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Versatile electrochemiluminescent organic emitters

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Abstract

Organic luminophores for electrochemiluminescence (ECL), namely polycyclic aromatic hydrocarbons, have been the first molecules investigated since the beginning of ECL studies. Moving from organic solvents to water-based solutions in view of analytical applications, the attention on ECL emitters shifted to soluble inorganic complexes, which prevailed in both fundamental and applied research. However, the investigation of organic molecules has recently revived owing to new synthetic procedures and concepts. Polymeric nanoparticles, surface functionalization, aggregation-induced emission (AIE), and thermally-activated delayed fluorescence (TADF) sparked the research with renovated interest for organic molecules. Here, we introduce and summarise these new concepts behind organic emitters for ECL.

Keywords

Electrochemiluminescence, AIE, TADF, π - π interactions, organic emitters, polymer nanoparticles

Introduction

The electrochemiluminescence (ECL), or electrogenerated chemiluminescence, is the emission of light from a molecular species following an electron transfer reaction that is triggered by an electrochemical reaction [1,2]. In the last 20 years ECL has proved to be a versatile and powerful analytical technique in different fields, ranging from fundamental research to commercial clinical and biological applications [1-8]. The efficiency of the signal strongly depends from many parameters such as electrode materials [9-11], reagents, i.e., type of coreactant [12,13] and luminophores [1,2]. Among luminophores, it is possible to distinguish inorganic complexes [1,2,14,15], nanomaterials (e.g., carbon-based, quantum dots, doped nanoparticles) [16-21] and organic molecules [1,2]. The latter has been the subject of investigation since the beginning of ECL studies [1,2], then leaving the way to inorganic complexes which are more suitable for sensing in water solutions, where ECL finds its application. However, new concepts such as aggregation-induced emission (AIE) and

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thermally-activated delayed fluorescence (TADF) brought a renewed interest for ECL organic emitters, in particular, the possibility to use water solutions and a hypothetical 100% internal conversion by up-conversion of triplet excitons in singlet excitons, respectively.

Design and synthesis of organic ECL dyes

Besides the “standard” polycyclic aromatic hydrocarbons (PAHs) such as 9,10-diphenylanthracene (DPA), rubrene, pyrene, and anthracene, many polyaromatic compounds have been investigated, showing how different substitution can influence the ECL emission in colour, efficiency, and stability.

The synthesis of these compounds often requires a precise molecular design in order to obtain the desired properties such as the fine-tuning of the ECL emission [22] (Figure 1) or the binding of the dye to the electrode surface [23]. In particular, red-shifted ECL curves have been obtained by enhancing the donor strength from fluorine, to methyl and methoxy substituents of diphenylamine (Figure 1B).

A general approach involves the functionalization of a π -core by adding lateral substituents. The choice of the aromatic core is pivotal to determining the nature of the emitting species. The use of a flat core, such as phenanthrene [24] and pyrene [25], allows to obtain ECL emission from excimers that can be tuned in colour and stability by introducing different aromatic substituents. Another family of planar molecules, such as the tetraphenylethylene, is used as central units to generate ECL with aggregate-induced emission (AIE) character [26]. Due to their peculiar properties, the AIE fluorophores are employed to generate ECL emission in aqueous environments, thus overcoming the low water solubility issue of many aromatic systems [27,28].

From the chemical point of view, the use of cross-coupling reactions is one of the most used approaches to extend the π -systems in PAHs ECL dyes. These reactions are generally catalysed by metals and require the presence of halide atoms on the core. The palladium-catalysed Suzuki-Miyaura cross-coupling reaction works under a large range of experimental conditions being more selective towards iodine than bromine, and for example has been used to introduce triphenylamine groups on different aromatic core units, such as spirobifluorene [29,30], or truxene [31]. Alternative donor groups, such as carbazole and diphenylamine, can be inserted using Hartwig-Buchwald palladium-catalysed, which allows to form C-N bonds. Due to the high costs of palladium, the employment of cross-coupling reactions based on Earth-abundant metals is a valued alternative. Among them, the Ullmann-type reactions and Chan-Lam coupling are based on copper, and they can work in presence of oxygen, thus decreasing the complexity of the experimental setup. On the other hand, the continued investigation of newly palladium-based catalysts offers a broad spectrum of conversions for the functionalization of PAHs.

