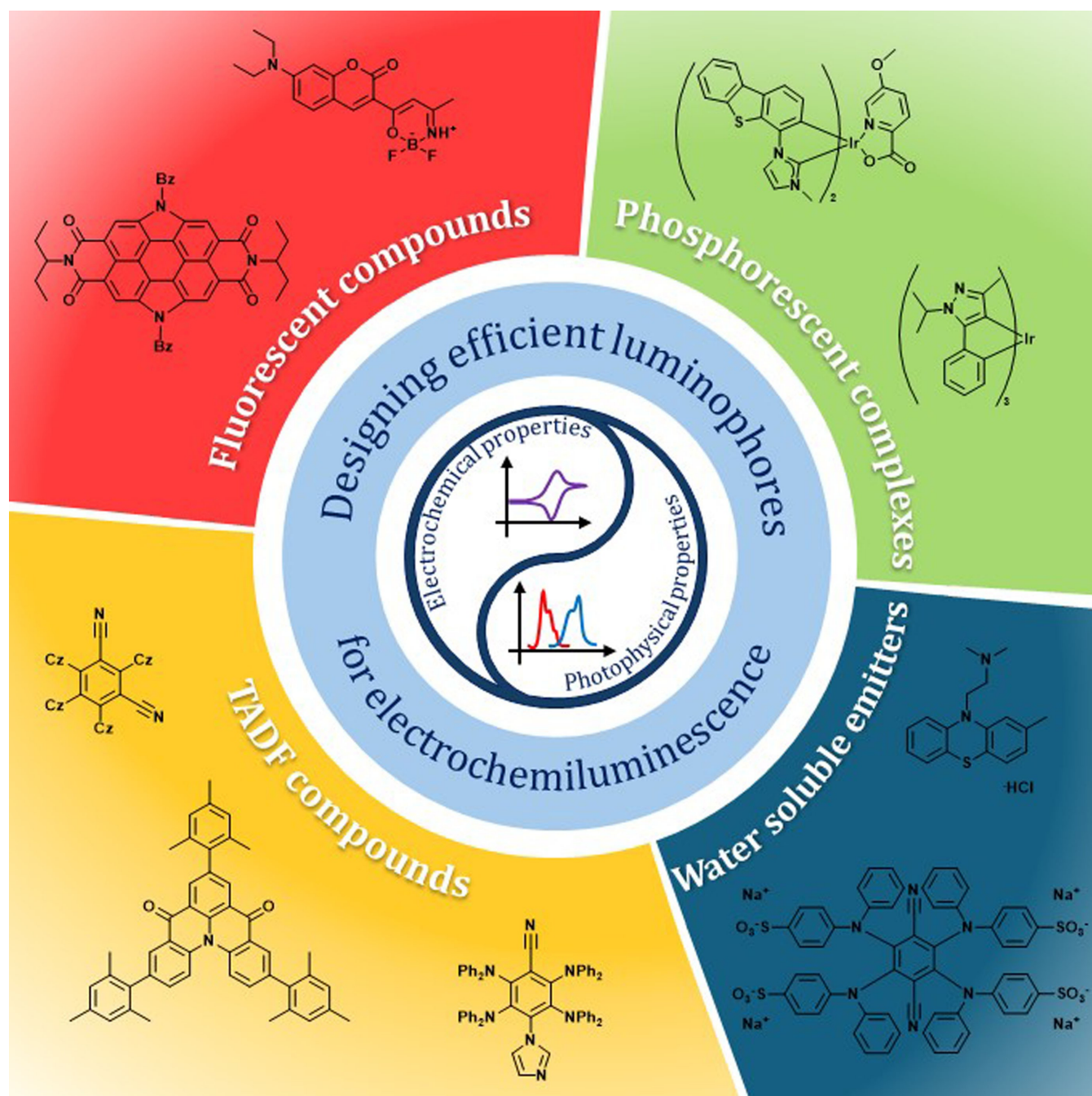# Critical Aspects and Challenges in the Design of Small Molecules for Electrochemiluminescence (ECL) Application

Chiara Alberoni[+],[a] Giulio Pavan[+],[a] Thomas Scattolin,[a] and Alessandro Aliprandi*[a]

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Electrochemiluminescence (ECL) has gained renewed interest due to the strong parallel development of luminophores in the field of organic light emitting diodes (OLEDs) with which this technique shares several aspects. In this perspective review we discuss the most relevant advances of the past 15 years in the study of organic and organometallic compounds as ECL emitters, by dividing them in three different classes: i) fluorescent emitters, ii) phosphorescent emitters and iii) Thermally Activated Delayed Fluorescence (TADF) emitters; then, water-soluble organic luminophores will be also discussed. We focus on how their design, their photo- and electrochemical properties and, in particular, the nature of the emitter, affect their efficiency in ECL. Regardless of the type of luminophore or the photoluminescence quantum yield (PLQY), the literature converges on the fact that the most determining aspect is the stability of the oxidized/reduced form of the emitter. Even if phosphorescent emitters can show outstanding efficiency, this often requires the absence of oxygen. In the case of TADFs, there is also a strong dependence of photoluminescence both in terms of PLQY and emission energy on the polarity of the media, so compounds, that appear promising in organic solvents, may be very inefficient in aqueous media.

1. Introduction

Electrochemiluminescence (ECL) is a process where reactive species formed on an electrode surface undergo high-energy electron-transfer reactions to generate luminescent species. Since its first report in 1929 by Harvey[1] and its theorization by Bard and coworkers in 1965,[2] electrochemiluminescence gained a growing interest since it is one of the most powerful analytical techniques available in many applications such as immunoassays, biomarkers,[3,4,5,6] environmental analysis[7] and imaging.[8,9] In fact, ECL presents high signal-to-noise ratio, large range of linearity, a nearly absent background and spatio-temporal control.[10,11]

In clinical settings, ECL has revolutionized diagnostic assays, enabling rapid and accurate detection of biomarkers for diseases such as cancer, infectious diseases and genetic disorders. Its exceptional sensitivity allows to the detection of analytes at extremely low concentrations, making it invaluable for early disease diagnosis and monitoring. Moreover, ECL has found widespread applications in pharmaceutical research and development, facilitating the analysis of drug compounds, pharmacokinetics, and drug-protein interactions with unprecedented sensitivity and specificity. Its compatibility with complex biological matrices and ability to detect multiple analytes simultaneously make it an indispensable tool in drug discovery and development pipelines.

In ECL, the generation of intermediates, that then form excited states, can occur in two different ways, named "annihilation ECL" and "co-reactant ECL", respectively. In annihilation ECL (Figure 1) two different voltages are applied subsequently to a luminophore to generate its oxidized and reduced species that undergo annihilation reaction to form an excited state that then decay with the emission of light.

