Efficient annihilation electrochemiluminescence of cationic helicene luminophores

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Abstract
The electrochemistry and annihilation electrochemiluminescence (ECL) of a series of chiral cationic helicene luminophores containing various substituents were investigated in acetonitrile solvent. The electrochemical characterization evidenced a systematic reversible reduction of cationic derivatives, whereas the oxidation could be reversible or not, depending on the nature of the core heteroatoms within the structure as well as the functional-group appendages. One of the key parameters governing the ECL intensity is, indeed, the formal redox potentials for the electrogeneration of the neutral radical and dication radical species, which will undergo the annihilation reaction. On that basis, a thermodynamic wall of efficiency was proposed in the case of ECL annihilation pathway to predict the formation efficiency of the emitting excited state and, eventually, the light emission’s strength. This very simple wall is constructed by plotting the difference of formal potentials in function of the fluorescence wavelength, thus delimiting two domains where ECL is thermodynamically possible or unfavorable.

Reference

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Efficient Annihilation Electrochemiluminescence of Cationic Helicene Luminophores


The electrochemistry and annihilation electrochemiluminescence (ECL) of a series of chiral cationic helicene luminophores containing various substituents were investigated in acetonitrile solvent. The electrochemical characterization evidenced a systematic reversible reduction of cationic derivatives, whereas the oxidation could be reversible or not, depending on the nature of the core heteroatoms within the structure as well as the functional-group appendages. One of the key parameters governing the ECL intensity is, indeed, the formal redox potentials for the electrogeneration of the neutral radical and dication radical species, which will undergo the annihilation reaction. On that basis, a thermodynamic wall of efficiency was proposed in the case of ECL annihilation pathway to predict the formation efficiency of the emitting excited state and, eventually, the light emission’s strength. This very simple wall is constructed by plotting the difference of formal potentials in function of the fluorescence wavelength, thus delimiting two domains where ECL is thermodynamically possible or unfavorable.

1. Introduction

ECL is a type of chemiluminescence involving the in-situ generation of an excited state at the electrode surface by electron transfer reactions.[1] ECL mechanisms have been established in two dominant pathways. In the co-reactant pathway, a co-reactant species is oxidized or reduced in order to produce very reactive radicals which react with the luminophore to generate the desired excited state. An alternative mode is based on the annihilation reaction between an oxidized and a reduced species of the luminophore that are electrochemically produced at a single electrode surface by applying alternating pulsed potentials or at different electrodes located in close vicinity.[2] Then, these two species react together according to an annihilation process to generate an electronically excited state. The latter relaxes to the ground state while emitting a photon. Thus, a possible mechanism for the ECL annihilation pathway can be presented as follows [Eqs. (1)–(6)]:

\[ A^- e^- \rightarrow A^+ \] (oxidation at the electrode) (1)

\[ A^- + e^- \rightarrow A^- \] (reduction at the electrode) (2)

\[ A^+ + A^- \rightarrow (2-\alpha) A + \alpha \ A^* \] (formation of the emitting excited state) (3)

or

\[ A^+ + A^- \rightarrow (2-\beta) A + \beta \ A^* \] (formation of the triplet excited state) (4)

\[ 3A^* + 3A^* \rightarrow (2-\gamma) A + \gamma \ A^* \] (triplet-triplet reaction) (5)

\[ A^* \rightarrow A + h\nu \] (ECL emission) (6)

where \( \alpha, \beta \) and \( \gamma \) are coefficients representing the efficiency of the excited state generation in reactions 3, 4 and 5, respectively.

