the anthracene core.[3] Although our interest was to explore the advantages of the sterically congested **DAA2** over **DAA1** as an ECL probe, the study of their photostability (**DAA1** and **DAA2**) allowed us to judge on the impact of the CH_3 groups at the 2,6-positions of the phenyl unit more clearly. Judging from the photo-oxygenation study, **DAA2** is much superior to **DAA1** with respect to photostability. It is understandable that steric repulsion between oxygen and the proximal *ortho*-CH_3 groups at the phenyl rings of **DAA2** disfavors 9,10-endoperoxide formation. A similar trend is reported for the *anti*-isomer of 9,10-bis(*o*-tolyl)anthracene, whose photostability was reported to be higher than that of **DPA**.[8c] **DAA1** not only lacks photostability but also undergoes ready oxygenation at the *meso*-positions, similar to **DPA** (Supporting Information). It is worth noting that the predominant formation of 9,10-endoperoxide in the case of **DAA1** implies that the C9 and C10 atoms of the anthracene core constitute the most electron-rich site, similar to the situation with **DPA**. In contrast, insensitivity of **DAA2** against oxygen is clearly a result of steric hindrance and not related to electronic effects.[8c]

The effect of steric hindrance induced by the 2,6-dimethylphenyl groups of **DAA2** on the reactive anthracene radical cations is illustrated by CV experiments. During the electrolysis, **DAA1** exhibits irreversible electron transfer in aqueous solution due to nucleophilic attack by water, resulting in the formation of byproduct 9,10-bis(*N*-methylimidazolium-3-propoxyphenyl)-9,10-dihydroanthracenediol as established by NMR analysis. In contrast, **DAA2** shows two consecutive one-electron oxidation waves in a reversible fashion to **DAA2**$^{+\bullet}$and partial reversibility to **DAA2**$^{2+}$, in aqueous solution (Figure 2). Normally, aromatic radical cations are extremely reactive species; therefore, only in few cases reversible redox behavior of either cation or dication has been reported in aqueous or acidic medium.[1,18,22] Our results clearly demonstrate that one may generate stable aryl cations in aqueous medium by installing appropriate shielding groups at the reactive positions of the chromophore/electrophore.

In order to understand the electrochemical behavior of **DAA1** and **DAA2** in non-aqueous medium, electrolysis was conducted in DMF solution. Reversible one-electron oxidation generates radical cations (**DAA1**$^{+\bullet}$ and **DAA2**$^{+\bullet}$), while further oxidation to the dication is successful exclusively for **DAA2**. In case of **DAA1**, an irreversible second oxidation wave is observed. The irreversible redox behavior of **DAA1** in non-aqueous DMF clearly indicates that the dication (**DAA1**$^{2+}$) is unstable on the time scale of CV. Therefore, it is likely that the dimethylphenyl substitution in **DAA2** not only is responsible for the suppression of nucleophilic attack but also blocks any annihilation process by stabilizing the radical ions via nonbonded interactions. This is further evidenced by the analogous substitution effect reported for several anthracene derivatives.[8,23] For example, cations of 9,10-diarylanthracenes were reported to be more stable than those of 9-arylanthracenes and anthracene. Likewise, 9-arylanthracenes form more stable cations than the unsubstituted anthracene.[23] Partial reversibility of the second electron oxidation as exhibited by **DAA2** in aqueous and dry DMF may be due to a lack of additional substitutions at C2 and C6 positions of the anthracene core. Electrochemical investigations of anthracenes functionalized at C2, C6, C9, and C10 positions show complete reversibility for both first and second electron transfer.[22,24] We expect that the instability and partial stability of **DAA1**$^{2+}$ and **DAA2**$^{2+}$, respectively, will not affect the quality of ECL since ECL is generated by spanning the electrode potential slightly beyond the first oxidation peak potential.[1] In particular, co-reactant-mediated ECL, if properly using the correct switching potential, is not usually affected by the second redox potential.[1b,19]

Due to the application of **DPA** as a precursor in different fields, the structures of neutral, cation, and anion radicals of **DPA** have previously been studied in great detail, utilizing different types of experimental and theoretical techniques.[17,18,22] The DFT-optimized geometries of **DAA1** and **DAA2** and their radical cations closely resemble previously published results. As depicted in Figure 4, the *ortho*-CH_3 groups of the phenyl unit in **DAA2**, due to severe steric interactions with protons 1H, 4H, 5H, and 8H of the anthracene, assume an orientation, in which the top and bottom of the reactive *meso*-carbons (C9 and C10) are well shielded against attack (e.g., $^1O_2$). Similar properties have been reported earlier for other sterically congested diarylanthracenes.[8,24]

