Electrogenerated Chemiluminescence of Cationic Triangulene Dyes: Crucial Influence of the Core Heteroatoms

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Electrogenerated chemiluminescence of cationic triangulene dyes: Crucial influence of the core heteroatoms

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Abstract: Trianguleniums are fascinating conjugated hexacyclic cations that exhibit interesting electronic and optical properties. Herein, the electrogenerated chemiluminescence (ECL) emission of this family of fluorescent dyes is reported for the first time. Redox behavior and fluorescence properties of eight cationic triangulene luminophores with different heteroatom patterns in the core structure and various pending substituents were examined to rationalize the ECL. Clearly, the more electron-rich the carbocations, the more efficient the corresponding ECL and two very distinct classes of triangulenes can be drawn from these studies using an ECL wall sufficiency formalism.

Conventional chemiluminescence (CL) is well-recognized for numerous bioassay applications based on the direct conversion of a chemical signal into light emission.[1] Electrogenerated chemiluminescence (ECL) belongs to the CL class of reactions but the generation of the excited state results from an initial electrochemical step.[2] Light emission occurs during the relaxation to the ground state. Benchmark luminescent techniques such as fluorescence or CL are potentially very sensitive because the output signal is produced in bulk solutions. Compared to other luminescent techniques, ECL is confined to an electrode surface but provides also advantageous features such as a high sensitivity combined with a low background signal. In addition, the excited state being produced locally at the surface of the electrode, manipulation of the luminescence can be achieved with excellent spatial and temporal resolutions using electrochemistry. Indeed, the time, the duration and the position of the light-emitting region is easily controlled electrochemically by producing *in situ* the reactive species involved in the global ECL process. In addition, it allows the simultaneous measurement of two experimental parameters (i.e., light intensity and faradaic current) *versus* potential and thus a great selectivity and control over the ECL phenomenon. ECL has found a large number of applications ranging from the development of ultrasensitive bioassays[3] to the design of light-emitting dynamic devices.[4] Currently, research is focusing on the development of new families of luminophores with tunable wavelength and capability.[5]

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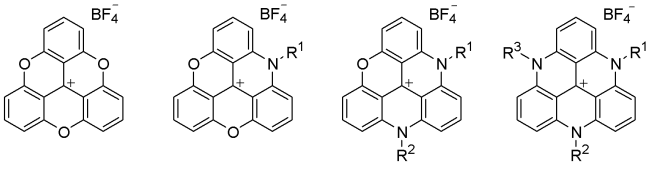
The expected features for these new moieties are low oxidation potential, high emission efficiency and good chemical stability. In this context, stabilized cations such as triaryl methyl carbenium ions are interesting as they have been widely explored for their remarkable optical properties despite an often-poor electron delocalization efficiency due to the non-planarity of the twisted phenyl rings.[6] To overcome this limitation, planarized cationic triangulene derivatives have been developed for instance.[7] The oxygen derivative **TOTA**$^+$, standing for trioxatriangulenium ion, was first described (Scheme 1).[8] The synthesis of the analogous mixed aza/oxa **ADOTA**$^+$ and **DAOTA**$^+$ and triaza **TATA**$^+$ derivatives was achieved only recently.[9] Thanks to high chemical stabilities and superior electronic properties, these compounds have enticed a large variety of applications from biology to physics.[7,9c,10] In fact, such triangulenium cations are useful dyes and luminophores exhibiting interesting (electro)chemical and (photo)physical properties that can be adjusted by tuning the heteroatoms within the core structures and also the nature of the side chains.[7,10a] However, to the best of our knowledge, their capability to promote ECL had never been disclosed. In this context, we report herein the electrochemical and fluorescence studies of a series of eight cationic triangulenes (Scheme 1) for which ECL is described for the first time. A comparison between the ECL and fluorescence behavior is drawn as well as a thermodynamic rationalization of the efficiency to generate the excited state. Finally, it appears that cationic triangulenes are suitable candidates for further development of ECL dyes, as their emission wavelengths can be advantageously tuned by the controlled incorporation of various heteroatoms into the molecular core.



Scheme 1. Cationic triangulene dyes and fluorophores. **TOTA**$^+$: trioxatriangulenium, **ADOTA**$^+$: azadioxatriangulenium, **DAOTA**$^+$: diazaoxatriangulenium, **TATA**$^+$: triazatriangulenium. **DCP** stands for 3,5-dichloro-2-hydroxyphenyl.