If the homogeneous electron transfer reaction between these electrogenerated species is exergonic enough, the annihilation process leads directly to the emitting excited state (generally, but not always, a singlet)[3] of the luminophore [Eqs. (1)–(3)]. In this case, the system has sufficient available energy and the emitted ECL follows the so-called “S-route”. But if the free enthalpy of the annihilation reaction is not sufficient to populate directly the emitting state, the system may follow the “T-route” where the triplet state is first produced (Eq. 4). For such an “energy deficient system”, triplet-triplet annihilation may eventually yield the singlet emitting state in a second step (Eq. 5). Both routes have been extensively studied with various molecular luminophores.[4] It is important to stress that S- and T-routes transcend the nature of the emitting states (i.e. singlet or triplet) but correspond only to energy sufficient systems or not. Indeed, the model tris(2,2’-bipyridine) ruthenium, Ru(bpy)_{3}^{2+}, luminophore is a triplet emitter but follows the “S-route”.[3] Whatever, the simplest “S-route” is the most relevant because the corresponding compounds exhibit the highest ECL.
efficiency which is particularly interesting for achieving sensitive analytical applications. ECL emission can arise from many luminophores including transition metal complexes based on iridium or ruthenium ions as well as from purely organic compounds. Many efforts are currently focused on the search for new organic ECL luminophores with high efficiency and/or tunable wavelengths. For example, Hogan, Francis and co-workers have recently reported the ECL color modulation by the annihilation of mixed metal chelates. The value of ECL efficiency \( \Phi_{ECL} \) is defined as the number of photons emitted per electrons transferred between the reduced and oxidized forms of the parent molecules in the annihilation pathway and is usually referred to a model system such as Ru(bpy)_3^{2+}. This value is function of the formation efficiency of the electronically-excited state and the photophysics of the radiative relaxation (reaction 6). Since ECL can be considered as the competition between a light-emitting and a non-radiative transition in the Marcus inverted region, the energetics of the bimolecular electron transfer reaction [Eqs. (3)–(5)] governs the efficiency of the excited state formation. Indeed, it may favor excited state formation over the ground state formation. ECL efficiency provides direct information on the homogeneous electron transfer reactions in both normal and inverted Marcus regions. Therefore, it is essential to study the energetic requirements which depend directly on the electrochemical properties of the luminophores (i.e. redox potentials) as well as the chemical stability of the electrogenerated anion and cation radicals.

Helicenes are ortho-fused polyaromatics which adopt well-defined helical (chiral) molecular structures. Among these derivatives, functionalized cationic [4] and [6]helicenes exhibit a relatively-large structural diversity (Figure 1) and these compounds are readily prepared via versatile late stage post-functionalization strategies. In relation to this study, these moieties are luminophores with original absorption and emission properties tunable up to the near-infrared wavelengths. More specifically, these derivatives contain nitrogen and/or oxygen heteroatoms that bridge the aromatic all-carbon rings within the helical core. A series of diaza [4]helicenes [4] DAH(X)^+, i.e. compounds 1–6 with four aza-bridged aromatic rings constituting the helical framework, was selected with various functional groups at the periphery (X=H, NH2, NMe2, N3, OH or CO2−). A cationic triazatriangulene analogue TATA^+ 7 was chosen as well as a series of hetero [6]helicenes 8–11. Within these latter structures, the helical skeletons contain either 2 nitrogen atoms as for [6]DAH(X)^+ 8–9 (with X=H and Br), one nitrogen and one oxygen with azaoxa [6]helicene [6] AOH^+ 10 or two oxygens for dioxa [6]helicene [6]DOH^+ 11.

In the present work, we gathered the electrochemical, optical and annihilation ECL properties of a series of extended organic cations featuring a helical shape (to the exception of planar derivative 7). These luminophores exhibit well-defined mono-electronic oxidation or reduction in acetonitrile with redox potential values \( E_{1/2}^\text{red} \) and \( E_{1/2}^\text{ox} \) (i.e. the electrochemical HOMO–LUMO gap which corresponds to the potential difference between the oxidation and the reduction waves) allows to predict quantitatively the efficiency of the excited state formation for the helicene compounds in the case of the annihilation “S-route” pathway.

**Experimental section**

**Materials**

Cationic [4] and [6]helicenes were synthesized according to previously reported procedures. Other reagents were purchased from Sigma-Aldrich and used without purification unless otherwise stated. Anhydrous acetonitrile (99.8%) was used as a solvent without further purification.

![Figure 1. Chemical structures of cationic [4]helicenes 1–6, triangulene analogue 7 and [6]helicenes 8–11.](image-url)
Instrumentation

Voltammetric experiments were performed with a PGSTAT30 Autolab potentiostat connected to a conventional three-electrode cell, consisting in a silver wire pseudo-reference electrode, a platinum-wire auxiliary electrode, and a 1 mm in radius platinum disk working electrode. Prior to measurements, Pt disks were polished with alumina slurry of different size, rinsed thoroughly with Milli-Q water between each polishing step, and sonicated in water and ethanol respectively, followed by a final rinse with acetonitrile and dried with N₂ stream. Voltammograms of ferrocene were also recorded in the same experimental conditions before and after the electrochemical characterization of the different helicene compounds. The ferrocene/ferroacenium (Fc/Fc⁺) redox couple shows an oxidation potential value of 0.42 V vs. Ag.

