

Circularly Polarized-Electrochemiluminescence from a chiral Bispirene Organic Macrocycle

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Abstract: The first observation of circular polarization of electrochemiluminescence (ECL) from a purely organic derivative is reported. A bis-pyrene scaffold mounted on a constrained polyether macrocycle displaying intense excimer fluorescence and highly circularly polarized (CP) photoluminescence has been selected for this purpose. Such compound displays an ECL dissymmetry factor of ca. $|8 \times 10^{-3}|$, in good agreement with the corresponding photoluminescence value. This observation is the first step towards the molecular engineering of bespoke suitable dyes acting both as ECL and CP-ECL reporters for (bio)analysis by bringing a new level of information when dealing with chiral environments. In addition, it provides an extra-dimension to the ECL phenomenon and opens the way to chiral detection and discrimination.

Electrochemiluminescence (ECL) is the production of light as a consequence of very exergonic electron-transfer reactions between electrogenerated species.^[1] Since the mid 1960's, a thriving scientific research has brought ECL to become one of the most highly sensitive techniques for the detection of bioanalytes.^[2] Indeed, the electrochemical stimulus permits a very precise control of the location and duration of the ECL emission whereas the optical readout makes the method extremely sensitive. Moreover, ECL offers many intrinsic advantages for (bio)analytical applications: wide linear dynamic range, selectivity and stability of the luminophore, extremely low background, simple instrumentation, low cost, high sensitivity at physiological pH, measurements in complex matrices such as serum or urine. In addition, ECL has the advantages of not requiring an excitation light source unlike techniques based on photoluminescence (PL) and thus to avoid interferences, as those caused by the autofluorescence of biological samples. Nowadays, ECL-based immunoassays are successfully commercialized and they have extensively used in clinical diagnosis and in food or environment investigations.^{[1][2]} Besides these well-established applications, thanks to the exceptional

spatial, temporal resolutions as well as intensity control of the emitted light, ECL systems have been employed in the development of new imaging methods, ranging from the quantification of relevant cancer biomarkers^[3] to single cell and cell membrane proteins visualization.^[4]

Being able to detect the circular polarization of the emission would add further advantage in (bio)assays in terms of selectivity, enhanced contrast and specific response in a chiral environment.^[5] It would provide original valuable information on the interaction between the molecular probe and the targeted analyte. In this context, circularly polarized photoluminescence (CP-PL), which consists in exciting the sample using unpolarized light, has been strongly evidenced.^[6] For example, lanthanide complexes able to modulate their CP-PL profile upon interaction with proteins or smaller chiral molecules were developed.^[5b, 5c, 7] Organic molecules, even achiral or racemic, can also signal their interaction with chiral (bio)analytes through CP-PL.

To the best of our knowledge, circularly polarized electrochemiluminescence (CP-ECL) was only evidenced once in a pioneering work by Blok et al. in 1987 with dextrorotatory $[\text{Ru}(\text{phen})_3][\text{ClO}_4]_2$ complex.^[8] So far, the question as to whether CP-ECL could be generalized and observed for organic systems has remained unaddressed, probably also due to the limited number of single molecules capable to give intense enough polarized response.

CP-ECL is a complementary phenomenon to CP-PL, and as such could be employed to widen the scope of the above-mentioned CP-PL assays. A further advantage is that circular polarization measurements can be made easier by avoiding excitation light. In fact, the exciting light source could induce fluorescence anisotropy artefacts due to photoselection, which can be a major problem in CP-PL, especially when dealing with large molecules.^[6b]

Herein, we report the first observation of CP-ECL on a purely organic dye. An ECL dissymmetry factor of ca. $|8 \times 10^{-3}|$ is obtained using a bis-pyrene scaffold mounted on a constrained polyether macrocycle; the result is self-consistent with the corresponding photoluminescence value.