The electrochemical properties of the triangulenium molecules were first investigated by cyclic voltammetry (CV) and the results are gathered in Figure 1 and Table 1.[11] These experiments have been performed in degassed CH_3CN solutions containing 1 mM of each triangulenium salts and 0.1 M *n*-

tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. CVs exhibited both oxidation and reduction waves in the potential window of the experiment. **TATA$^+$** presents the most negative reduction potential with a typical $E°_{red}$ = −1.20 V *vs.* Fc/Fc^+ (Figure 1). This process is a reversible monoelectronic transfer generating a neutral radical from the cation. It is noteworthy that repetitive cleaning and polishing of the electrode surface is mandatory to record accurate and reproducible CVs as these compounds have a strong tendency to adsorb at the surface of the working electrode.[10o] On the other hand, the oxidation process of **TATA$^+$** is more complex exhibiting three partially-reversible waves that have been defined by the corresponding anodic peaks centered at E_{ox} = 1.34, 1.68 and 1.87 V *vs.* Fc/Fc^+, respectively. The first oxidation was assigned to the removal of an electron to generate the corresponding radical dication. Further anodic behavior shows that at least two additional electrons can be sequentially removed from **TATA$^+$**, thus yielding to highly oxidized species. Changing either the nature of the heteroatoms or the pending substituents had a strong influence on both oxidation and reduction potentials of the dyes (Table 1). The presence of an electron donating group brings a larger electron density and renders the reduction more difficult. From Figure 1, it is obvious that the reduction potential becomes sequentially more positive along the series **TATA$^+$**, **DAOTA$^+$**(**Pr**), **ADOTA$^+$**(**Pr**), and **TOTA$^+$** (see Table 1). In fact, the reduction becomes easier when replacing successively the electron donating nitrogen by 1, 2 or 3 oxygen atoms with $E°_{red}$ = −0.73 V, −0.33 V and −0.12 V *vs.* Fc/Fc^+, respectively. The cyclic voltammograms revealed that the reduction process appear to be electrochemically reversible for all studied compounds. However, dimerizations of TOTA radical and related triarylmethanes prepared by chemical reduction with chromous chloride have been disclosed.[12] Herein we observed a reversible electrochemical reduction of the cationic triangulenes into neutral species. However, this characteristic feature is probably very much dependent on the time scale of the experiments (in our study, typically a few seconds using cyclic voltammetry at a scan rate of 0.1 V s^{-1}). By contrast, the structure/activity relationship (SAR) for the anodic part is not straightforward as the oxidation of the **DAOTA$^+$**, **ADOTA$^+$** and **TOTA$^+$** appears to be irreversible and occurring at higher potential values by comparison to **TATA$^+$**. Nevertheless, these results are consistent with that reported in the literature.[11-13] A SAR study was also possible for both **ADOTA$^+$** and **DAOTA$^+$** sub-families for which three different moieties were compared; *n*-propyl (**Pr**), phenyl (**Ph**) or 3,5-dichloro-2-hydroxyphenyl (**DCP**) appendages being introduced on one nitrogen atom for each series (Scheme 1). A similar trend was observed in both families as the reduction potential becomes more negative from **Pr** to **Ph** and then to the **DCP** group. Comparing **Pr** and **DCP** affords a difference in $E°_{red}$ of about 0.29 V and 0.26 V for **ADOTA$^+$** and **DAOTA$^+$** respectively. The increased electron donating capability of the side chains (**DCP** > **Ph** > **Pr**) explains readily this trend. In summary, these results evidence that substituting oxygen by nitrogen atom(s) has a major influence on the electrochemical properties of these electro-active molecules. Moreover, the fine tuning of the redox properties can also be achieved through a careful choice of the nature of chemical functions pending on the nitrogen heteroatoms.