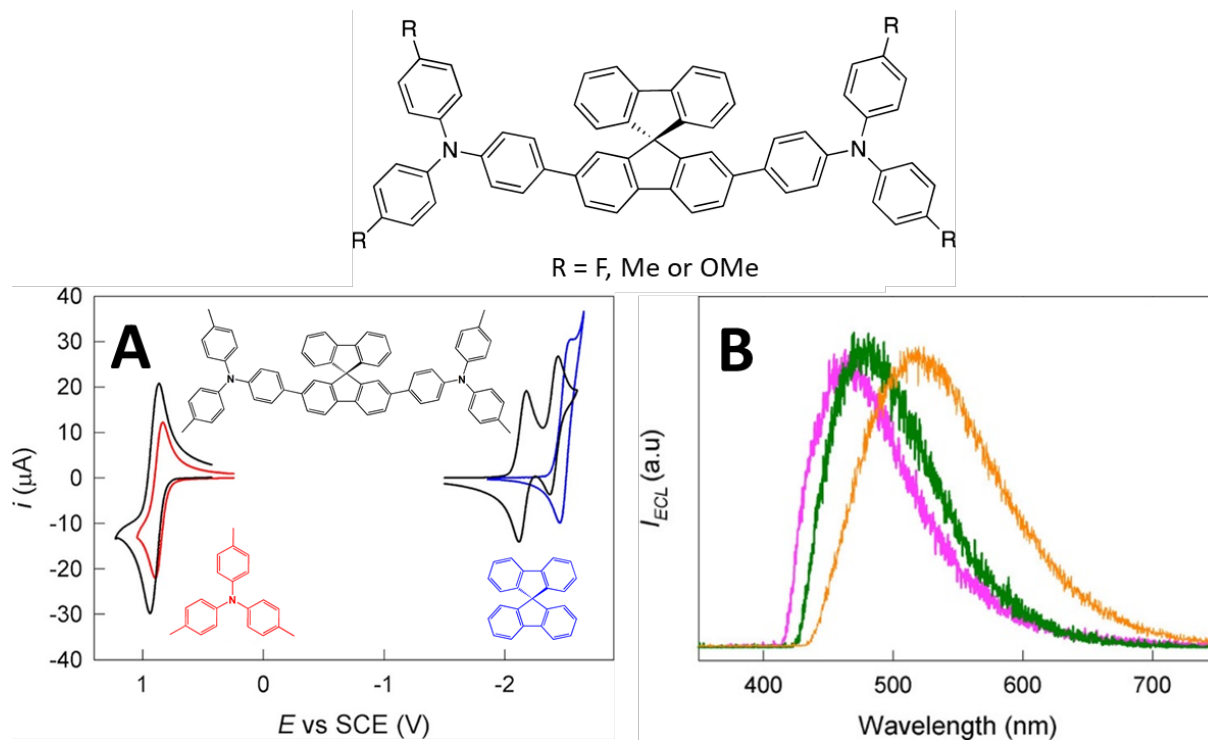
The synthesis of extended aromatic systems by means of cross-coupling reactions is a useful strategy for the preparation of organic dyes with a donor-acceptor (D-A) structure. The use of substituents with different donor strengths allows tuning the emission ECL colour. Moreover, if the D-A system is designed to reduce the overlap between HOMO and LUMO orbitals in the ground and excited states, it is possible to observe the thermally activated delayed fluorescence (TADF) phenomenon [32,33]. Indeed, the small energy gap between singlet and triplet excited states arising from the HOMO-

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LUMO separation allows the occurrence of reverse intersystem crossing process (rISC), thus the enhancement of the ECL emission as a consequence of the conversion of triplet excitons into singlet excitons, [34] as described by pioneering Kapturkiewicz in the '90s [35].

Figure 1



Molecular structure of spirobifluorene derivative. (A) CVs of 1 mM spirobifluorene derivative with R=Me (black), spirobifluorene core (blue), and tris(4-methylphenyl)amine (red) in DMF/0.1 TBAP. Scan rate 0.2 Vs⁻¹. (B) ECL spectra in DMF/0.1 M TBAP of spirobifluorene derivative with R=F (purple), R=Me (green), and R=OMe (orange) (adapted from Rizzo et al [Errone. Il segnalibro non è definito.22] with permission from the American Chemical Society).

ECL properties of organic ECL dye

The ECL from organic molecules has generally relied on organic solvents to overcome the solubility issue, while the solid state has been a viable alternative approach.

Covalent-organic frameworks (COFs), crystallization, or π - π stacking interactions inducing aggregation are the main strategies to achieve ECL from organic dyes in water solution, which might find application in the development of bioanalytical sensing strategies.

COFs provide stable long-range ordered arrangements of ECL luminophores and a strategy to assemble organic molecules on the surface of the electrode with stable structures [36,37].