The optimized geometry of **DAA1**$^{+\bullet}$ and **DAA2**$^{+\bullet}$ shows a change in the orientation of the phenyl groups for **DAA1**$^{+\bullet}$ only. The torsional angle changes from 67 to 53° upon oxidation of **DAA1**, due to the need of charge delocalization in **DAA1**$^{+\bullet}$,[18b] as apparent from ESR analysis in related cases.[8,18a] In contrast, the dihedral angle remains unaltered for **DAA2** (89°), and its radical cation **DAA2**$^{+\bullet}$ (88°) as an angle change would cause severe intramolecular steric hindrance. As in the neutral molecule, **DAA2**$^{+\bullet}$ is well shielded against attack.[24]

Good ECL behavior of **DAA1** and **DAA2** is realized in aqueous and DMF solution containing TPrA as a co-reactant.[19] At a scan rate of 100 mV s^{-1} (potential range = 0.15 to 0.95 V), **DAA1** and **DAA2** in DMF provide ECL signals that are similar to that for **DPA**, indicating that the imidazolium substituents do not affect the electronic situation.[12] The comparable emission energies detected in the PL and ECL spectra indicate that the same excited state is formed in both experiments. In the case of **DAA1**, ECL is not stable for subsequent scans in aqueous and DMF solution. Even when the electrode is repolished for each scan, ECL emission is not restored, suggesting that the decay is caused by formation of byproducts, such as 9,10-bis(*N*-methylimidazolium-3-propoxyphenyl)-9,10-dihydroanthracenediol. Furthermore, the decomposition of **DAA1** with each scan in ECL may be monitored by PL, as the initial fluorescence intensity of **DAA1** decreases versus the number of repeated scans. Even in DMF, **DAA1**$^{+\bullet}$ undergoes decomposition to unstable products as revealed by NMR (^1H NMR shows highly complicated aromatic region). So far, the exact reason for the loss of ECL efficiency in non-aqueous DMF is unknown, but a similar behavior was observed previously with other diarylanthracene derivatives in non-aqueous CH_3CN, $C_2H_4Cl_2$, fluorobenzene, etc.[1,2,25] On the other hand, the sterically hindered anthracene **DAA2** produces a stable ECL emission for more than 100 repetitive scans, independent of the medium. Thus, ECL, photochemical, and electrochemical results of **DAA2** in aqueous and non-aqueous medium clearly indicate that steric hindrance caused by the 2,6-dimethylphenyl groups actively protects the reactive C9 and C10 positions of the anthracene core against nucleophilic attack and intermolecular annihilation. Similar features have been reported for two other sterically congested ECL emitters, namely, *meso*-tetrakis(3-sulfonatomesityl)-porphyrin[26] and 2,6-bis(9-[1,1′-biphenyl]-9-[*p*-tolyl]fluoren-2-yl)-9,10-di[*p*-tolyl]anthracene[24] in aqueous and organic solution, respectively. The values of relative ECL intensities $\Phi_{\text{rel'ECL}}$ for **DAA1** and **DAA2** in aqueous and DMF solutions are given in Table 1. It should be noted that both **DAA1** and **DAA2** exhibit higher ECL efficiency than the standard $[\text{Ru(bpy)}_3]^{2+}$, in agreement with their higher PL quantum yields.[24,27] Comparing **DAA1** and **DAA2**, the former shows a 10% higher efficiency than latter due to the absence of $-CH_3$ substitutions that may cause energy dissipation by rotation.

As mentioned at the onset, only $[\text{Ru(bpy)}_3]^{2+}$-based ECL emitters have commercially been used in bioanalysis.[1b,c] Usual drawbacks for other reported ECL luminophores are limited water solubility and lack of photo- as well as electrochemical stability.[1b] As an alternative, hydrophobic ECL luminophores were encapsulated in either nanoparticles or polymer blends to enable ECL in aqueous media.[4,6,28] Using appropriately shielded molecular luminophores that are inert under aqueous conditions seems to be a much more straightforward strategy.[26] Water-soluble organic fluorophores, including **DAA1** and **DAA2** as reported here, exhibit higher ECL efficiency and readily overcome the disadvantages existing with the more familiar ruthenium (inorganic)-based ECL emitters, such as environment unfriendliness, limited availability, etc.[29]