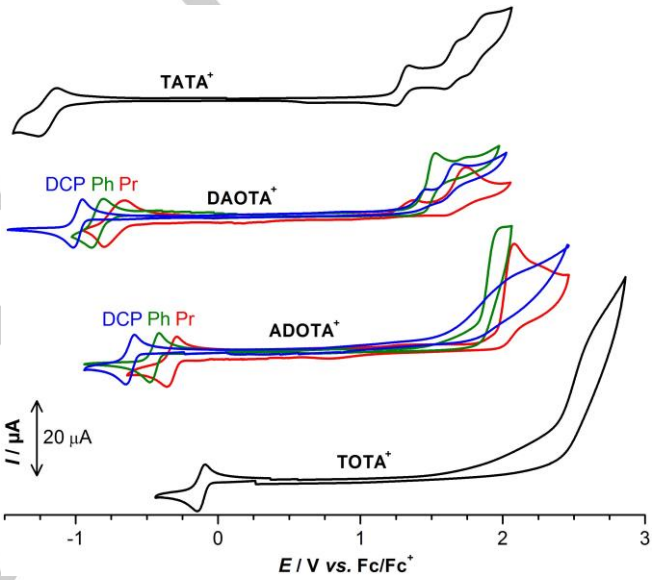


Figure 1. Cyclic voltammograms recorded in CH_3CN solutions with 0.1 M $TBAPF_6$ as supporting electrolyte and 1 mM of triangulenium salts. Scan rate 0.1 V s^{-1}.

Table 1. Electrochemical characterization, fluorescence and ECL data in CH_3CN.

Compounds	E / V *vs.* Fc/Fc^+		Fluo	ECL[c]	Φ_{Fluo}[d]	*Relative* Φ_{ECL}[e]	$\Delta G°$[f]
	$E°_{red}$[a]	E_{ox}[b]	λ_{max} / nm		%	%	/ eV
TATA$^+$	–1.20	1.34	558	585	19	35	–0.48
DAOTA$^+$(**Pr**)	–0.73	1.37	591	598	47	15	–0.13
DAOTA$^+$(**Ph**)	–0.84	1.53	590	598	36	21	–0.24
DAOTA$^+$(**DCP**)	–0.99	1.47	599	606	40	46	–0.42
ADOTA$^+$(**Pr**)	–0.33	2.08	558	566	52	< 10^{-4}	0.39
ADOTA$^+$(**Ph**)	–0.45	~ 2	563	567	48	10^{-4}	0.25
ADOTA$^+$(**DCP**)	–0.62	n.d.	570	579	31	2.10^{-4}	0.06
TOTA$^+$	–0.12	n.d.	524	n.d.	11	< 10^{-4}	0.75

[a] Reduction potentials calculated as the mean value of the cathodic and anodic peaks for the monoelectronic reduction process. [b] Oxidation processes are mostly irreversible therefore the potential value refers to the first anodic peak. [c] ECL spectra have been recorded in CH_3CN solutions containing 1 mM of triangulenium salts, 10 mM of BPO co-reactant and 0.1 M $TBAPF_6$. [d] The quantum yield (Φ_{Fluo}) values were measured in CH_3CN containing 50 µM trianguleniums

and 0.1 M $TBAPF_6$. [e] The ECL efficiency has been calculated by comparison with $Ru(bpy)_3^{2+}$ as a reference and is therefore denoted as a "relative ECL yield". [f] The values of $\Delta G°$ were calculated using eq 6.

Of interest for this study, cationic triangulenes are also effective dyes which usually absorb light in the visible region (450 to 600 nm) with extinction coefficients varying from 8200 to 18200 M^{-1} cm^{-1}, from **TOTA**$^+$ to **TATA**$^+$. Significant and gradual red-shifted absorptions are observed at low energy when replacing successively oxygen by nitrogen atoms in the cationic cores, *i.e.* from **TOTA**$^+$ to **DAOTA**$^+$. However, for **TATA**$^+$ derivatives, the influence of the symmetry is predominant compared to the electronic parameters and these compounds absorb at higher energy than **DAOTA**$^+$.[9b,9c] The photophysical properties of the cationic triangulenes were then recorded to be able to compare classical fluorescence with ECL. Contrary to fluorescence which starts by the absorption of a photon, the production of light by ECL requires an initial electrochemical step that brings *in fine* the luminophore to the excited state. Several chemical pathways can be used to promote ECL. For this study, rather than generating the excited state by an annihilation process,[2b,3a,14] a sacrificial co-reactant was utilized. In this later strategy, the co-reactant is used to produce a highly reactive radical that can directly react with the luminophore to afford the excited state. However, two approaches are then possible. On one hand, an oxidative-reductive approach consisting in the generation of a strong reductant by an electrooxidation step can be followed. For example, tri-*n*-propylamine (TPA) is oxidized at the surface of the electrode to generate, after dissociation, the TPA radical which is a strong reductant. This is used routinely to promote the ECL of tris(2,2'-bipyridine) ruthenium(II) complexes.[2b,3a] However, since triangulene cations display systematically well-reversible reduction waves but irreversible oxidations (see above), this approach was not pursued. Instead, a reductive-oxidative approach was chosen (eqs 1 to 5). First, the benzoyl peroxide (BPO) co-reactant is reduced simultaneously with the cationic triangulenes at the surface of the electrode (eqs 1 and 2). After dissociation (eq 3), BPO produces a strong oxidant $Ph\text{-}CO_2^{\bullet}$ that oxidizes the reduced luminophore to generate the excited state (eq 4). Finally, radiative de-excitation generates the desired ECL emission (eq 5).