Recently, synthetic protocols have been developed for the synthesis of unsaturated macrocycles via (i) $[3+6+3+6]$ condensations of cyclic ethers and α -diazo- β -ketoesters and (ii) tandem amidation – olefin transpositions.^[9] These macrocycles comprise a constrained polyether ring and two aromatic subunits positioned rigidly. A compound like **pyrene-18C6** can be obtained in combined 43% yield from 1,4-dioxane as a racemate (Scheme 1).^[10] The two enantiomers can be conveniently and

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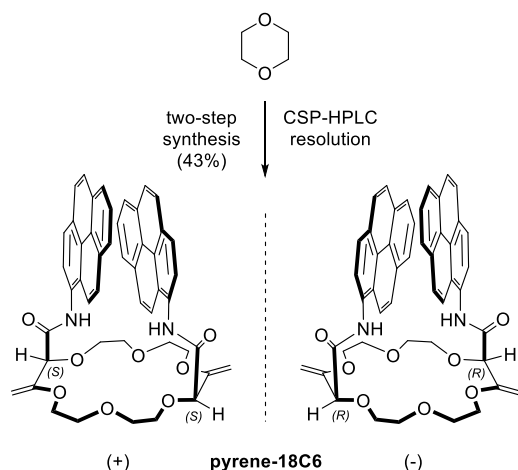
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effectively separated *via* semi-preparative chiral stationary phase (CSP) HPLC.^[11]

Pyrene-18C6 shows a photoluminescence profile dominated by a strong excimer band around 490 nm as well as good photoluminescence quantum yield (24% in CH₃CN, relative to anthracene).^[10-12] Such strong excimer is formed intramolecularly thanks to the peculiar molecular geometry, which brings the two pyrene moieties in close spatial proximity. Moreover, the chiral elements of the macrocyclic ring induce a defined configuration of the skewed arrangement of the two pyrene units, resulting in highly CP-PL (Figure S1).^[11]



Scheme 1. Molecular structure of pyrene-18C6.

To determine the appropriate conditions for ECL generation, the electrochemical properties of the **pyrene-18C6** were first investigated in acetonitrile with a glassy carbon (GC) working electrode. Indeed, the stability of the electrogenerated luminophore radicals is of fundamental importance to produce strong ECL intensity. Due to the known instability of the cation radical of pyrene resulting from the electrochemical oxidation,^[13] we focused our study in the cathodic domain. As shown in Figure 1 (top), the voltammogram exhibits two stepwise reversible reduction waves, at $E_{1,red} = -1.92$ V, and $E_{2,red} = -2.24$ V vs Ag pseudo-reference electrode. The peak current of the first reduction wave is equal to the second one. By contrast, the voltammetric response of pyrene shows a single 1-electron reduction wave at -2.1 V vs Ag (Figure S2) in the same potential window, in good accordance with previous works.^[13b, 14] The shift of $E_{1,red}$ to less cathodic potential in comparison to pyrene means that the first pyrene in the complex is easier to reduce than the pyrene alone. The two successive cathodic waves of **pyrene-18C6** can be attributed to the stepwise 1-electron reduction of each pyrene in the complex (Scheme 2). Indeed, the formation of the pyrene dianion (Py^{2-}) occurs at more negative potentials as reported by Heinze and co-workers^[14b] with two reduction waves for pyrene at -2.13 and -2.86 V vs SCE (Scheme 2). After the first reduction step, the second pyrene is

more difficult to reduce ($E_{1,red} > E_{2,red}$) and it indicates that there is an electronic communication between both pyrene moieties. In any case, it shows that both the mono-anion and the di-anion of **pyrene-18C6** produced during the cathodic processes, are stable in solution during at least the time scale of the voltammetric experiments. This reversible reduction behavior should therefore enable the ECL generation following the reductive-oxidation pathway with an appropriate co-reactant.