Conversely, in co-reactant ECL, a single and fixed potential is applied to a luminophore in the presence of a co-reactant, which is a sacrificial compound that generates, upon reduction or oxidation, a reactive intermediate. The co-reactant mode can be subdivided in two additional mechanisms: "reductive-oxidation" and "oxidative-reduction" (Figure 2). In the first case a negative potential is applied and inorganic and organic peroxides such as persulfates, benzoyl peroxide (BPO) and hydrogen peroxide are used as co-reactants. After the application of a negative potential, radical-anions of both luminophore and co-reactant are formed, then the latter degrades into the reactive intermediate (benzoyl radical, BO•), an oxidizing agent that extracts an electron from the SOMO of the reduced luminophore (Ru(I)) to generate the excited state species (Ru(II)* in Figure 2 – left).

In the oxidative-reduction mechanism a positive potential is applied and various co-reactants, such as tertiary amines, are used (Figure 2 – right). In this case, after the application of a positive potential, radical-cations of both luminophore and co-reactant are formed and, if tripropylamine is used as co-reactant, the reactive intermediate is a tripropylamino radical (TPA•), a highly reducing species that inject an electron in the LUMO of the oxidized luminophore (Ru(III)).
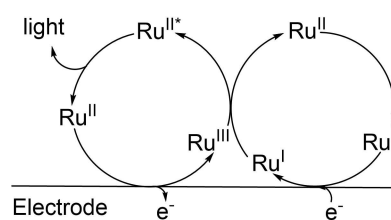
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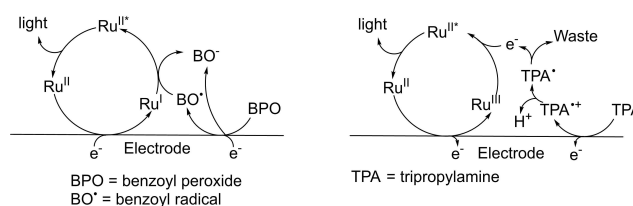[+] *These authors contributed equally.*

Figure 1. Annihilation ECL pathway.

Figure 2. Co-reactant ECL pathways: reductive-oxidation mechanism (left) and oxidative-reduction mechanism (right).

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Since electrochemiluminescence is widely used in biomedical applications, the matrices investigated are almost always water-based, which follows that the luminophore must be water-soluble to a certain extent.

Moreover, in order to be used as ECL emitters, luminophores have to show other important properties such as reversible electrochemistry, good chemical stability (of both the neutral form and radicals) and a low quenching from the co-reactant. Many of these requirements can be found in [Ru-(bpy)$_3$]$^{2+}$ (bpy = 2,2'-bipyridine), which is in fact extensively used in combination with tripropylamine (co-reactant) in biomedical applications.

A very important aspect of electrochemiluminescence is the fact that it is a charge-recombination process, as in the cases of chemiluminescence and electroluminescence, consequently singlet (S$_1$) and triplet (T$_1$) states are formed in a 1:3 statistical ratio.[12] From this ratio it follows that harvesting triplet excitons is of fundamental importance for improving ECL efficiency and many efforts were made during the last 50 years to find highly performing luminophores. A first solution was the use of phosphorescent organometallic complexes, which nevertheless present some problems as environmental issues and high costs, which can be limited by using organic luminophores.

Recently, a new class of carbon nitride (CN) with rigid 2D backbones are reported in the literature as an emerging model luminophore of different color with high Φ_{ECL}[13–16] for ultra-sensitive multiplexed bioassays.[17,18]

In this work, we will discuss the most relevant progresses obtained in the last 15 years in the study of organic and organometallic luminophores as ECL emitters, by dividing them in three different classes: *i)* fluorescent emitters, *ii)* phosphor-escent emitters and *iii)* Thermally Activated Delayed Fluorescence (TADF) emitters; then, water-soluble organic luminophore will be discussed. In this perspective review we focus not only on the design and photo-electrochemical characteristics that a good ECL emitter should have, but also what are the weaknesses/advantages of each class towards practical applications, since in other reviews these aspects have not been covered thoroughly.[19,20]

2. Fluorescent Compounds

Fluorescent compounds are the first examples of organic dyes applied in ECL, owing to their high stability, low toxicity and ease of synthesis. For these characteristics they are also used in the biological analysis and environmental monitoring as mentioned in the Introduction section.[21,22] As anticipated, according to spin statistics both singlet and triplet excitons can be formed, however it has been demonstrated that, if the annihilation reaction is exergonic enough, the emitting singlet excited state can be directly populated and the ECL follows the so-called singlet route (also called 'S-route'), while non-emissive triplet states can contribute through triplet-triplet recombination eventually yielding the singlet emitting state in a second step. This second scenario is commonly observed for "energy deficient system" where the annihilation reaction is insufficient to populate directly the singlet state (the so-called 'T-route'). Another possible pathway involves the formation of excimer/exciplex (denoted as 'E-route') which are typically characterized by a bathochromically shifted emission compared to the monomers.

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Chiara Alberoni completed her PhD in 2022 at University of Trieste in Inorganic Chemistry focusing on the development of homogeneously catalysts based on Pd(II) complexes for the synthesis of functionalized polyolefins. In 2023 she occupied a Post-Doc position under the supervision of Prof. Alessandro Aliprandi in the ERC-STG project "BioPoweredCL" at University of Padova. She is focused on the synthesis and the characterization of organic TADF emitters as dyes in regenerative chemiluminescence.

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Thomas Scattolin completed his PhD in Chemistry in 2019 under the supervision of Prof. Fabiano Visentin at University of Trieste. In 2019 he was a visiting scientist in the laboratories of Prof. Antonio Togni at the ETH in Zurich. In 2020, he joined the group of Prof. Steven P. Nolan at Ghent University as a postdoc researcher. Since 2022, he is assistant professor in Inorganic Chemistry at the University of Padova. His research activity primarily focuses on the synthesis and reactivity of late transition metal complexes with applications in homogeneous catalysis and medicinal chemistry.

Historically, polycyclic aromatic hydrocarbons, such as anthracene, pyrene, rubrene and its derivatives, were the first compounds to produce ECL signals and, in particular, the substitution at C9 and C10 of anthracene with dimethylamine or a phenyl group, protects the radical cation and prevents the formation of decomposition products.[23]

In recent years some examples of perylenes were reported in the literature, but most of them are applied in OLED devices or for biological purposes (*e.g.* compound **1** in Figure 3).[24,25]

In general, perylene derivatives are typical n-type organic semiconductors with high fluorescence and photostability properties, good electron-withdrawing character and good light absorption. The perylene tetracarboxylic dianhydride opened a way for the synthesis of interesting perylene-based compounds which were mainly tetracarboxylic diamide derivatives. Modifications on the *N*-amide substituents or in the bay positions of the backbone allow to finely tune both electrochemical and photophysical properties of these compounds (Figure 3).