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

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

$$BPO^{\bullet -} \rightarrow Ph\text{-}CO_2^- + Ph\text{-}CO_2^{\bullet} \quad (3)$$

$$Triangulene^{\bullet} + Ph\text{-}CO_2^{\bullet} \rightarrow Triangulenium^{+*} + Ph\text{-}CO_2^- \quad (4)$$

$$Triangulenium^{+*} \rightarrow Triangulenium^+ + h\nu \quad (5)$$

Using such a reductive-oxidative pathway, it was possible to collect successfully the ECL spectra for the whole series of compounds except **TOTA**$^+$ (Figures 2 and S1). Surprisingly though, while some cationic triangulenes displayed strong ECL characters (**TATA**$^+$ and **DAOTA**$^+$), others only exhibited very weak ECL intensity, and derivatives **ADOTA**$^+$ and **TOTA**$^+$ in particular.

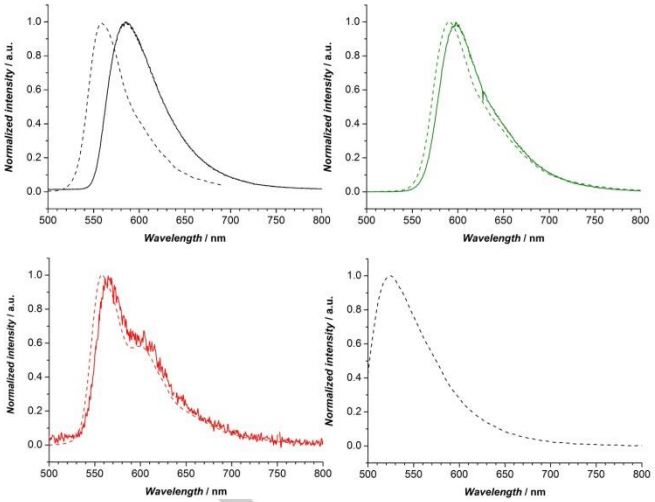


Figure 2. Representative fluorescence (dashed lines) and ECL (solid lines) spectra recorded in CH_3CN solutions. ECL performed under electrochemical control with 0.1 M $TBAPF_6$ and 1 mM of triangulenium salts. Fluorescence spectra have been recorded with solutions containing 10 µM of the triangulenium dye. Top left: **TATA**$^+$; Top right: **DAOTA**$^+$(**Ph**); Bottom left: **ADOTA**$^+$(**Pr**); Bottom right: **TOTA**$^+$, no recordable ECL spectrum in the latter case.

Comparison with the fluorescence spectra showed similar maxima and shapes (Figure 2). The natural inference is therefore that the same excited states are reached with both methods (electrochemical initiation and photon absorption). As previously reported, **TATA**$^+$ and **ADOTA**$^+$ were found to emit around 560 nm and, in the latter case and as noticed earlier, a marked shoulder at *ca.* 610 nm is observed on the fluorescence and ECL spectra of the **ADOTA**$^+$ derivatives.[10d,10m,13] For **DAOTA**$^+$ compounds, the emission is centered around 590 nm.[10k] **TOTA**$^+$ has the most energetic luminescence but only when irradiated (λ_{max} 524 nm) as the corresponding ECL spectra is not recordable. The introduction of the **DCP** group induces a ~ 10 nm red shift in all cases (λ_{max} = 570 nm for **ADOTA**$^+$ and 599 nm for **DAOTA**$^+$). Finally, when comparing the maximum emission on the fluorescence and ECL spectra, a small red shift is noticeable most of the time, typically between 5 and 25 nm. Such a shift is classically observed when comparing ECL and fluorescence spectra. It is mainly attributed to the inner-filter effects of the solution due to the very different concentration range of the dye used in ECL and fluorescence experiments (*i.e.* mM *vs.* µM, respectively) and also to the slight differences in the instruments used to collect ECL and PL data.[15]