ECL intensity was measured using a Hamamatsu photomultiplier tube (PMT) R5070 A with a Hamamatsu C9525 high voltage power supply. The PMT detector was held at 750 V and placed at a constant distance of 5 millimeters in front of the working electrode. The output signal was amplified by a Keithley 6485 Picoammeter before acquisition via the second input channel of the PGSTAT30 Autolab potentiostat.

ECL spectra were recorded using a Princeton Instruments Acton SpectraPro 2300i. The cell is built with a glass slide at the bottom in order to record the ECL signal. The optical fiber connected to the device was placed close to this glass slide in front of the working electrode. The potential was controlled by a potentiostat (µ-Autolab type III), the pseudo-reference electrode was a silver wire and the counter electrode was a platinum wire. Before each experiment, the solution was deoxygenated using nitrogen for 5 min. To record the ECL spectra by annihilation, the electrode potential was alternatively pulsed from the first oxidation potential (Eox₁/₂ + 100 mV) to the first reduction potential (Ered₁/₂ − 100 mV). Only for the compound 3 which presents a second irreversible oxidation wave characterized by a more anodic half-wave potential Eox₂ (entry 3 in Table 1), the electrode potential was alternatively pulsed from the second oxidation potential (Eox₂ + 100 mV) to the first reduction potential (Ered₁/₂ − 100 mV). Fluorescence spectra were collected on a Varian Cary Eclipse spectrophotometer, using a 1 cm-path length quartz cuvette.

2. Results and Discussion

The series of [4], [6]helicenes and triangulene 1–11 was investigated by recording cyclic voltammetry in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. The electrochemical behavior of some of the compounds was previously described in several independent contributions[5g, h, 10b, 13] and they were gathered here with new voltammetric characterizations in order to draw a full structure/activity relationship. Briefly, the 1-electron reduction of the cation forms a neutral species and the electron transfer reaction is reversible at a scan rate of 0.1 V s⁻¹. The corresponding redox potential Eox₁/₂ is found to vary between −0.12 V vs. Ag pseudo-reference for 11 which is the easiest to reduce to −1.20 V vs. Ag for 7 which is indeed the more stable cation in the series. The permution from N to O core heteroatoms (10 and 11) markedly weaken the stability of the cation whereas the introduction of electron donating groups in the northern part of the chromophore (2–5) enhances the cation stability and shift therefore the redox potential toward more negative values. On the other hand, it is also possible to remove an electron from the cation and generate the corresponding dicatonic species. This oxidation is in fact reversible for most of the studied molecules except luminophores 6, 10 and 11. When reversible, the corresponding redox potential Eox₁/₂ is spread between 0.91 V vs. Ag for 3 and 1.56 V vs. Ag for 9. The oxidation process characterized by the Eox₁/₂ value could eventually be even more positive, especially in the case of an irreversible process (10–11). It is also noteworthy that 3 shows two sequential reversible oxidation waves, yielding a stable trication oxidized species, 3３⁺, during the timescale of the voltammetric experiments.

The structure/activity relationship reveals also the major influence of core heteroatoms at bridge positions and of the pending groups interfering directly on the stability of singly or doubly charged structures, respectively. The difference ΔE₁/₂ is