In particular, Ding and Welch reported examples of *N*-annulated perylene diimide dimers **2–4**, which are graphene-model compounds.[26,27] Their full characterization was reported together with their performances in ECL. As far as concerned the ECL annihilation pathway, the obtained efficiencies are very low with respect to [Ru(bpy)₃]²⁺ (Table 1). Interestingly, **3** generated ECL signals at both positive and negative potentials, while **4** showed ECL signal only in the anodic scan. This is due to the different stability and lifetimes of both the radical anion and radical cation that induced the formation of an excited state.

In the case of compound **3**, comparable ECL efficiencies were determined in the presence of BPO and TPA (Table 1), thus confirming that the radical anions were as stable as the radical cations.
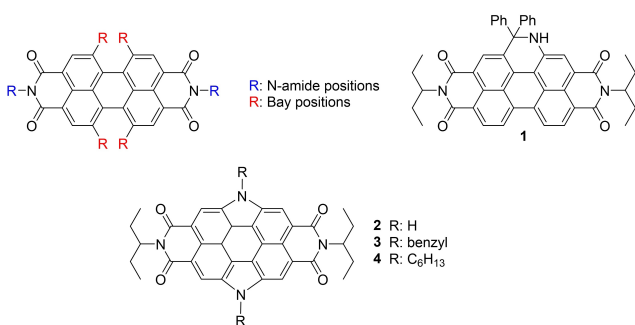
By comparing the ECL behavior of **3** with **4** in the presence of TPA, the lowest ECL efficiency was observed in the case of compound **3**. The authors supposed that this might be due to the increase in the steric hindrance around the bay positions that reduces the diffusion on the electrode.

Over the past decade, a wide range of BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) derivatives were studied in electrochemiluminescence (ECL) using organic solvents such as dichloromethane and acetonitrile. The electrochemical and photophysical characteristics of these compounds can be modulated by structural modifications like the introduction of various substituents at the *meso*, α, and β positions of the backbone, including methyl or *tert*-butyl groups,[28,29] as well as by varying the conjugation length with an appropriate spacer.[30]

In this context, Bard and colleagues have systematically investigated compounds, **6–12**, demonstrating that the location and nature of the substituents played a crucial role in predicting the ECL behavior. The electrochemical studies show reversible reduction and oxidation waves in both positive and negative directions. This means that both radicals, anion and cation, are quite stable because of the block of dimerization and polymerization processes with the introduction of substituents on the BODIPY backbone. In particular, compounds bearing ethyl or *tert*-butyl or *n*-pentyl groups (**8**, **9** and **10**, respectively) show the highest values of Φ_{ECL}. The enhanced stability of substituted BODIPY derivatives was assessed by means of both annihilation and co-reactant ECL modes, where tripropylamine (TPA) or benzoyl peroxide (BPO) were employed as co-reactants (Figure 4 and Table 2).

Notably, the bipyridine BODIPY derivatives **13** and **14** show a reversible redox behavior (both in oxidation and in reduction) suggesting a good stability of both the radical cation and anion. In addition, the calculated frontier molecular orbitals confirm that the bipyridine spacer of each compound does not facilitate

Figure 3. Examples of perylene derivatives reported in the literature.

Table 1. ECL reported for perylene derivatives.

Compound	Φ_{ECLann}[a]	Φ_{ECLBPO}[a]	Φ_{ECLTPA}[a]	λ_{ECL} (nm)
3	< 0.01	0.16	0.46	675
4	0.04	n. r.	0.64	637

Setup and conditions: WE: Pt disk (2 mm); RE and CE: Pt wire coils. [Dye] = 0.2 mM, [TBAPF₆] = 0.1 M, [BPO] = 5 mM, [TPA] = 20 mM. Solvent: benzene: acetonitrile (1:1). [a] Calculated assuming the ECL efficiency of [Ru(bpy)₃]²⁺ = 1. n. r. = not reported.

Figure 4. Examples of BODIPY derivatives reported in the literature.

Table 2. Electrochemical and ECL properties recorded for BODIPY derivatives.

Compound	Φ_{FL}[a]	λ_{FL} (nm)	Φ_{ECL}[a]	λ_{ECL} (nm)
6	19.8	512	0.04	534
7	20.0	541	0.12	540
8	20.0	537	4.20	551
9	15.0	566	3.00	572
10	18.4	572	3.80	566, 706
11	10.0	623	1.00	600
12	5.60	655	0.20	630
13	7.80	545	0.12	570, 740
14	9.40	543	0.20	571, 741
15	n. r.	450	2.60	670, 745
18	9.70	658	0.13	670, 745

Setup and conditions: WE: glassy carbon (0.07 cm^2) or platinum disk (0.07 mm^2); RE: Pt or Ag wire; CE: platinum spiral, ferrocene as internal standard. [TPA] = 25 mM. Solvent: acetonitrile or benzene. [a] Calculated assuming the ECL efficiency of [Ru(bpy)$_3$]$^{2+}$ = 1. n. r. = not reported.
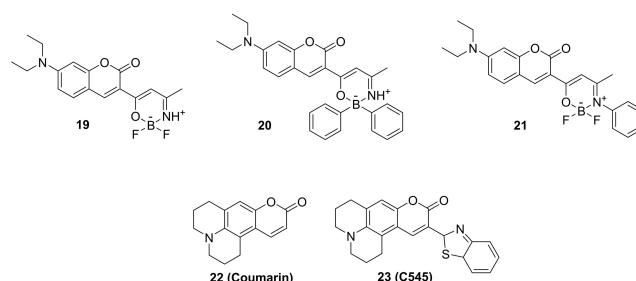
efficient electronic communication between the tethered indacene units. In the presence of a co-reactant, bipyridine BODIPY derivatives **13** and **14** exhibit strong ECL signals and produce emission spectra that are very similar to their corresponding fluorescence profiles.

As far as concerned BODIPY derivatives bearing thiophene moieties (**15–17**), they display a first reversible oxidation process of the BODIPY core, a second oxidation process of the thienyl substituents and an irreversible reduction process due to the instability of the radical anion. Interestingly, while in compounds **15** and **16** the irreversible oxidation of the thiophenes results in their electropolymerization, increasing the number of thiophene rings increases the stability of the radical dication, resulting in a reversible oxidation process. However, only compound **15** showed a decent ECL emission.[31]

More recently, ring-expanded BODIPY derivatives were investigated in ECL with tripropylamine (TPA) as a co-reactant (**18**).[32] The authors observed an ECL efficiency of ca. 10 times lower than that of Ru(bpy)$_3^{2+}$/TPA system.