The ECL intensities of all the studied triangulenium salts were also compared. A quantitative SAR was drawn by a direct measurement of the ECL intensity with a PMT detector (Figures S2). The corresponding ECL yields are referred to $Ru(bpy)_3^{2+}$ as a standard exhibiting arbitrary an ECL yield of 100%[16] (Table 1). As the ECL yields are calculated as referring to the efficiency of $Ru(bpy)_3^{2+}$, these values can be compared among the triangulenium series. However, no direct comparison of the ECL yield and fluorescence quantum yield can be drawn because the excitation processes are fundamentally different. Moreover, the photophysical contribution (i.e. quantum yield) is taken into account when measuring the ECL efficiency which is indeed a combination of the thermodynamic generation of the excited

state (eq. 4) and subsequent radiative emission to return to the ground state (eq. 5). **TATA$^+$** has a very good relative ECL yield of 35% while the **DAOTA$^+$** series are equally efficient with values ranging from 15% (**Pr**), 21% (**Ph**) and up to 46% (**DCP**). It could be underline that the ECL capability of these four dyes are quite high when compared to other organic luminophores.[3a] In contrast, **ADOTA$^+$** and **TOTA$^+$** derivatives show very low ECL capability that could only be detected on a highly sensitive calibration range. The corresponding relative ECL yields are typically 4 to 5 orders of magnitude smaller with **ADOTA$^+$**(**DCP**) exhibiting a yield of only 2 × 10^{-4} %. The ECL decreased to 10^{-4} % in the case of **ADOTA$^+$**(**Ph**) and is even lower for **ADOTA$^+$**(**Pr**) and **TOTA$^+$**. As already mentioned above, a direct comparison between fluorescence and ECL data should be done with cautions also because the classic experimental conditions are quite different (10 µM *versus* 1 mM dye concentration, respectively). However, two sets of controls were performed to validate such a comparison. First, we verified that the presence of the supporting electrolyte (0.1 M $TBAPF_6$) and also the co-reactant (10 mM BPO) does not affect the fluorescence behavior by recording the corresponding spectra with a selection of triangulenium molecules (Fig. S3). It is noteworthy that no relevant quenching was observed due to the presence of these additive chemicals in solution. Moreover, relative ECL yields were also measured by using 10 µM of triangulenium instead of 1 mM and the discrepancy between both experimental conditions was always smaller than 2 % which is typically ranging within the accuracy of the measurements (Fig. S4).

In order to deconvolute the photophysical contribution in the overall ECL process, the fluorescence quantum yields (Φ_{Fluo}) were measured in CH_3CN solutions containing the supporting electrolyte (Table 1). The experimental values found are in good agreement with previous reports,[13,17] and notably, the symmetry group has as expected a strong influence on the quantum yield. **ADOTA$^+$** ($0.31 < \Phi_{Fluo} < 0.52$) and **DAOTA$^+$** ($0.36 < \Phi_{Fluo} < 0.47$) of C_{2v} symmetry group are more efficient luminophores than **TOTA$^+$** ($\Phi_{Fluo} = 0.11$) and **TATA$^+$** ($\Phi_{Fluo} = 0.19$) of D_{3h} symmetry group).[7,9a,10a]

As observed experimentally, the cationic triangulene family is split into two distinctive categories showing either strong or dramatically low ECL capability. This kind of threshold energetic requirement can be rationalized by considering the free energy $\Delta G°$ associated to the homogeneous reaction giving the excited state (eq 6).

$$\Delta G° = E°_{red}(triangulenium) - E°_{ox}(Ph\text{-}CO_2^{\bullet}/Ph\text{-}CO_2^{-}) + E_{FI} \quad (6)$$

$$E_{FI} = 1239.81 / \lambda_{max} \quad (7)$$

The formation of the excited state occurs by reaction between the reduced triangulene species and the strongly oxidizing benzoyloxy Ph-$CO_2^{\bullet}$ radical and its energy is given by equation 6 in which $E°_{ox}(Ph\text{-}CO_2^{\bullet}/Ph\text{-}CO_2^{-})$ is a constant that has been reported to be 1.5 V *vs.* SCE (i.e. 1.36 V *vs.* Fc/Fc^+),[18] and E_{FI} is the energy of the excited state in eV. At room-temperature, in a first approximation, this latter could be calculated from the fluorescence emission data by equation 7, where λ_{max} is the maximum emission wavelength (Table 1). The corresponding estimated values for the lowest singlet excited state of the studied analytes are comprised between E_{FI} = 2.1 eV and E_{FI} = 2.4 eV so its variation is relatively low. The cathodic potentials $E°_{red}$ vary more drastically from −0.12 V to −1.2 V *vs.* Fc/Fc^+ so this must be the major factor governing the efficiency of the excited state formation in ECL, as indicated by the significant differences observed in the $\Delta G°$ values of each compounds (see Table 1).