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>Ered₁/₂ [V] vs. Ag</th>
<th>Eox₁/₂ [V]</th>
<th>ΔE₁/₂ [V]</th>
<th>λmax [nm]</th>
<th>ΦECL [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[4]DAH(H)⁺</td>
<td>−0.70</td>
<td>1.40</td>
<td>2.10</td>
<td>670</td>
<td>1.85</td>
</tr>
<tr>
<td>2</td>
<td>[4]DAH(NH₂)⁺</td>
<td>−0.60</td>
<td>0.96</td>
<td>1.56</td>
<td>−775²⁶</td>
<td>1.60</td>
</tr>
<tr>
<td>3</td>
<td>[4]DAH(Me₂)⁺</td>
<td>−0.62</td>
<td>0.91</td>
<td>1.53</td>
<td>−710³⁶,⁷</td>
<td>1.75</td>
</tr>
<tr>
<td>3³⁺</td>
<td>[4]DAH(NMe₂)⁺</td>
<td>−0.62</td>
<td>1.26</td>
<td>1.88</td>
<td>−665³⁶,⁷</td>
<td>1.86</td>
</tr>
<tr>
<td>4</td>
<td>[4]DAH(NH)⁺</td>
<td>−0.70</td>
<td>1.18</td>
<td>1.88</td>
<td>−705²⁶</td>
<td>1.76</td>
</tr>
<tr>
<td>5</td>
<td>[4]DAH(OH)⁺</td>
<td>−0.52</td>
<td>0.98</td>
<td>1.50</td>
<td>−690²⁶</td>
<td>1.80</td>
</tr>
<tr>
<td>6</td>
<td>[4]DAH(CO)⁺</td>
<td>−0.71</td>
<td>1.29²⁶</td>
<td>2.00</td>
<td>−690²⁶</td>
<td>1.80</td>
</tr>
<tr>
<td>7</td>
<td>TATA⁺</td>
<td>−1.20</td>
<td>1.34</td>
<td>2.54</td>
<td>558</td>
<td>2.22</td>
</tr>
<tr>
<td>8</td>
<td>[6]DAH(H)⁺</td>
<td>−0.72</td>
<td>1.40</td>
<td>2.12</td>
<td>657</td>
<td>1.89</td>
</tr>
<tr>
<td>9</td>
<td>[6]DAH(Br)⁺</td>
<td>−0.38</td>
<td>1.56</td>
<td>1.94</td>
<td>680</td>
<td>1.82</td>
</tr>
<tr>
<td>10</td>
<td>[6]AOH⁺</td>
<td>−0.45</td>
<td>1.93²⁶</td>
<td>2.38</td>
<td>616</td>
<td>2.01</td>
</tr>
<tr>
<td>11</td>
<td>[6]DOH⁺</td>
<td>−0.12</td>
<td>2.14²⁶</td>
<td>2.26</td>
<td>592</td>
<td>2.09</td>
</tr>
<tr>
<td>12</td>
<td>Ru(bpy)₃²⁺</td>
<td>−1.19</td>
<td>1.41</td>
<td>2.61</td>
<td>620</td>
<td>2.00</td>
</tr>
</tbody>
</table>

The potentials Ered₁/₂ and Eox₁/₂ are referred vs. Ag pseudo-reference. The efficiency ΦECL of the ECL annihilation was calculated by comparison with Ru(bpy)₃²⁺ as a reference (ΦECL = 100%). The fluorescence wavelength is given approximately for the poorly emitting compounds (entries 2–6). Fluorescence data were generally recorded at 10 μM or at a higher concentration of 0.1 mM (entries 3 and 4). The entry 3 corresponds to the data of compound 3 but considering its second reversible oxidation wave (Eox₂ = −1.26 V) for the calculations of −ΔHรม, ΔG and ΦECL. The formal oxidation potential is calculated as the half-wave potential Eox₁/₂ except when the oxidation is not reversible at a scan rate of 0.1 V s⁻¹ (entries 6, 10 and 11).
also reported in Table 1 as it will be used later as a key parameter to describe the ECL proficiency in the annihilation pathway. This difference between the formal oxidation and reduction processes is found to be maximal for 7 (ΔE$_{1/2}$ = 2.54 V), providing thus the highest annihilation free enthalpy. At the opposite, [4]DAH(X)$^+$ 5, 3 and 2 (with X=OH, NMe$_2$ and NH$_2$) exhibit the lowest ΔE$_{1/2}$ values (1.50, 1.53 and 1.56 V, respectively). Therefore, the available enthalpy of the annihilation (Eq. 3 or 4) will be dramatically lower for these three luminophores.

As already presented, the ECL emitting excited state may be reached directly via the “S-route” or indirectly via the “T-route”. In the first case, the energy of the system is high enough to populate the emitting state which could be singlet or triplet. For the second case, the triplet state is produced first and the triplet-triplet annihilation may generate the singlet emitting state. To clarify the involved route for our systems, we compared the energy of the electronically excited state, $E_s$ obtained from the fluorescence spectrum with the enthalpy provided by the annihilation reaction, $-ΔH_{ann}$. The values of the energy required to populate the first singlet excited state is given by the Equation (7):

$$E_s \text{ (in eV)} = \frac{1239.8}{λ_{nuo}} \tag{7}$$

where $λ_{nuo}$ (in nm) is the wavelength at the maximum fluorescence intensity.