Two years later, the same research group reported three efficient pyrrolopyrrole aza-BODIPYs able to electrogenerate chemiluminescence in the NIR region by using tripropylamine as a co-reactant in acetonitrile. They represent a rare example of efficient NIR ECL organic emitters as most of the literature on NIR ECLs involve nanoclusters.[33]

Another example of new donor-acceptor chromophores was represented by coumarin derivatives bearing an oxazaborine moiety (**19–21**, Figure 5).[34] The electrochemical properties were influenced by the different substituents, that shift the first reduction potential to less negative values moving from fluorine (**19** and **21**) to phenyl (**20**), as well as by the delocalization of electron density. As far as concerned their photophysical properties, the compound having a diphenylboron fragment (**20**, see Table 3) reached the highest PLQY (74%). Finally, ECL performances in annihilation mode have been investigated (Table 3). Compound **20** showed the lowest ECL efficiency due to its observed decomposition in diluted

Figure 5. Examples of coumarin derivatives reported in the literature.

Table 3. Electrochemical and luminescence data of reported coumarin derivatives.

Compound	Φ_{PL}	λ_{PL} (nm)	Φ_{ECL}[a]	λ_{ECL} (nm)
19	69.0	518	1.4	521
20	74.0	513	0.4	–
21	72.0	540	4.0	553

Setup and conditions: WE: platinum disk (2 mm^2); RE: Ag wire; CE: platinum spiral. [Dye] = 5·10^{-4} M, [TBAPF$_6$] = 0.1 M, scan rate: 100 mV/s. Solvent: acetonitrile. [a] Calculated assuming the ECL efficiency of [Ru(bpy)$_3$]$^{2+}$ = 1.

solution of acetonitrile, while the Φ_{ECL} of **21** is four times higher than that of the standard [Ru(bpy)$_3$]$^{2+}$ in the same operative conditions.

Other research groups are focused on structural modification of compound **22** (Figure 5).[35] In this context, coumarin derivative **23** shows a strong yellow fluorescence at 584 nm and the donor-acceptor rigid structure facilitate the charge transport. It tends to a coplanar aggregation and acquires an improved ECL efficiency of 23% with respect to [Ru(bpy)$_3$]$^{2+}$ in PBS solution with triethanolamine (TEA) as a co-reactant. Authors supposed that the radical cation and radical anion are stable and easily generated.

Recently, coumarins are synthesized as organic nanoparticles (nanorods or nanowires) that can provide a metal-free alternative for traditional semiconductor quantum dots in developing new ECL emitters and the corresponding sensing systems.[35]

In 2020, star-shaped dyes with spirofluorene or truxene cores were synthesized (**24** and **25**), and their photophysical and ECL properties were explored (Figure 6).[36] The initial unit for the design and preparation of more complex star-shaped dyes, consisting of a truxene core bearing di- or tri-phenylamine moieties with or without a thiophene connector, is the quadrupolar spirofluorene system. The electrochemical and photophysical characteristics are tuned by the introduction of a thiophene bridge and electron-donor substituents at their terminal branches. For **25**, a reversible oxidation process was detected in DMF associated to the oxidation of the triphenylamine and the presence of this functionality together with thiophene to the truxene core makes reduction of the molecule significantly easier. These results indicate the formation of stable radical cations and radical anions related to the charge delocalization by π-conjugation in the thiophene bridge. Notably, the highest ECL performance is achieved by annihilation and co-reactant (BPO) pathways with the blue-emitting truxene dye, which is 2 and 4.5 times greater than that of $[Ru(bpy)_3]^{2+}$ (Table 4). Based on their good performances reported in ECL, these structures can represent the starting point to design highly efficient blue-emitting ECL dyes with a truxene core.

3. Phosphorescent Compounds

The advent of phosphorescent compounds, thanks to the pioneer work of Tokel and Bard in 1972,[37] who demonstrated efficient ECL from the transition metal complex $[Ru(bpy)_3]Cl_2$, had a profound impact in ECL opening a new era in this field, full of applications and opportunities.[38] The parallel growth of the OLED technology that is based on electroluminescence, a process that shares many distinct similarities, in particular the role of the spin statistics in the formation of the exciton, has further boosted the research. Indeed, after realizing that phosphorescent emitters outperform fluorescent dyes many OLED phosphorescent emitters have been successfully used as ECL luminophores.[39] This is particularly true for the highly emissive and color tunable Ir(III) complexes,[40] as well as for the more recent fully organic compounds based on the Thermally Activated Delayed Fluorescence (TADF) process.[41] Some recent examples of iridium(III) complexes (**26**–**36**) are shown in Figure 7, showing promising photophysical and electrochemical properties.[42]

Complexes **26**–**34** displayed an intense orange phosphorescence (586–600 nm).[42] The substitution of the picoline moiety with H, F or methoxy groups, reduced the stability of the cyclometallated iridium(III) complexes. In general, all complexes exhibited high PL quantum yields in the range of 66.4–86.3% in deaerated dichloromethane, with the exception of complexes **30** and **31** that reach PLQYs of 17.5% and 15.8%, respectively (Table 5). The ECL was studied with the co-reactant pathway using triethanolamine (TEA) as co-reactant. The highest ECL efficiency (11 times higher than that of $[Ru(bpy)_3]^{2+}$) is reached with **33**, which is a cyclometallated iridium(III) complex bearing a 3,5-dimethoxy picolinate ligand, while **30** exhibited the lowest ECL intensity among these studied cyclometallated iridium(III) complexes. Unfortunately, the lack of complete electrochemical data does not allow to rationalize the low
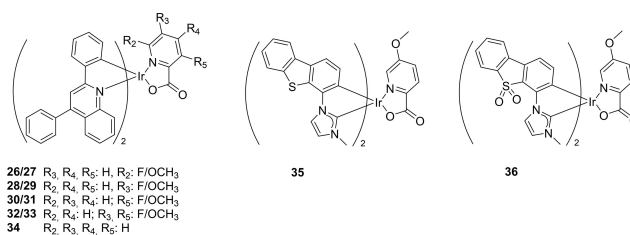

26/27 R_3, R_4, R_5: H; R_2: F/OCH$_3$
28/29 R_2, R_4, R_5: H; R_3: F/OCH$_3$
30/31 R_2, R_3, R_4: H; R_5: F/OCH$_3$
32/33 R_2, R_4: H; R_3, R_5: F/OCH$_3$
34   R_2, R_3, R_4, R_5: H

Figure 7. Examples of phosphorescent Ir(III) complexes.
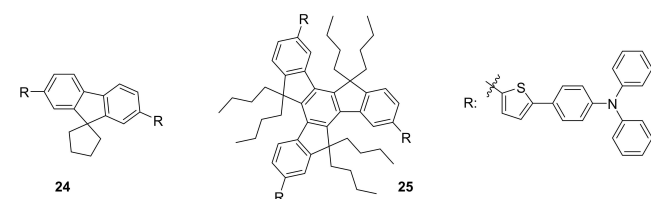
Figure 6. Examples of phosphorescent spirofluorenes derivatives.

Table 4. ECL efficiencies of phosphorescent spirofluorenes derivatives under investigation.