In summary, the water-soluble diarylanthracenes **DAA1** and **DAA2** are successfully prepared by introducing positively charge imidazolium groups at remote positions of the luminophore. Both **DAA1** and **DAA2** exhibit optical and electrochemical properties similar to that of the parent blue emitter 9,10-diphenylanthracene. The dimethylphenyl substitution in **DAA2** imparts substantial photochemical and electrochemical stability to the anthracene unit. As a result, stable ECL emission of **DAA2** is observed even in aqueous medium during co-reactant-mediated oxidation. These findings illustrate that the use of steric hindrance as a tool to protect active sites of a luminophore against undesired electrochemical reactions is a successful addition to ECL design strategies.

■ EXPERIMENTAL SECTION

General Aspects. All reactions were performed under a nitrogen gas atmosphere in oven-dried glassware. Dry tetrahydrofuran, benzene, and toluene were freshly distilled over sodium prior to use. All reactions were monitored by analytical thin layer chromatography (TLC) on silica gel. Column chromatography was conducted with silica gel (60−120 mesh). All commercial chemicals were used as received. All measurements were carried out at ambient conditions unless stated otherwise. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer in deuterated solvents.

UV−vis absorption spectra were recorded using a 10 μM solution of **DAA1** or **DAA2** in either methanol or aqueous buffer solution. PL spectra and quantum yields (Φ_{PL}) were measured with excitation and emission slits of either 1.5 or 2.5 nm. The concentration used was 10 μM, and Φ_{PL} values were determined using 9,10-diphenylanthracene as a standard (Φ = 0.9 in cyclohexane, λ_{exc} = 365 nm).[15] The following equation was used for the calculation of Φ_{PL} for **DAA1** and **DAA2**:

$$\phi_u = \phi_s(I_u/I_s)(A_s/A_u)(\eta_u/\eta_s)^2$$

where the subscripts "s" and "u" refer to standard and unknown samples, A_u and A_s to absorbances of the sample and the standard at the excitation wavelength, I_u and I_s to the integrated emission intensities (i.e., areas under the emission curves) of the sample and the standard, and η_u and η_s to the refractive indexes of the corresponding solutions (pure solvents are assumed; water 1.333, methanol 1.329, and cyclohexane 1.427).

Cyclic voltammograms were obtained using a standard three-electrode setup, that is, a 1 mm platinum disk working electrode, a platinum wire counter electrode, and a silver wire as pseudoreference electrode. The working electrode in each case was polished on a felt pad with alumina slurry and then rinsed with water followed by acetone and subsequently dried with air. The potentials were measured at a scan rate of 100−200 mV s^{-1}. All solutions for the electrochemical experiments contained the compounds of interest, **DAA1** or **DAA2** at 5×10^{-4} M and tetra-*n*-butylammonium hexafluorophosphate (TBAP) as the supporting electrolyte (0.1 M). Ferrocene (Fc) was used as the internal standard in non-aqueous DMF solution.

Electrochemiluminescence measurements were performed using a 5×10^{-4} M solution of **DAA1** and **DAA2** in DMF or aqueous buffer solution containing additionally tris-*n*-propylamine (TPrA, 50×10^{-3} M) as a co-reactant. A similar electrode setup as in the CV experiment was used. To generate ECL, the potential was swept across the first oxidation potential (0.15−0.95−0.15 V with respect to a silver wire as a quasi-reference electrode) at 100 mV s^{-1}. The resulting emission spectra were recorded with a CCD camera cooled at −130 °C. The relative ECL efficiency of **DAA1** and **DAA2** was determined by using the equation[30]

$$\Phi_{\text{rel'ECL}} = \Phi°_{\text{ECL}}(I/Q)(Q°/I°)$$

where $\Phi_{\text{rel'ECL}}$ and $\Phi°_{\text{ECL}}$ are the ECL efficiency of the target and standard samples, I and $I°$ are the integrated ECL intensities (area under a curve) of the target and standard systems, and Q and $Q°$ are the charges consumed by the target and standard, respectively. We used $[\text{Ru(bpy)}_3]^{2+}$ as a standard with the $\Phi_{\text{rel'ECL}}$ value of 1.[30] In order to maintain an equal charge transfer for the target emitter co-reactant and standard co-reactant systems during ECL,[30] we performed experiments at exactly similar conditions (i.e., same electrode, solvent, electrolyte, co-reactant, and concentrations).