The calculated values of $E_s$ span from 1.60 to 2.22 eV for the analyzed compounds (Table 1). The energy of the lowest emitting state for each helicene cation has to be compared with the enthalpy of the annihilation reaction. Its value depends on the difference between the oxidation and reduction potentials of the helicenes and it is described by Equation (8):

$$-ΔH_{ann} \text{ (in eV)} = E_{ox}^{1/2} - E_{red}^{1/2} - T.AΔS \tag{8}$$

with an estimated entropy effect of 0.1 eV.

By comparing both values in Table 1, one can see that the energy of the annihilation reaction is larger than the energy required to populate directly the first singlet excited states for 1, 6–11. Therefore these latter helicene moieties can be defined as energy sufficient systems following the “S-route”. On the other hand, compounds 2–5 are contrarily energy-deficient as the value calculated for $-ΔH_{ann}$ is lower than $E_s$. Therefore, the corresponding [4]DAH(X)$^+$ luminophores are supposed to be ECL-inactive in the annihilation pathway.

To further investigate the stability of the ECL and radical ions of the [6]helicenes, potential pulsing ECL transients were recorded. Transient ECL for 8 depicted in Figure 3c shows that a constant ECL emission is observed upon each individual pulsing step, indicating that almost the same quantities of neutral (i.e. 8) and dicaticionic (i.e. 8$^{2+}$) radicals are formed per pulse and both electrogenerated species appear to be stable during the time of the annihilation reaction. Besides, the ECL transient process of 8 is comparable to the one recorded for 1 (Figure 3). Such a comparable behavior is very much expected as both molecules feature similar electrochemical reactions and redox potentials (Figure 3a) and fairly comparable emission properties ($λ_{nuo} = 657$ nm for 8 and 670 nm for 1, respectively). However, 10 and 11 also gave non-negligible ECL emission by annihilation even though their electrochemical oxidation appears irreversible. It means that the annihilation reaction is kinetically in competition with the follow-up chemical reaction and that the oxidized intermediate is stable enough to react with the reduced form and thus to yield the excited state. As shown in Figure 3d, the annihilation of 10 performed by potential pulses shows asymmetric ECL transients in which the intensity corresponding to the cathodic pulse is always much smaller than the anodic one. This kind of ECL transient reveals that the oxidized form (6$^{2+}$) is unstable and depleted in solution, as already mentioned, leaving only a small fraction available for generating ECL when the following anodic pulse occurs. For the annihilation of 11 (data not shown), the shape and intensity of ECL maximum intensity is very different to the other tested compounds. ECL does not occur immediately after the anodic pulse but with a time delay and increases steadily until the reduction pulse. This behavior may possibly involve an adsorption step with formation of an emitting film on the electrode. Finally, transient ECL for 7 is presented on Figure 3b and the measured ECL intensity is remarkably higher compared to the other tested compounds. Indeed, the ECL signal is 3 to 8 times stronger than those from 1 and 10. It results in a very efficient ECL process with a $Φ_{ECL}$ value reaching almost 40% in comparison to the reference compounds, Ru(bpy)$_3^{2+}$ (Table 1). This value is notably high as compared to those observed in the other tested helicenes (Table 1). Indeed, 7 gave the strongest ECL efficiency among the tested compounds. It is due to the more exergonic reaction populating the emitting excited state (i.e. the more negative value of the free enthalpy $ΔG^*$) as well as to the better stability of the oxidized dicaticionic radicals. Indeed, even if 10 presents a more important driving force $ΔG^*$ (~0.27 eV and ~0.22 eV for 10 and 7, respectively), its oxidation wave is partially irreversible indicating that the electrogenerated dicaticionic radical is not stable enough in solution. These both criteria have to be fulfilled at least to obtain efficient ECL process.