Compound	$\Phi_{ECLann}{}^a$	$\Phi_{ECLBPO}{}^a$	λ_{ECL} (nm)
24	1.6	2.3	504
25	3.1	4.5	494

Conditions: [BPO] = 10 mM; [TBAPF$_6$] = 0.1 M. Solvent: DMF. [a] Calculated assuming the ECL efficiency of $[Ru(bpy)_3]^{2+}$ = 1.

Table 5. Photoluminescence quantum yields and ECL efficiency of the iridium(III) complexes **26**–**34**.

Compound	Φ_{PL} (%)	$\Phi_{ECL}{}^a$
26	72.0	8.7
27	84.6	9.9
28	75.0	9.9
29	72.9	7.8
30	17.5	0.6
31	15.8	1.6
32	66.4	1.6
33	86.3	11.3
34	80.7	5.5

Setup and conditions: WE: gold disk (3.1 mm²); RE: Ag/Ag⁺ saturated KCl solution; CE: Pt plate. [Ir^{III}] = 5·10⁻⁹ M, [TEA] = 0.025 M, scan rate: 100 mV/s. Solvent: acetonitrile. [a] Calculated assuming the ECL efficiency of $[Ru(bpy)_3]^{2+}$ = 1.

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Table 6. Photoluminescence and ECL data of iridium(III) complexes containing two NHC ligands.

Compound	Φ_{PL} (%)	Φ_{ECLann}[a]	Φ_{ECLBPO}[a]	Φ_{ECLTPA}[a]
35	79.8	$1.45 \cdot 10^{-2}$	$0.25 \cdot 10^{-2}$	$0.83 \cdot 10^{-2}$
36	19.2	$1.50 \cdot 10^{-2}$	$0.48 \cdot 10^{-2}$	$0.97 \cdot 10^{-2}$

Setup and conditions: WE: glassy carbon electrode (3 mm); RE: Pt wire; CE: Pt wire. [Dye] = 0.1 mM. [TBAPF$_6$] = 0.1 M, [BPO/TPA] = 40 mM, scan rate: 50 mV/s. [a] Calculated assuming the ECL efficiency of [Ru(bpy)$_3$]$^{2+}$ = 1.

efficiency in ECL of compound **34** compared to its analogue present in Table 5.

Heteroleptic iridium(III) complexes containing two NHC ligands with a dibenzothiophene moiety (**35** and **36**) showed emission peaks centered at 530 nm and a remarkable PLQY of 79.8 % in the case of complex **35**.[43] These Ir-NHC complexes were tested in ECL both in annihilation and co-reactant modes (with BPO and TPA). Unfortunately, the overall ECL efficiency of the two Ir(III) complexes is very low compared with the benchmark [Ru(bpy)$_3$]$^{2+}$ (Table 6).

Despite the abovementioned compounds being excellent candidates for electrochemiluminescence (ECL) applications, with the Ru(bpy)$_3^{2+}$ complex serving as the gold standard for calculating the efficiencies of other compounds, they exhibit drawbacks attributed to the cost of the heavy atom incorporated into the complexes. These disadvantages extend not only to economic considerations, but also have geopolitical implications.

4. TADF Compounds

Even if some phosphorescent emitters show better electrochemical and electrochemiluminescence properties and higher water solubility than fluorescent emitters, they suffer from many drawbacks as previously mentioned.[44] For these reasons the OLED industry, to which ECL research is linked, began to search for more economic and efficient compounds to be used in these devices, and the most promising solution was "Thermally Activated Delayed Fluorescence" (TADF) emitters.[45–48]

The TADF phenomenon can be observed in purely organic compounds made of electron-rich moieties (donors) and electron-poor moieties (acceptors) that can be directly linked (D—A) or separated by a π-linker (such as a phenylene group) (D-π-A) and with a tilted structure. From this structure, it follows that HOMO and LUMO are spatially separated and a small energy gap ($\leq$ 100 meV) between the lowest-lying singlet state and the lowest-lying triplet state (ΔE_{ST}) is present;[49] this gap makes possible a reverse intersystem crossing (RISC) process at room temperature whereby triplet excitons can up-convert into the excited singlet state, which can decay radiatively resulting in an internal quantum efficiency (IQE) up to 100 %. Moreover, an interesting advantage of TADF emitters is the fact that their optical and electrochemical properties can be tuned by judicious selection of the donor and acceptor moieties.

First reports about ECL from TADF molecules were published by Imato and colleagues, where they studied carbazoyldicyanobenzene derivatives in annihilation conditions (Figure 8).[50,51]

They found that all the investigated molecules showed ECL emission (Table 7) and, in some cases, such as for compound **39**, the ECL emission exceeded the limitation of spin statistics.[51] In particular, compound **39** showed a Φ_{ECL} of nearly 10 times higher than that of [Ru(bpy)$_3$]$^{2+}$ in dichloromethane, thus making this compound the state of art.

Moreover, it was observed that the ECL emission of these compounds are superimposable with their PL emissions, excluding the generation of excimers, with the exception of compounds **37** and **38**, for which excimers were suspected. Finally, it was observed that carbazole derivatives undergo electro-polymerization in presence of an anodic potential and this polymerization led to lower ECL emissions.[52]

Comparing Φ_{PL} and Φ_{ECL} of these compounds, it can be observed that compound **37** shows the lowest ECL yields, which can be due to a lower heterogeneous rate constant value (k^0 = 0.012 cm s^{-1}). Conversely, the higher k^0 of compound **40** (0.014 cm s^{-1}) results in higher ECL yields.

After this initial investigation, the same group chose the best-performing compound, **39**, and systematically examined how different substituents on the carbazole moieties would affect the electrochemical and photophysical properties. From this examination, they found a direct correlation between ECL efficiency and electrochemical stability. Indeed, as shown in Figure 8, the presence of *tert*-butyl groups in **42** stabilize better the oxidized form with respect to the methyl (**41**) and phenyl groups (**43**) leading to higher efficiencies (see Table 8).

After these two seminal works, the attention was turned to ECL properties of TADF polymers, polymer dots or
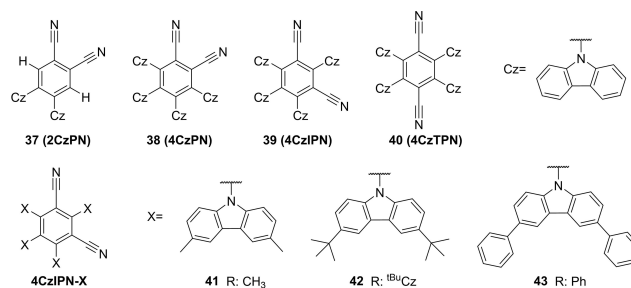
Figure 8. First row: carbazoyldicyanobenzene derivatives investigated by Imato and colleagues in 2014; Second row: isophthaloderivatives investigated by the same group later on.