Preparation of 9,10-Bis(4-methoxyphenyl)anthracene. 9,10-Dibromoanthracene (1.0 g, 3.0 mmol), 4-methoxyphenylboronic acid (1.0 g, 6.6 mmol), and $[\text{Pd(PPh}_3)]_4$ (0.21 mg, 6.0 mol %) were introduced into an initially oven-dried pressure tube under N_2. To this mixture were added toluene (20 mL) and saturated $NaHCO_3$ solution (7 mL). The reaction mixture was refluxed at 90−100 °C for 12 h. Then the contents were extracted with CH_2Cl_2, dried over Na_2SO_4, and the solvent was evaporated. The resultant material was purified by silica gel column chromatography using 5−10% CH_2Cl_2 in hexane, yielding 9,10-bis(4-methoxyphenyl)anthracene as a pale yellow solid (0.92 g, 82%): mp 272−274 °C (mp 274 °C);[31] R_f 0.22 in hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (s, 6H, 5-H), 7.15 (d, J = 8.8 Hz, 4H, 3-H), 7.32−7.34 (m, 4H, 2-H), 7.40 (d, J = 8.8 Hz, 4H, 4-H), 7.73−7.75 (m, 4H, 1-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.1, 113.5, 124.6, 126.7, 129.9, 130.8, 132.1, 136.4, 158.7.

Preparation of 9,10-Bis(4-methoxy-2,6-dimethylphenyl)-anthracene. This compound was prepared according to a previously reported protocol.[13] To a solution of 9,10-dibromoanthracene (1.0 g, 3.0 mmol) and dry $NiCl_2(PPh_3)_2$ (0.30 mg, 10.0 mol %) in 50 mL of THF at −35.0 °C was added 4-methoxy-2,6-dimethylphenylmagnesium bromide (2.4 equiv) in THF over 1.5 h. The resultant dark green solution was brought to room temperature and refluxed at 80 °C for 36 h. Subsequently, the reaction mixture was quenched with 10% aqueous HCl and extracted with ethyl acetate, dried over Na_2SO_4, and the solvents were evaporated. The brown residue was purified by column chromatography over silica gel using 5−10% CH_2Cl_2 in hexane to furnish 9,10-bis(4-methoxy-2,6-dimethylphenyl)anthracene as a white powder (0.42 mg, 32%): mp 247−251 °C; R_f 0.18 in hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 12H, 4-H), 3.91 (s, 6H, 5-H), 7.11 (s, 4H, 3-H), 7.33−7.35 (m, 4H, 2-H), 7.75−7.77 (m, 4H, 1-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.2, 59.9, 124.8, 127.1, 130.0, 130.6, 131.7, 134.4, 136.9, 156.3. Anal. Calcd for $C_{32}H_{30}O_2$: C, 86.06; H, 6.77. Found: C, 86.08; H, 6.53.

Preparation of 9,10-Bis(4-hydroxyphenyl)anthracene. To a solution of 9,10-bis(4-methoxyphenyl)anthracene (0.90 g, 2.3 mmol) in 15.0 mL of CH_2Cl_2 at 0 °C was added dropwise 1.0 M BBr_3 solution in

CH_2Cl_2 (5.1 mL) under N_2 gas atmosphere. The reaction mixture was allowed to stir overnight. Subsequently, it was quenched with 10% aqueous HCl, extracted with ethyl acetate, dried over Na_2SO_4, treated with charcoal, filtered, and concentrated. The pure product was obtained as a colorless solid after filtration over a short pad of silica gel using 50% ethyl acetate in hexane, followed by recrystallization from ethyl acetate and hexane furnishing 9,10-bis(4-hydroxyphenyl)anthracene as a greenish-yellow solid (0.71 g, 87%): mp 278−282 °C dec.; R_f 0.31 in ethyl acetate−hexane, 4:1 ratio; IR (KBr, cm^{-1}) 3366 (b, −OH); ^{1}H NMR (400 MHz, CD_3OD) δ 6.98 (d, J = 12.4 Hz, 4H, 3-H), 7.14 (d, J = 12.4 Hz, 4H, 4-H), 7.21−7.23 (m, 4H, 2-H), 7.61−7.63 (m, 4H, 1-H); ^{13}C NMR (100 MHz, CD_3OD) δ 116.3, 125.8, 128.0, 131.2, 131.6, 133.4, 138.2, 158.1. Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01. Found: C, 86.07; H, 5.12.