It is also noteworthy that the electrochemical oxidation of 7 features several separated waves as shown in the corresponding voltammogram (Figure 2). The ECL transient reported in Figure 3b were recorded with an oxidation step potential slightly after the first anodic wave. ECL transients were also recorded after the second anodic wave but were unfortunately much weaker. This degradation of ECL intensity is probably link to the relative instability of the electrogenerated trication 7$^{3+}$ compared to the more stable dication 7$^{2+}$.

Moreover, ECL emission recorded for the compounds 1, 8, 10 and 11 was stable with time and strong enough to collect ECL spectra using the annihilation method. ECL spectra of 1 and 8 are very similar with their band centered around 650–670 nm (Figure 4). It is not surprising since, as already discussed, their oxidation and reduction potentials are almost the same and therefore the energy gap is similar. By comparison, 11 shows a hypsochromic shift with a band centered at 600 nm, similarly to the fluorescence spectrum.
Therefore, the same excited state is generated by photoexcitation and by the annihilation between the electrogenerated neutral and dicationic radicals. The behavior of 10 is similar to 11 and its emission is shifted to a longer wavelength of 616 nm (data not shown). But considering the ECL of 8 and 11, a red-shift of ~10 nm in comparison to fluorescence was observed experimentally and attributed to an inner-filter effect and/or aggregation caused by the higher concentration used in ECL compared to fluorescence.[16]

In the annihilation pathway, the bimolecular electron-transfer reaction occurring between the electrogenerated neutral and dicationic helicene radicals leads competitively to an emitting excited state with a low exergonicity or to the formation of the ground state with a high exergonicity.[17] The free enthalpy $\Delta G^\circ$ associated to the ECL annihilation process corresponds directly to the difference between the energy provided by the bimolecular electron-transfer reaction $-\Delta H_{\text{ann}}$ and the energy of the emitting excited state $E_s$. Thus the formation of the excited state depends mainly on this enthalpic term $-\Delta H_{\text{ann}}$ which is directly related to the potential difference $\Delta E_{1/2}$ as well as on the stability of the electrogenerated radicals.

In brief, it is essential to consider the exergonicity of the ECL process by comparing the energy provided by the annihilation reaction described by $\Delta E_{1/2}$ and the energy released by the light emission from the excited state. Both can be easily calculated from their experimental features: $\Delta E_{1/2}$ and $\lambda_{\text{flu}}$. This energetic requirement has been nicely presented in the form of an “ECL-wall” by Hogan and co-workers for different heteroleptic Ir(III) complexes in the case of an oxidative-reduction pathway involving tri-n-propylamine as a co-reactant.[11] Recently, we

![Figure 2](image2.png)

**Figure 2.** Cyclic voltammograms of 1 mM 1, 3, 7, and 9, recorded in deoxygenated CH$_3$CN solution containing 0.1 M TBAPF$_6$ as supporting electrolyte. Scan rate 0.1 V s$^{-1}$.

![Figure 3](image3.png)

**Figure 3.** Chronoamperometric curves and ECL transients of a) 1 mM 1, b) 1 mM 7, c) 1 mM 8, and d) 1 mM 10 in deoxygenated CH$_3$CN solution containing 0.1 M TBAPF$_6$ pulsed between the first reduction potential ($E_{1/2}^- = -100$ mV) and the first oxidation potential ($E_{1/2}^+ = +100$ mV), respectively. Pulse duration: 0.1 s.
reported the ECL capability of different helicene compounds with the same formalism with either anodic or cathodic co-reactants and resulting thus in a “double ECL-wall” figure. In the present work for the annihilation ECL, the energetic threshold is illustrated by plotting the potential difference $\Delta E_{1/2}$ versus emission maximum wavelength $\lambda_{\text{em}}$ (Figure 5). In this case, the direct formation of the emitting excited state was solely considered (Eq. 3) without taking into account the “T-route” which is possible in some systems (Eq. 5). Indeed, the triplet excited state is usually non-emissive in solution for organic systems and the process is much less efficient in the “T-route”. The luminophore is energy sufficient for excited state formation when it is located on the right side of the dashed line (Figure 5). This dashed line materializes the frontier between energy-sufficient and energy-deficient systems. The equation corresponding to the dashed line is obtained by solving $\Delta G^\circ = 0$ for the annihilation (combination of Eqs. 7 and 8). On the left side, the compounds fall in the grey zone where they do not generate ECL emission following the annihilation pathway. The proposed ECL wall on Figure 5 shows the dependence of the energetic criteria on the emission wavelength. For emission closer to infrared, the required potential difference $\Delta E_{1/2}$ is obviously lower. On one hand, one can notice that the values $\Delta E_{1/2}$ varied from 1.53 eV to 2.54 eV for 3 and 7, respectively. On the other hand, the tested helicenes emitted fluorescence over a wide wavelength range, from 558 nm to 775 nm so from the green color to the near-infrared. It corresponds to energy levels spanning from 2.22 eV to 1.60 eV for 7 and 2, respectively.