As discussed above, the ECL overall efficiency (relative Φ_{ECL}) is govern by two contributions that are the thermodynamics associated to the generation of the excited state ($\Delta G°$) and the photophysics of the radiative de-excitation (Φ_{Fluo}). One can then calculate the ratio Φ_{ECL}/Φ_{Fluo} in order to remove the quantum yield contribution in the ECL emission (Table S1). By doing so, the observed trend is very comparable to the previous thermodynamic comparison, meaning that the free enthalpy of eq. 4 is the determining criterion except when comparing two dyes with the same $\Delta G°$ value, namely **TATA$^+$** and **DAOTA$^+$**(**DCP**). In that case, the best ECL-active molecule is the one with the higher quantum yield (**DAOTA$^+$**, C2v symmetry) because the photophysical contribution becomes preponderant.

The energetic criterion could be nicely represented by the plot reported recently by Barnard, Hogan *et al*.[19] The authors characterized a whole family of Ir complexes bearing *N*-heterocyclic carbene ligands. They defined a so-called ECL wall of energy sufficiency for the electrochemical promotion of the excited state *via* the co-reactant (TPA) oxidative-reductive pathway. In the present study, the results using organic dyes instead of organometallic species and BPO as co-reactant (reductive-oxidative pathway) can still be treated according to the above formalism (see Figure 3) and they strongly support this simple thermodynamic requirement. The energy sufficiency of ECL processes could also be compared by drawing energy diagrams of the corresponding reductive-oxidative pathways. Such a comparison between ECL-active **TATA$^+$** and ECL-inactive **TOTA$^+$** can be found in the Supporting Information (see Figure S5).[19] Moreover, thanks to a fine analysis of the ECL yields, the ECL wall allows a qualitative discrimination of which dyes are able, or not, to reach their respective excited state and thus to emit light through ECL. Even more interestingly, the energetic distance between each data point and the threshold limit represented by the dotted line directly represents the thermodynamic easiness for generating the excited state according to eq. 4. This means that the experimental sequence **TOTA$^+$** < **ADOTA$^+$**(**Pr**) < **ADOTA$^+$**(**Ph**) < **ADOTA$^+$**(**DCP**) < **DAOTA$^+$**(**Pr**) < **DAOTA$^+$**(**Ph**) < **DAOTA$^+$**(**DCP**) ~ **TATA$^+$** could be predicted from the electrochemical and fluorescence data, without conducting ECL experiments. This trend is the ECL manifestation of the inverted Marcus region in the case of highly exergonic redox reactions. Indeed, the increase of the ECL efficiency with the more cathodic reduction potentials (*i.e.* distance from the "ECL wall" in the cathodic direction on Figure 3) is mainly related to the kinetic inhibition of the ground state formation.[20] In other words, increasing the available free energy of the system favors kinetically the less exergonic formation of the excited state over the competing highly exergonic reaction leading to the ground state (inverted region). Finally, it should be stressed that the ECL wall is solely a schematic way to illustrate the energetic criterion necessary to generate the excited state. Such formalism does not take into account the quantum yield contribution related to the subsequent radiative relaxation to the ground state. In other words, the ECL wall does not represent directly the ECL yield but only the thermodynamic efficiency of the dye/co-reactant system to generate electrochemically the excited state. The overall value of the ECL yield is indeed a combination of the electrochemical steps (diffusion of the chemical species and electrode surface reactions), of this energetic criterion (efficiency

to populate the excited state) and of the fluorescence quantum yield.

Figure 3. ECL wall of energy sufficiency for BPO co-reactant. The dashed line materializes the reduction potential threshold value necessary for a given emission wavelength (see Eq. 6 in the case of BPO). Each data point on the ECL wall is defined by λ_{max} (x) and $E°_{red}$ (y) and the dotted line is the equation $E°_{red} = E°_{ox}(Ph\text{-}CO_2^{\bullet}/Ph\text{-}CO_2^{-}) - 1239.81/\lambda_{max}$. It means that the distance between the dotted line and a data point is indeed the ΔG° values (in eV).Therefore, the molecules located below the dashed line are ECL-active.