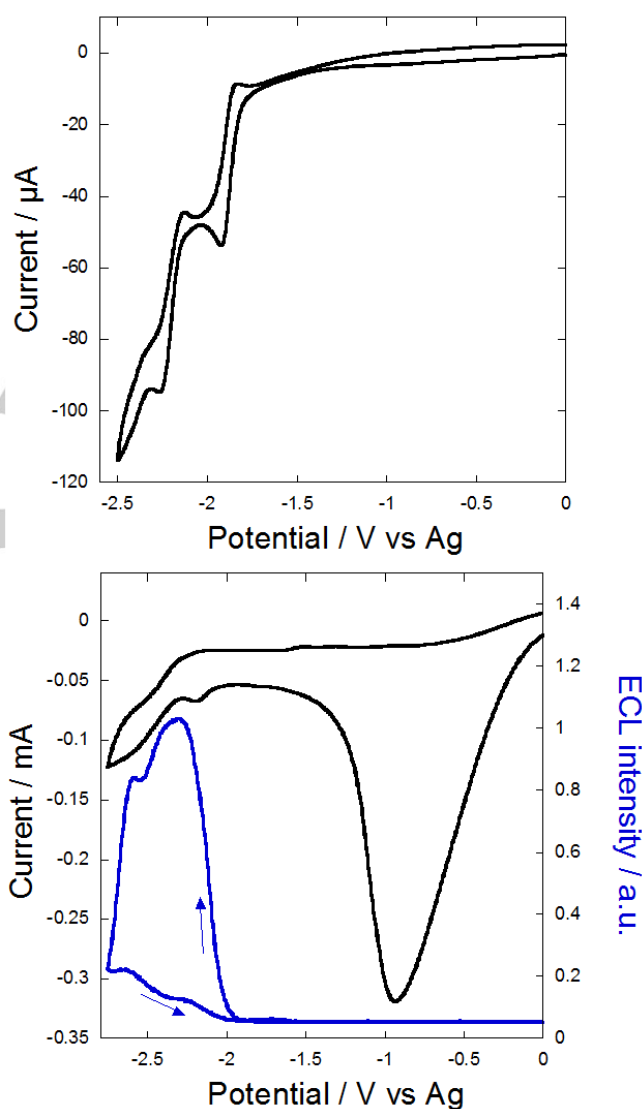
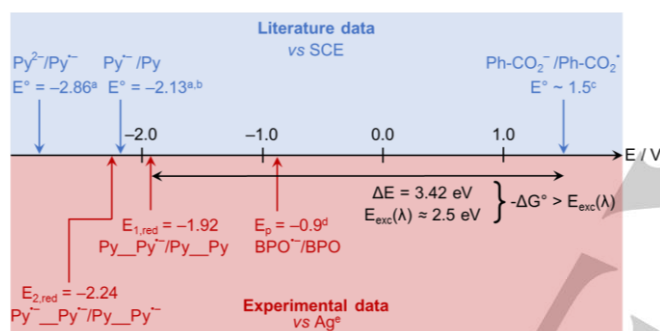


Figure 1. (Top) Voltammetric characterization of 1 mM **pyrene-18C6** in degassed CH₃CN solution with 0.1 M TBAPF₆ as supporting electrolyte. (Bottom) Cyclic voltammogram (black curve) and corresponding ECL signal (blue curve) recorded in CH₃CN solution containing 0.5 mM **pyrene-18C6**, 50 mM BPO and 0.1 M TBAPF₆. A GC disk and a Ag wire were used as working electrode and pseudo-reference electrode, respectively. Scan rate: 0.1 V/s.

In the present work, the good stability of the reduced forms of **pyrene-18C6** was exploited and ECL emission was thus tested using benzoyl peroxide (BPO) as a sacrificial co-reactant.^[1, 2b, 15] In a BPO solution, the potential of the GC working electrode was

swept from 0 V to -2.75 V vs Ag (Figure 1, bottom). Reduction of BPO (black curve) is visible with a wave peaking at -0.9 V but ECL emission (blue curve) occurs only at the potentials where the pyrene moieties of the complex are reduced. In addition, it is noteworthy that ECL signal is composed of two overlapping peaks with a maximum at -2.35 V vs Ag (Figure 1, bottom). Afterwards, it decays very rapidly. These two peaks are most probably related to both reduction waves of the pyrene moieties. The reduction of BPO leads to its dissociative cleavage, which produces a strong oxidant radical Ph-CO_2^\bullet . Several competitive mechanistic pathways have been proposed for the ECL emission using BPO^[13b, 15-16] co-reactant with several luminophores including pyrene. The possible mechanisms for **pyrene-18C6** are detailed in the Supporting Information (Schemes S1-S2). In the simplified BPO mechanism that is usually reported,^[17] the benzoate radical Ph-CO_2^\bullet oxidizes the reduced forms of the **pyrene-18C6** and generates the excited state, herein the excimer.^[2] Finally, radiative relaxation of the excimer to the ground state produces the ECL emission.