By applying this approach to the series of helicene dyes, two typical groups are easily distinguished. The first one corresponds to ECL-inactive molecules as the enthalpy of the annihilation is insufficient to populate the singlet excited state. Most of the [4]DAH(X)+ 2–5 luminophores fall in this category and do not generate ECL due to this energetic criteria. Only 1 and 6 were able to produce ECL by annihilation. Since 3 displayed a second reversible oxidation wave at 0.76 V, we also tried to generate ECL by pulsing the potential between the first reversible reduction wave and the second irreversible oxidation wave, and not between the first reduction and oxidation ones. Even if this case corresponds obviously to a more exergonic annihilation process noted 3′ in Table 1 (i.e. higher $\Delta E_{1/2}$ compared to 3), it was not high enough to generate ECL. Contrarily, the other one gathered ECL-active molecules according to the S-route because the enthalpy of the annihilation reaction was found to be larger than the energy of the excited state. The [6]DAH(X)+, [6]AOH+ and [6]DOH+ (i.e. 8–11) compounds belong to this category even if the anodic wave is not reversible for all of them. But the lifetime of the dicaticionic radicals in this case seems long enough to allow to a sufficient fraction of them to participate to the annihilation reaction (Eq. 3). It is also noteworthy that 1 and 8 are ECL-active with comparable ECL efficiency. One can directly visualize this on Figure 5 and it is directly related to the similar electrochemical features (stability of the electrogenerated radicals, $E'_{\text{cat}}$, $E'_{\text{red}}$, $E'_{2/1}$ values) as well as emission wavelength. This is rather expected as both have a comparable structure only differentiated by 2 additional fused benzene rings which do not change notably the electronic properties. 7 generated a strong ECL signal as it can be expected from his position which is far from the energetic threshold. Finally, if one considers a wavelength of 800 nm, the corresponding HOMO–LUMO gap of 1.65 eV is electrochemically accessible in water which is relatively rare in the annihilation pathway. In fact, as already mentioned, it illustrates the simple fact that luminophores

Figure 4. Typical fluorescence (dashed line) and annihilation ECL (solid line) spectra for a) 1 and b) 8 in CH$_3$CN solution.

Figure 5. ECL wall of energy sufficiency for the cationic [4] and [6]helicene luminophores in the annihilation mode. The dashed line materializes the potential difference threshold of a luminophore required to populate the excited state for a given emission wavelength. Filled circles are for ECL-efficient molecules exhibiting either a reversible (black) or irreversible oxidation (grey) behavior whereas unfilled circles correspond to ECL-inactive dyes.
emitting further in the infrared require lower $\Delta E_{1/2}$ values to reach the excited state. This kind of plot may help to find new ECL luminophores in the infrared with oxidation and reduction potentials electrochemically compatible with water and thus to open original perspectives for the annihilation pathway in the analytical field.

3. Conclusions

In this contribution, the electrochemical and annihilation ECL properties of a series of eleven cationic helicene molecules were studied in acetonitrile. A new visual formalism was proposed to predict the efficiency of the excited state formation in the annihilation pathway by considering solely the HOMO-LUMO electrochemical gap ($\Delta E_{1/2}$) and the emission wavelength ($\lambda_{em}$). These two very simple features are readily accessible by recording a cyclic voltammogram and a fluorescence spectrum. Considering both characteristics together allows estimating quantitatively the ECL capability of a given compound. Indeed, the energetic threshold indicates precisely the minimum electrochemical gap necessary to achieve ECL at a given wavelength. The proposed wall of energy sufficiency could be in principle applied to any redox-active luminophore which could be oxidized and reduced electrochemically. This will therefore help to identify easily new potential ECL probes with appropriate redox and photophysical characteristics.

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Conflict of Interest

The authors declare no conflict of interest.

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