In this work, the electrochemical, fluorescence and ECL properties of eight cationic triangulenes have been investigated. ECL generation according to the reductive-oxidative pathway was studied by using BPO as a co-reactant. The maximum emission wavelengths were determined and ECL featured only a small red shift when compared to fluorescence which is consistent with the same excited state for both approaches. All the data evidenced a noticeable influence of the nature of the heteroatoms inside the triangulenium cores as well as the pending chemical groups. However, the efficiency of the ECL is dramatically contrasted from one molecule to the other. The dyes containing two and three nitrogen atoms, **DAOTA$^+$** and **TATA$^+$** respectively, exhibited high relative ECL yields whereas **ADOTA$^+$** (one nitrogen) and **TOTA$^+$** (none) showed dramatically small ECL intensities. Such a dichotomy was rationalized and illustrated using the new ECL wall presentation that can predict the feasibility of ECL generation from the redox and fluorescence data. Furthermore, the present study reveals that the symmetry group only marginally influences the relative ECL yield unlike in fluorescence. By contrast, the main key parameters governing ECL efficiency are the electron-donating effects which control the mono-cation stabilization and therefore the corresponding redox potential values. However, when comparing two dyes with similar $\Delta G°$ values like **TATA$^+$** and **DAOTA$^+$**(**DCP**), the symmetry group also plays a role because the quantum yield contribution is not negligible anymore and therefore the C_{2v} molecule exhibits a higher ECL yield than the D_{3h} one. Finally, as the properties of cationic triangulenes are readily tailored by the selection of the heteroatoms within the core and their peripheral substituents, further fruitful applications of these dyes towards ECL can be expected, in particular as biomarkers.

Experimental Section

All triangulenium salts used in the present study were synthesized according to previous reports (see Supporting information, sections 1-3).

Electrochemical data were recorded using a μ-Autolab type III. Cyclic voltammetry was recorded using a Pt disk as working electrode, a Pt wire as counter electrode and a silver wire as a pseudo-reference. The triangulenium solutions (1 mM) were prepared in acetonitrile with *n*-tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. Prior to the experiment, the solution is degassed using nitrogen for 5 min.

Emission spectroscopy was recorded on a Cary Eclipse fluorescence spectrophotometer from Varian.

ECL spectra were recorded using a Princeton Instruments Acton SpectraPro 2300i. The electrochemical cell is built with a glass slide at the bottom in order to collect ECL signal *in-situ*. An optical fiber is connected to the device and placed in front of the glass slide at close vicinity of the working electrode. The potential is controlled by a potentiostat (μ-Autolab type III). Before the experiment, the solution is degassed using nitrogen for 5 min. BPO (Luperox A75FP, Benzoyl peroxide, 75% Sigma) is used as co-reactant. ECL intensity was recorded using a Hamamatsu photomultiplier tube R5070 with a Hamamatsu C9525 high voltage power supply. The PMT detector was placed a few millimeters in front of the working electrode and the output signal was amplified by a Keithley 6485 Picoammeter before acquisition *via* the second input channel of the Autolab potentiostat (PGSTAT 30)

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Keywords: triangulene • luminescence • electrochemistry • electrogenerated chemiluminescence

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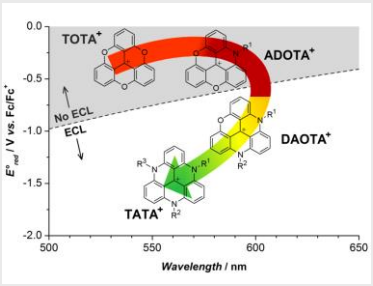
FULL PAPER

Electrochemiluminescence structure/activity relationship: Electrogenerated chemiluminescence (ECL) of cationic triangulene dyes is reported here for the first time. The nature of the heteroatom patterns in the core structure influences strongly the ECL capability. Triaza- and diazatriangulenium ($TATA^+$ and $DAOTA^+$) exhibit strong ECL unlike dioxa- and trioxatriangulenium ($ADOTA^+$ and $TOTA^+$). Such a structure/activity dichotomy is rationalized by considering the electrochemical and photochemical properties of the dyes.



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