Scheme 2. Potential scale gathering the redox species involved in the ECL mechanism. The top part refers to literature data whereas the bottom part shows the experimental data reported in this work. Py₂Py represents **pyrene-18C6**. a) Reduction potentials of pyrene (noted Py) reported by Heinze and co-workers.^[14b] b) Data self-consistent with our results and with Bard and co-workers.^[13b, 14a] c) Value estimated from the irreversible oxidation of Ph-CO_2^- by Maran and co-workers.^[18] d) Peak potential of the irreversible reduction of BPO, which is a slow redox couple and its position depends on the BPO concentration, scan rate, and electrode material. e) The difference of potential between SCE reference and Ag pseudo-reference is negligible.^[19] Indeed, we measured a standard potential of -2.1 V vs Ag for the first reduction wave of pyrene in acetonitrile (Figure S2), very close to the reported value of -2.13 V vs SCE.^[13b, 14]

As mentioned, the energy available to produce the excited state results from the exergonic electron-transfer reaction between the benzoate radical and the reduced luminophore (Scheme 2). This value should be compared with the energy to reach the excimer state. The excimer band at 490 nm corresponds to an energy $E_{\text{exc}}(\lambda) = 1239.8 / \lambda$ (λ in nm) equal to 2.5 eV. The free enthalpy of the electron-transfer reaction may be estimated from the relationship:^[1, 2b]

$$\Delta G^\circ (\text{eV}) \approx - [E^\circ(\text{Ph-CO}_2^\bullet/\text{Ph-CO}_2^-) - E_{1,\text{red}}] = -\Delta E \quad (1)$$

where $E^\circ(\text{Ph-CO}_2^\bullet/\text{Ph-CO}_2^-)$ was previously estimated to 1.5 V vs SCE,^[15, 18] and the value of $E_{1,\text{red}}$ has been extracted from the voltammograms (Figure 1, Top). The entropic term, which is usually unknown but estimated to be 0.1 ± 0.1 eV^[1, 2b] can be neglected. Therefore, the calculated free enthalpy ($-\Delta G^\circ \sim 3.4$ eV) is much larger than the energy required for the excimer generation $E_{\text{exc}}(\lambda) \approx 2.5$ eV and the direct generation of the excimer is possible (see Schemes 2 and S1). For pyrene, other mechanisms involving triplet-triplet annihilation and anion-cation annihilation have also been presented in the literature (see detailed mechanistic description in Supporting information and Scheme S2).^[13b, 16, 20] Whatever, **pyrene-18C6** produces a strong and stable ECL emission by applying a potential of -2.1 to -2.5 V vs Ag in presence of BPO.

The ECL spectrum (Figure 2, middle) was self-consistent with the PL spectrum collected under 366 nm irradiation (*vide infra*). As expected, the main spectral feature was the excimer emission, as already observed in photoluminescence, while the weak monomer contribution remained hidden under the broad excimer band. As already reported, monomeric pyrene gives only a very weak ECL signal.^[13a, 13b]

With these experimental conditions in hand, we verified that the ECL emission was stable at least for the time of acquisition of the spectra (~240 s, Figure S3, bottom). Then we proceeded to measure the circular polarization of ECL of the two enantiomers of **pyrene-18C6** by using our home-made spectrofluoropolarimeter (Figure S4).^[21] The spectroelectrochemical cell was accommodated into the sample holder of the instrument, and the instrumental parameters (slit width, PMT voltage, integration time, see ESI) were optimized for the measurement. A clear positive CP-ECL signal was unambiguously observed for (-)-**pyrene-18C6**, allied with the electrogenerated excimer chemiluminescence, while a negative band was observed for (+)-**pyrene-18C6**. At least 6 measurements for each enantiomer were carried out to check the reproducibility. The persistence of CP-ECL signal (Figure S3, top) indicated the chemical stability of the compounds during the measurement. Both enantiomers gave indeed mirror image spectra, as expected. The corresponding averaged CP-ECL spectra are reported in Figure 2, (top). Moreover, as a control experiment, the CP-ECL of racemic **pyrene-18C6** was measured in the same conditions and no significant polarization was observed. All these results excluded the presence of artefacts due to linearly polarized components of light in the CP-ECL measurements.