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Table 7. ECL efficiencies of carbazoyldicyanobenzene derivatives under annihilation conditions investigated by Imato and colleagues.

| Compound	Solvent	Φ_{PL} (%)	λ_{PL} (nm)	Φ_{ECL}[a]	λ_{ECL} (nm)
37	DCM	34	533	0.90	550
	ACN	10	560	0.22	585
38	DCM	29	583	2.80	595
	ACN	7.5	609	0.42	610
39	DCM	54	544	9.40	555
	ACN	18	565	3.00	565
40	DCM	15	581	1.20	600

Conditions: [Dye] = 1 mM or 0.4 mM (for compound **40**). [a] Calculated from integrated ECL intensity at λ_{ECL} and charge compared with that of the 1 or 0.4 mM [Ru(bpy)$_3$]$^{2+}$ system with Φ_{ECL} = 1.

Table 8. ECL efficiencies of substituted tetracarbazoylisophthalonitriles under annihilation conditions investigated by Imato and colleagues.

Compound	Solvent	Φ_{PL} (%)	λ_{PL} (nm)	Φ_{ECL}[a]	λ_{ECL} (nm)
41	DCM	18	577	2.60	585
	ACN	3.7	603	1.50	595
42	DCM	44	585	7.00	572
	ACN	8.5	588	1.84	587
43	DCM	17	588	2.60	595
	ACN	3.7	611	0.64	610

Conditions: [Dye] = 1 mM. [a] Calculated by using [Ru(bpy)$_3$]$^{2+}$ in ACN with Φ_{ECL} = 1.
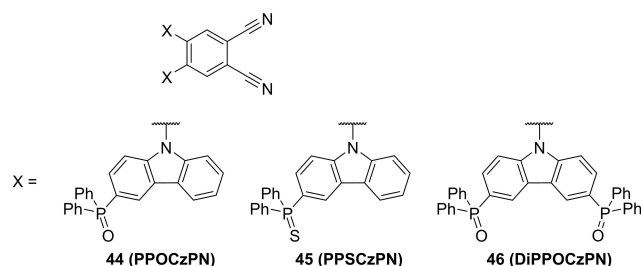
Figure 9. Chemical structure of phthalonitrile derivatives investigated by Zysman-Colman and colleagues.

nanoparticles.[53–55] In 2022 Niu and co-workers gave new significant information about annihilation and co-reactant ECL of **39**.[54] In that article, it was observed that, under annihilation conditions, the radical-anion of **39** (4CzIPN$^{\bullet-}$) is more stable than the radical-cation 4CzIPN$^{\bullet+}$, a behavior that is compatible with its electrochemical properties and that is supported also by the ECL efficiencies in presence of tripropylamine (TPA) and benzoyl peroxide (BPO): 12% of the standard [Ru(bpy)$_3$]$^{2+}$/TPA

in the first case while ca. two times the same standard in the second case. These results corroborate the theory that good electrochemical reversibility is critical to achieving good ECL efficiencies.

In the same year, the Zysman-Colman group reported the investigation of ECL from phthalonitrile derivatives containing diphenylphosphine chalcogenide-substituted carbazole donors (Figure 9) under annihilation and co-reactant pathways.[56]

As for **37**, these compounds do not show high ECL efficiencies under annihilation conditions or with benzoyl peroxide (BPO) as co-reactant (see Table 9) because of the instability of their radicals.

Then, the same group reported ECL from compounds **47**[57] and **48** (Figure 10).[58] More in detail, compound **47** is a Multiresonance TADF (MR-TADF) molecule, which is characterized by having HOMO and LUMO alternated in the molecule, while compound **48** is a through-space charge transfer TADF compound, an alternative approach to design TADF molecules.[24]
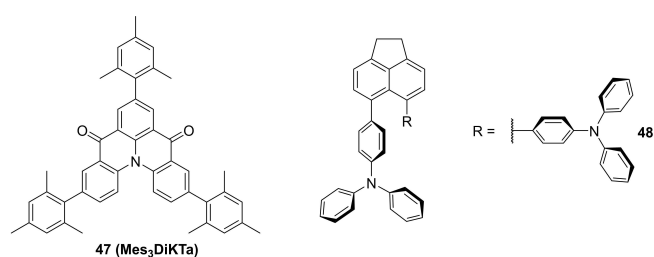
Table 9. ECL efficiencies under annihilation and co-reactant (BPO) conditions of compounds investigated by Zysman-Colman and colleagues.

Compound	Φ_{PL} (%)	λ_{PL} (nm)	$\Phi_{ECL, ann}$	$\lambda_{ECL, ann}$ (nm)	$\Phi_{ECL, BPO}$	$\lambda_{ECL, BPO}$ (nm)
44	51	498	0.01	520	0.17	520
45	47	501	0.01	500	0.06	500
46	61	565	0.10	475	0.01	545
48	67	470	0.03	630	22	610

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Table 10. ECL efficiencies of monoimidazole derivative in presence of BPO as co-reactant.

Compound	Solvent	Φ_{PL} (%)[a]	λ_{PL} (nm)	Φ_{ECL}[b]	λ_{ECL} (nm)
49	DCM	65.0	532	28.0	533
	ACN	9.8	536	12.0	528
50	DCM	58.0	525	11.0	529
	ACN	22.0	540	4.70	545
51	DCM	69.0	500	1.30	514
	ACN	40.0	513	0.38	522
52	DCM	37.4		5.0	557
	ACN	46.0		3.0	550

Conditions: [Dye] = 50 μM, [BPO] = 1 mM. [a] Ar-purged solution. [b] Calculated assuming the ECL efficiency of $[Ru(bpy)_3]^{2+} = 1$.

Figure 10. Structures of TADF dyes investigated by Zysman-Colman and colleagues.

Figure 11. 4-(1H-imidazol-1-yl)benzonitrile based TADF emitters studied by our group.

Figure 12. TADF red emitters.

Interestingly, these molecules (for efficiencies see Table 9) show a delay in the ECL-onset and a buildup of ECL signal, that was already observed by other authors.[59]
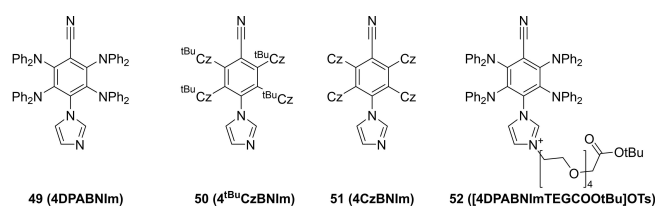
However, authors excluded that these delays could be caused by a decrease in the electron-transfer constants or diffusion issues, so they attributed them to the so-called "Organic Long ElectroChemiLuminescence" (OLECL), a phenomenon similar to the so-called "Organic Long PhotoLuminescence" (OLPL).[47]

The authors attributed these delays to either large ΔEST for compounds **45** and **46**[56] or aggregate/excimers formation for compounds **47** and **48**,[57,58] as large red-shifts can be observed for ECL emission.
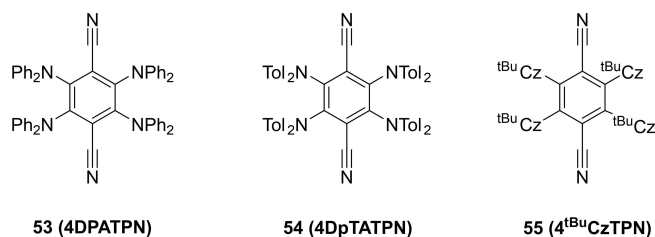
However, with the aim of practical application, most of the TADF molecules reported so far exhibit two main issues: *i)* the absence of bioconjugable groups necessary and *ii)* lack of water solubility.