Preparation of 9,10-Bis(4-hydroxy-2,6-dimethylphenyl)-anthracene. This compound was prepared from 9,10-bis(4-methoxy-2,6-dimethylphenyl)anthracene following the same procedure as described above (yield 89%): mp 271−273 °C; R_f 0.30 in ethyl acetate−hexane (4:1); IR (KBr, cm^{-1}) 3426 (b, −OH); ^{1}H NMR (400 MHz, CD_3OD) δ 2.34 (s, 12H, 4-H), 6.96 (s, 4H, 3-H), 7.26−7.29 (m, 4H, 2-H), 7.68−7.71 (m, 4H, 1-H); ^{13}C NMR (100 MHz, CD_3OD) δ 16.9, 125.6, 125.8, 128.2, 131.5, 131.6, 132.3, 138.4, 153.9. Anal. Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 86.06; H, 6.15.

Preparation of 9,10-Bis(4-bromopropoxyphenyl)-anthracene. 9,10-Bis(4-hydroxyphenyl)anthracene (0.70 g, 1.9 mmol) was dissolved in 30 mL of acetone. After adding potassium carbonate (1.6 g, 11.6 mmol) and 1,3-dibromopropane (0.6 mL, 5.8 mmol), the resultant heterogeneous solution was stirred for 8 h at room temperature. Afterward, acetone was removed and the solid was extracted with CH_2Cl_2. After drying over Na_2SO_4 and evaporation of the solvents, the crude product was purified by silica gel column chromatography using CH_2Cl_2 yielding 9,10-bis(4-bromopropoxyphenyl)anthracene as a colorless solid (0.90 g, 76%): mp 243−246 °C; R_f 0.18 in hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (quint, J = 6.0 Hz, 4H, 6-H), 3.72 (t, J = 6.4 Hz, 4H, 7-H), 4.27 (t, J = 5.8 Hz, 4H, 5-H), 7.15 (d, J = 8.8 Hz, 4H, 3-H), 7.32−7.35 (m, 4H, 2-H), 7.39 (d, J = 8.8 Hz, 4H, 4-H), 7.73−7.76 (m, 4H, 1-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.8, 32.2, 65.1, 114.1, 124.6, 126.7, 129.9, 131.1, 132.1, 136.4, 157.8. Anal. Calcd for $C_{32}H_{28}Br_2O_2$: C, 63.59; H, 4.67. Found: C, 63.37; H, 4.62.

Preparation of 9,10-Bis(4-bromopropoxy-2,6-methylphenyl)anthracene. This compound was prepared from 9,10-bis(4-hydroxy-2,6-dimethylphenyl)anthracene by the same procedure as described above (yield 79%): mp 219−224 °C; R_f 0.16 (n-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 12H, 4-H), 2.45 (quint, J = 6.0 Hz, 4H, 6-H), 3.80 (t, J = 6.4 Hz, 4H, 7-H), 4.10 (t, J = 6.4 Hz, 4H, 5-H), 7.11 (s, 4H, 3-H), 7.32−7.35 (m, 4H, 2-H), 7.73−7.75 (m, 4H, 1-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.4, 30.4, 33.6, 69.2, 124.8, 127.1, 129.9, 130.7, 131.7, 134.5, 136.8, 154.8. Anal. Calcd for $C_{36}H_{36}Br_2O_2$: C, 65.47; H, 5.49. Found: C, 65.49; H, 5.48.

Preparation of DAA1. A solution of 9,10-bis(4-bromopropoxyphenyl)anthracene (0.90 g, 1.4 mmol) and N-methylimidazole (0.51 g, 5.6 mmol) in 60 mL of acetone was refluxed under N_2 for 10 h. After this period, a colorless precipitate formed and was isolated by filtration. The solid was dissolved in DMF (4−5 mL), and NH_4PF_6 (0.50 g, 3.1 mmol) was added. The mixture was stirred for about 30 min and poured in acetone (15 mL). The precipitate formed was isolated by filtration and washed with small portions of cold water. The imidazolium salt was purified by recrystallization from a water/acetone mixture to yield 0.71 g (66%): mp 297−300 °C dec.; R_f 0.12 in methanol; IR (KBr, cm^{-1}) 3388, 3138, 3049, 2931, 2858, 1571, 1466, 1380, 1337, 1172, 1019, 890, 767, 655, 625; ^{1}H NMR (400 MHz, CD_3OD) δ 2.49 (quint, J = 6.0 Hz, 4H, 6-H), 3.98 (s, 6H, 8-H), 4.24 (t, J = 5.6 Hz, 4H, 5-H), 4.56 (t, J = 7.2 Hz, 4H, 7-H), 7.17 (d, J = 8.4 Hz, 4H, 3-H), 7.30−7.34 (m, 8H, 2\4-H), 7.62−7.65 (m, 6H, 1\9-H), 7.77 (t, J = 5.6 Hz, 2H, 10-H), 9.1 (s, 2H, 11-H); ^{13}C NMR (100 MHz, CD_3OD) δ 30.9, 36.6, 48.5, 65.9, 115.6, 124.1, 125.1, 126.1, 127.9, 131.5, 132.9, 133.6, 137.9, 138.3, 159.5; ESI-MS m/z (%) 753.3 (100) $[M - PF_6]^+$. Anal. Calcd for $C_{40}H_{40}F_{12}N_4O_2P_2$: C, 53.46; H, 4.49; N, 6.23. Found: C, 53.19; H, 4.61; N, 6.27.