Analogously to photoluminescence, CP-ECL can be quantified by an ECL dissymmetry factor (g_{ECL}), defined as $2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the intensities of the left and right circularly polarized components of the electrogenerated emission.^[6] The g_{ECL} values observed around 490 nm, on the maximum of excimer emission, were $+8.4 \times 10^{-3} \pm 1.4 \times 10^{-3}$ and $-7.3 \times 10^{-3} \pm 2.0 \times 10^{-3}$ for (-) and (+)-**pyrene-18C6** respectively (Figure 2, bottom). As expected, the g_{ECL} associated with the racemic ECL

mixture is erratic and becomes vanishingly small when averaged throughout the spectrum, with a maximum g_{ECL} values around $0.3 \cdot 10^{-3} \pm 1.4 \cdot 10^{-3}$. This defines a lower limit of quantitation for CP-ECL in the conditions employed and ensures that the signals measured for the enantiopure compounds are significant (~30 times higher than the racemic signal).

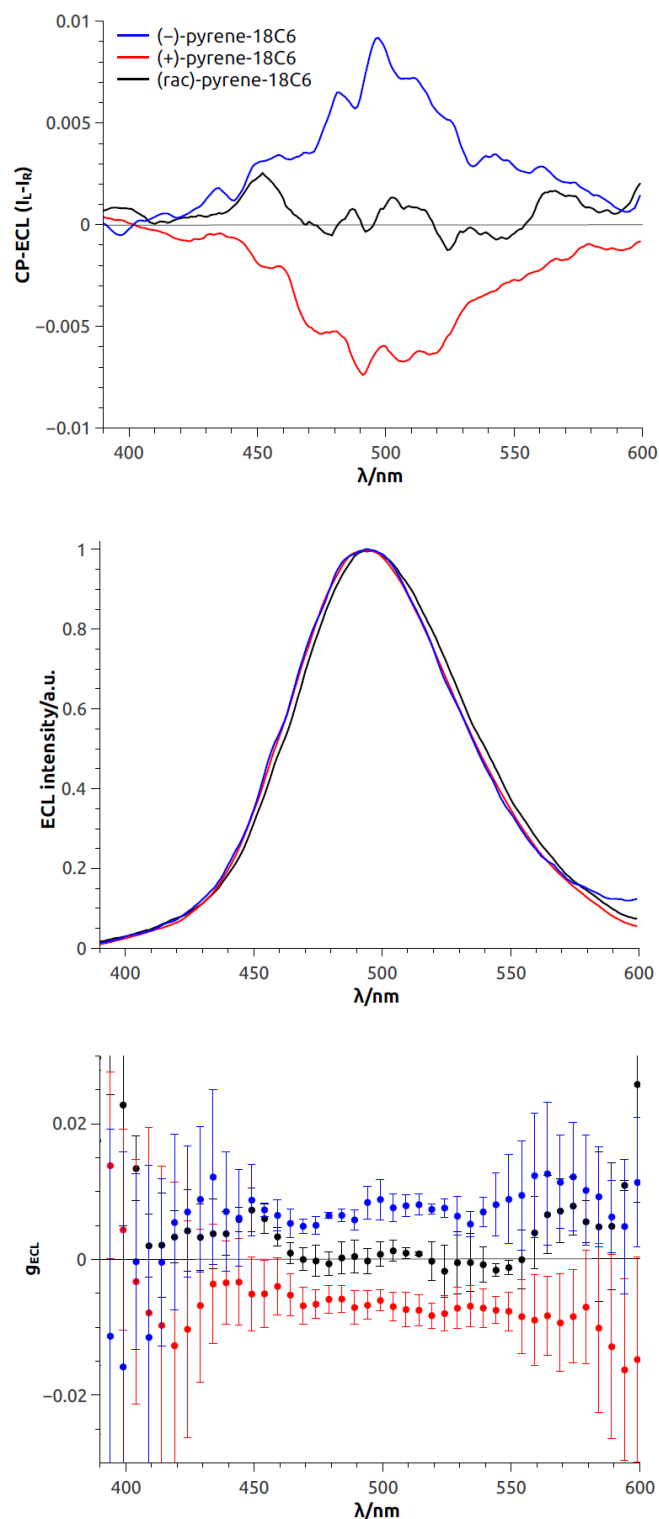


Figure 2. CP-ECL (top), ECL (middle) and g_{ECL} (bottom) of pyrene-18C6 (both enantiomers and racemic mixture). In g_{ECL} plot, the error bars represent \pm one standard deviation and are generated over 6 replicates for each enantiomer and 3 for the racemic mixture. Note that errors on g_{ECL} diverge on the edges of the spectra, where total emission intensity becomes vanishing small.

The CP-ECL profile closely retraces the one measured for CP-PL (see Figure S5), moreover g_{ECL} and the photoluminescence dissymmetry factor g_{PL} (measured under 366 nm irradiation) are well-comparable ($g_{\text{PL}} = +9.0$ and -8.8×10^{-3} for (-) and (+) enantiomers, respectively). These observations confirm that the same electronic state is involved in both PL and ECL. Finally, the aforementioned g_{ECL} values are almost one order of magnitude higher than the one measured by Blok et al. for (+)-[Ru(Phen)₃][ClO₄]₂ in the only report so far on CP-ECL.^[8, 22]