Starting from these premises our group recently reported a class of novel TADF molecules bearing an imidazole moiety (Figure 11) that was also alkylated with a polyethylene glycol chain bearing a *tert*-butyl ester group to obtain the imidazolium derivative **52**, [4DPABNImTEGCOOtBu]OTs.[62] From the systematically variation of donor moieties, we observed that a reversible electrochemistry both at anodic and cathodic regions was fundamental to achieve high ECL efficiencies and that the alkylation of imidazole moiety, even if slightly decreases ECL efficiencies, did not quench them at all (Table 10).

Moreover, as observed Zysman-Colan and colleagues, we also noticed delays on ECL-onsets and buildup of ECL signals, but by comparing PL and ECL emissions (that are super-

imposable), we were able to exclude excimers, and we attributed them to the presence of a complex mechanism of ECL generation.

However, these monoimidazole derivatives show emission in the blue-yellow region and their ECL efficiencies were evaluated under the "reductive-oxidation" mechanism mainly for two reasons: *i)* the electrochemical reversibility of the acceptor moiety and *ii)* the very low reduction potential, which would cause low ECL efficiencies with TPA as co-reactant. Therefore, we changed the acceptor moiety in order to shift the reduction processes of acceptor towards more anodic potentials and to shift the emission in the orange-red region. To achieve this goal we used terephthalonitrile as acceptor while *tert*-butyl carbazole, diphenylamine and di-*para*-tolylamine were used as donors (Figure 12).[63] All these compounds were ECL-active, but their ECL efficiencies, apart for compound **53**, were a third of the standard ($[Ru(bpy)_3]^{2+}$/TPA) (Table 11) and, moreover, they do not show any hydrophilic and functionalizable group.

If we then look at the results reported so far, it can be stated that, in organic media, TADF emitters can be excellent alternatives to phosphorescent emitters because of their higher

Table 11. ECL efficiencies of terephthalonitrile derivative in presence of TPA as co-reactant.

Compound	Φ_{PL} (%)[a]	λ_{PL} (nm)	Φ_{ECL}[b]	λ_{ECL} (nm)
53	49.43	597	1.72	595
54	14.98	625	0.33	621
55	6.61	593	0.30	601

Conditions: [Dye] = 50 μM, [TPA] = 1 mM, solvent: DCM. [a] Ar-purged solution. [b] Calculated assuming the ECL efficiency of [Ru(bpy)$_3$]$^{2+}$ = 1.

Figure 14. Structures of the water-soluble dimethylamino cationic and [4] and [6] helicenes investigated by Sojic and colleagues.
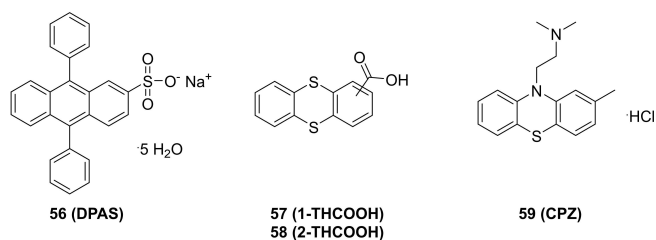
ECL yields (in absence of oxygen). However, their PLQY significantly drop when increasing solvent polarity making challenging their application in aqueous media unless alternative strategies such as the formation of nanoparticles or nanoaggregates are used.[64,65]
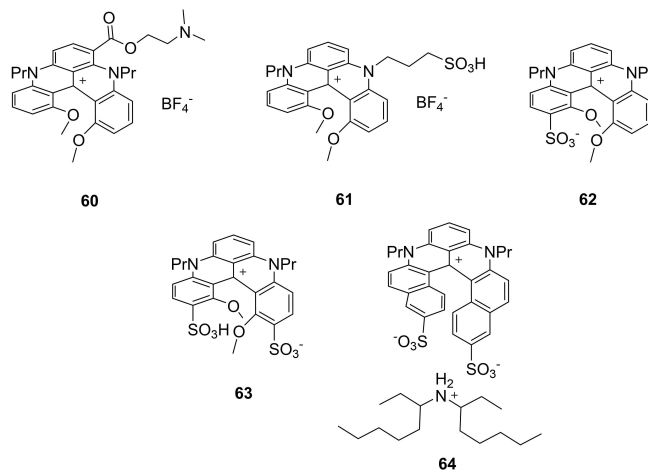
5. Water-Soluble Compounds

As already mentioned in the introduction, ECL is widely used in aqueous solution, where phosphorescent Ru(II) and Ir(III) complexes are widely used[66,67] both because some of them are intrinsically water-soluble and because their ligands can be functionalized with water-soluble/bioconjugable groups or encapsulated within water-soluble nanoparticles.[68,69]

On contrast, there are few reports about ECL from water-soluble organic molecules. The first report about ECL from water-soluble organic molecules was published by Richards and Bard.[70] In that report, ECL emission of **56** (sodium 9,10-diphenylanthracene-2-sulfonate (DPAS)), **57** and **58** (1- and 2-thiantiirene-carboxylic acid (1-THCOOH and 2-THCOOH), respectively) and **59** (chlorpromazine (CPZ)) in sodium phosphate buffer with TPA and S$_2$O$_8$$^{2-}$ as co-reactants were studied (Figure 13). Unfortunately, no ECL yields were reported.

An interesting aspect of that work is the behavior of chlorpromazine, which showed a kind of "self-annihilation" ECL process, where the dimethylamino group, upon oxidation, generates a reducing group that transferred electrons to the dye core. This phenomenon was also observed by Sojic and colleagues 15 years later, when they reported anodic-ECL in the red region from a cationic helicene bearing a dimethylamino group in absence of co-reactant, **60** (Figure 14).[71]

These results are very interesting and can open new research lines since the presence of a dye incorporating the co-reactant can simplify and decrease costs of sensors.

The same group also reported near-infrared ECL from water soluble compounds **61**–**64** by inserting sulfonate groups (Figure 14).[72] All these compounds show emission at ca. 700 nm and, as expected, they do not exhibit high PLQYs due to energy-gap law (Φ_{PL} from 0.6% (**63**) to 6.8% (**64**)). Notably, Φ_{ECL} trend (Table 12) is not consistent with Φ_{PL} trend, since compound **65** show a Φ_{ECL} lower than **61** and **63**. This behavior was reconducted to a better stability of the oxidized form of **61**.