Preparation of DAA2. This compound was prepared starting from 9,10-bis(2,6-methyl-4-bromopropoxyphenyl)anthracene by following the procedure described above (yield 71%): mp 286−290 °C dec.; R_f 0.12 in methanol; IR (KBr cm^{-1}) 3170, 3125, 2934, 2862, 1575.6, 1469, 1382, 1169, 1113, 839, 740, 651, 624, 558; ^{1}H NMR (400 MHz, CD_3OD) δ 2.40 (s, 12H, 4-H), 2.53 (quint, J = 6.4 Hz, 4H, 6-H), 4.00 (s, 6H, 8-H), 4.09 (t, J = 6.0 Hz, 4H, 5-H), 4.64 (t, J = 7.2 Hz, 4H, 7-H), 7.08 (s, 4H, 3-H), 7.30−7.32 (m, 4H, 2-H), 7.62−7.67 (m, 6H, 1\9-H), 7.83 (t, J = 2 Hz, 2H, 10-H), 9.13 (s, 2H, 11-H); ^{13}C NMR (100 MHz, CD_3OD) δ 16.7, 32.1, 36.6, 48.6, 69.9, 123.9, 125.1, 126.0, 127.9, 131.3, 132.2, 132.9, 136.2, 138.0, 156.5; ESI-MS m/z (%) 809.3 (100) $[M - PF_6]^+$. Anal. Calcd for $C_{44}H_{48}F_{12}N_4O_2P_2$: C, 55.35; H, 5.07; N, 5.87. Found: C, 55.28; H, 5.01; N, 5.87.

Photo-oxidation of Diarylanthracenes DAA1 and DAA2. To a solution of **DAA1** or **DAA2** in either water or methanol was added methylene blue (catalytic amount: <1.0 mg) followed by bubbling oxygen through the solution over 15−20 min. The resultant clear solution was irradiated with a xenon lamp at 20 °C. Progress of the reaction was monitored for up to 16−20 h by fluorescence decay. After completion of the reaction, the solvent was removed under vacuum at room temperature and the crude product was purified by recrystallization in a water/acetone mixture. Molecule **DAA2** did not yield any endoperoxide, as concluded from NMR and fluorescence monitoring.

9,10-Endoperoxide from DAA1: Yield 96%; R_f 0.15 in methanol; IR (KBr cm^{-1}) 3059, 2920, 1491, 1458, 1437, 1383, 1246, 1024, 942, 767, 751, 666; ^{1}H NMR (400 MHz, CD_3OD) δ 2.39 (quint, J = 6.0 Hz, 4H, 6-H), 3.91 (s, 6H, 8-H), 4.10 (t, J = 5.6 Hz, 4H, 5-H), 4.45 (t, J = 6.8 Hz, 4H, 7-H), 6.96 (d, J = 8.4 Hz, 4H, 3-H), 7.12 (d, J = 8.8 Hz, 4H, 2-H), 7.49−7.59 (m, 10H, 1\4\9-H), 7.68 (d, J = 2.0 Hz, 2H, 10-H), 9.02 (s, 2H, 11-H).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional UV−vis, PL, CV, and ECL figures, and NMR reproduction for arbitrates and **DAA1** and **DAA2**, atomic coordinates and absolute energies of all structures are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: natarajan@chemie.uni-siegen.de, schmittel@chemie.uni-siegen.de.

Notes

The authors declare no competing financial interest.

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