In conclusion, we have shown that it is possible to obtain and measure highly circularly polarized ECL from purely organic molecules. We disclosed a new nature of the ECL signal, showing for the first time that this analytical technique can discriminate enantiomers. These findings can be generalized to other appropriate molecules and tailored structures can be developed to be used as selective CP-ECL reporters for (bio)analytes and other chiral systems of interest.

Acknowledgements

F.Z., E.B., A.H. and J.L. thank the University of Geneva and the Swiss National Science Foundation for financial support (SNF 200020-172497). The support of the Société Académique de Genève (travel grants) is also acknowledged. S.V. thanks the Agence Nationale de la Recherche (Moly ANR-15-CE19-0005-02) for financial support. L.D.B. thanks the University of Pisa PRA_2018_23 for financial support.

Keywords: Circularly polarized electrochemiluminescence • Circularly polarized luminescence • CPL • excimer fluorescence • pyrene

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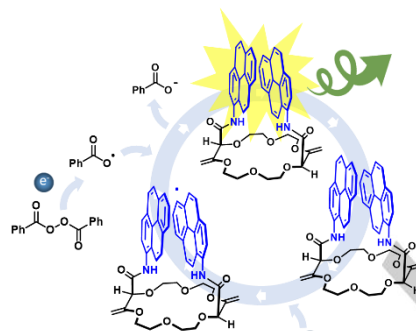
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- [22] Attempts to measure CP-ECL in CH₃CN of the enantiomers of [Ru(bpy)₃][PF₆]₂ (prepared following ref. [23]), were performed in similar conditions. A signal could not be detected despite an intense and stable ECL signal. In the report by Blok et al. (see ref. [8]), neither the exact ECL experimental conditions nor the corresponding ECL data were clearly displayed; only the ECL dissymmetry factor value was given. In addition, only the dextrorotatory enantiomer of [Ru(phen)₃][ClO₄]₂ was tested.
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Entry for the Table of Contents

Layout 1:

COMMUNICATION

Circularly polarized electrochemiluminescence is observed from a chiral organic molecule. The chiral macrocyclic scaffold leads to efficient excimer formation between two pyrene moieties mounted on it. Thus, highly polarized emission is obtained upon electrochemical excitation.

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