However, there were no reports of water-soluble TADF dyes and their applications in electrochemiluminescence. To this end, we recently reported the characterization of a water-soluble TADF dye, namely Na$_4$[4DPASO$_3$TPN], **64** (Figure 15), and its application in oxidative-reduction ECL.[63]
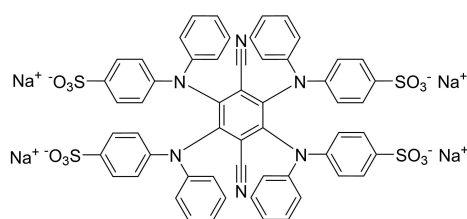
Even if this compound keeps TADF features in aqueous media, the drop of Φ_{PL} (only 2.9%) and, more importantly, a scarce electrochemical reversibility, leads to a quite low ECL efficiency (2% of [Ru(bpy)$_3$]$^{2+}$) compared to the unsulfonated analogue **53** which was 172%. Despite the negative results obtained with this compound, it is a demonstration that TADF dyes retain in water their TADF properties and they are ECL-active.

This compound may therefore open a new line of research, in which TADF dyes with good electrochemical stabilities and

Figure 13. Structures of water soluble dyes investigated by Richards and Bard.

Table 12. PL and ECL efficiencies of water-soluble helicene derivatives synthesized by Sojic and colleagues using TPA as co-reactant.

Compound	Φ_{PL} (%)	λ_{PL} (nm)	Φ_{ECL}[a]	λ_{ECL} (nm)
61	2.8	672	0.34	671
62	1.3	693	0.22	688
63	0.6	710	0.05	708
64	6.8	661	0.20	661

Conditions: Solvent: 0.1 M PBS, [Dye] = 20 μM, [TPA] = 0.05 M. [a] ECL efficiencies are calculated assuming ECL efficiency of [Ru(bpy)$_3$]$^{2+}$ = 1.

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62 (Na₄[4DPASO₃TPN])

Figure 15. Structure of the water-soluble TADF dye synthesized by our group.

photoluminescent properties can be investigated as water-soluble ECL emitters with the aim of overcoming the standard $[Ru(bpy)_3]^{2+}$ to make more efficient (bio)sensors.

6. Conclusions and Outlook

In summary, this perspective review has comprehensively examined emitters utilized in electrochemiluminescence (ECL) over the past decade. We compared the efficiencies from traditional fluorescent and phosphorescent compounds to emerging organic molecules with Thermally Activated Delayed Fluorescence (TADF) properties. The review has emphasized the crucial correlation between electrochemical properties and ECL efficiency of these compounds. As far as concerned the electrochemical characterization, samples have to show suitable reduction and oxidation potentials and these processes have to be reversible; consequently, the investigated compounds, if characterized by good PLQYs, usually exhibit enhanced ECL efficiency compared to the standard $[Ru(bpy)_3]^{2+}$. Interestingly, the stability of the oxidized/reduced form of the luminophore has the greatest impact on ECL efficiency with respect to photoluminescence quantum yields, the nature of the excited state (fluorescence or phosphorescence) or the ability to harvest triplet excited states efficiently. Fluorescent organic compounds have the advantage of being easily functionalized and of being little influenced by the medium and the presence of oxygen. Indeed, some BODIPY derivatives can, in some cases, outperform $[Ru(bpy)_3]^{2+}$ by up to 4x in terms of ECL efficiency despite a PLQY of only 20%, suggesting that there is still room for improvement. In the case of phosphorescent compounds and TADF, therefore where triplet excited states contribute to the emission, they can significantly outperform $[Ru(bpy)_3]^{2+}$, but in oxygen-free conditions. Since the most relevant applications of ECL are in biological media where oxygen is present, the efficiency of ECL should also be evaluated under air conditions. In the case of TADF there is also a further problem, the strong dependence of photoluminescence both in terms of PLQY and emission energy on the polarity of the medium, so compounds that appear promising in organic solvents may be extremely inefficient in aqueous media. Furthermore, most of these compounds typically exhibit photocatalytic activity. Excited states are known to be stronger reducing and oxidizing agents than the ground state, and it is therefore possible for photo-

induced reactions to occur with the co-reactant. Analytical applications of ECL typically require bioconjugable groups, whose introduction can dramatically change the optical and electrochemical properties of the compound, sometimes in unpredictable ways. We would like to underline that even if the trends may be clear within a homogeneous series of compounds or within the work of a research group, it becomes quite complex to rationalize the behaviors in a more absolute way due to the presence of numerous variables, not least the different concentrations of the luminophores, of the co-reactants, the role of pH and finally the setup used to carry out the measurements. Moreover, the efficiency is always determined by a comparison with a standard, typically $[Ru(bpy)_3]^{2+}$, whose efficiency in turn depends on the solvent and operative conditions. For this last problem new strategies have been proposed to obtain absolute measures.[73,74] In our opinion, the photoluminescence quantum yield of the emitters in the ECL operating conditions should be measured to ensure that the efficiency is not reduced by photoinduced processes. We also believe that an interesting direction could be based on the functionalization of the most efficient scaffolds with bioconjugable and/or water-solubilizing groups in order to estimate how effectively the studies conducted in organic solvent can be translated into aqueous media and understand which ones may be the most "innocent" moieties at the photo and electrochemical level.

Acknowledgements

Conflict of Interests

The authors declare no conflicts of interest.

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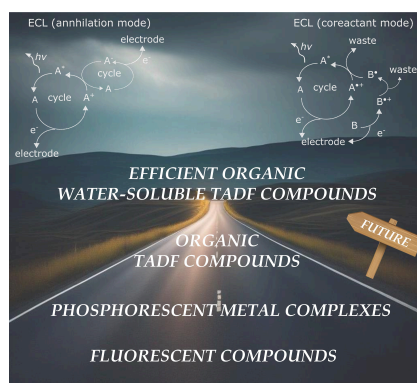[8] J. Dong, Y. Lu, Y. Xu, F. Chen, J. Yang, Y. Chen, J. Feng, *Nature* **2021**, *596*, 244–249.

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REVIEW

In this perspective review, the most relevant progresses obtained in the last 15 years in the study of organic and organometallic luminophores as ECL emitters were discussed. Examples of fluorescent and phosphorescent emitters, Thermally Activated Delayed Fluorescence (TADF) emitters and finally, water-soluble organic luminophore were reported.

EFFICIENT ORGANIC
WATER-SOLUBLE TADF COMPOUNDS

ORGANIC
TADF COMPOUNDS

PHOSPHORESCENT METAL COMPLEXES

FLUORESCENT COMPOUNDS

Dr. C. Alberoni, G. Pavan, Dr. T. Scattolin, Prof. Dr. A. Aliprandi*

Critical Aspects and Challenges in the Design of Small Molecules for Electrochemiluminescence (ECL) Application