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Crystallization of 2-thienyl-benzo[b]siloles on the electrode leads to enhanced ECL which differs for electrodes modified with luminophores that exist as crystalline films or amorphous aggregates, thus differentiating crystallization-induced emission enhancement ECL (CIEE-ECL) [38] from aggregation-induced emission ECL (AIE-ECL) [39]. The transposition of Aggregation-Induced Emission (AIE) in the ECL field opened a new range of applications for organic dyes which had been precluded previously. Tetraphenylethylene units [40], thiophene [41], 1,1-disubstituted 2,3,4,5-tetraphenylsiloles [42], and carboranyl carbazoles [43] are examples of moieties that induce the aggregation of the ECL emitters. Substitution of tetraphenylethylene for 4-(phenoxazin-10-yl)benzoyl (PXZ) unit on 1,3-bis(carbazol-9-yl)benzene (mCP-BP-PXZ) resulted in aggregation-induced delayed electrochemiluminescence by exploiting the thermally activated delayed-fluorescence of PXZ [27].

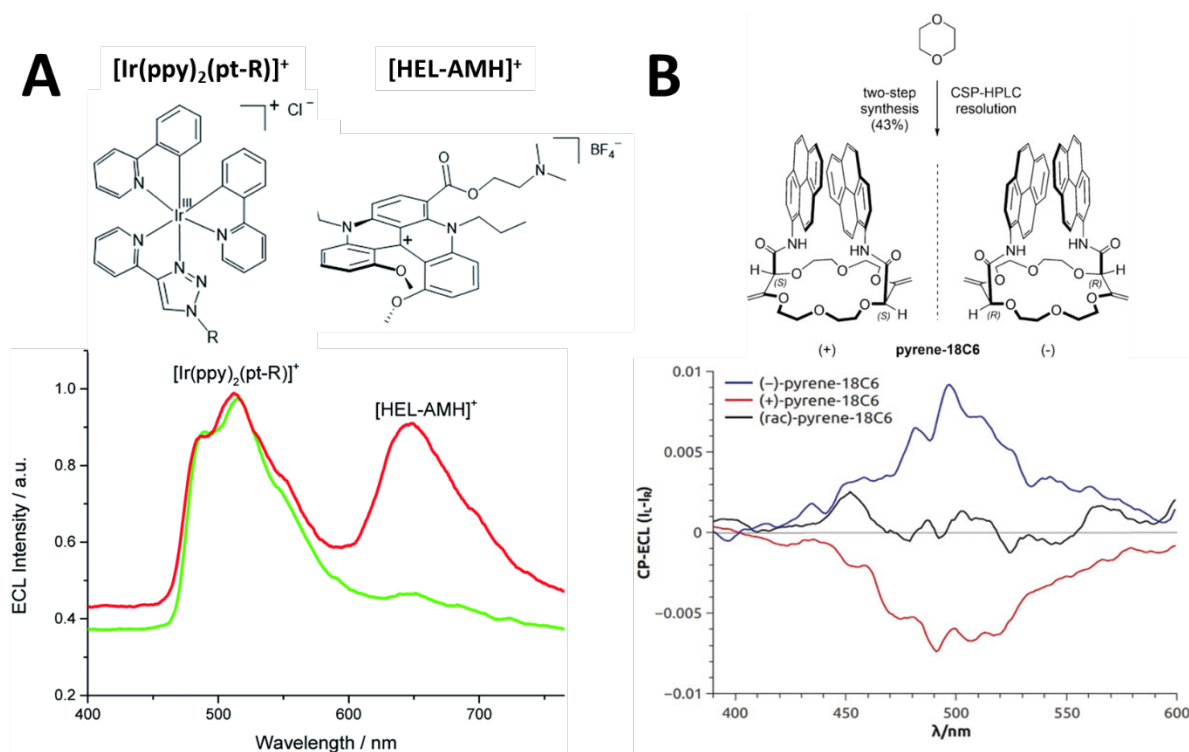
By careful design of the molecular structure, Yang et al. investigated the ECL from the N-annulated PDI dimer (tPDI2N-hex), a graphene quantum dot analogue. The dimer structure halts further dimerization, thus improving the ECL efficiency, while a simple electronic structure leads to pure luminescence without surface-state emission. Moreover, the twisted structure, although aromatic, prevents strong π - π stacking which alleviates the aggregation-caused quenching [44]. Structure tunability gives significant advantages in the development of readily accessible ECL luminophores, as in pyrido[1,2- α]pyrimidine derivatives, where the presence of the aromatic chain rings provides a high possibility for π interaction, which is expected to stabilize the electrogenerated radicals required for the generation of the excited state, and therefore affords high ECL activity [45].

Sojic's group demonstrated that organic molecules can be used A) to provide multicolour electrochemiluminescence by competitive electron-transfer processes or B) for chiral detection and discrimination (Figure 2). In the first example, a chiral red-emitting cationic diaza[4]helicene connected to a dimethylamino moiety by a short linker integrates bifunctional ECL features (i.e., luminophore and coreactant) and each function may be operated either separately or simultaneously. Multicolour ECL emission, from red to blue with tuneable intensity, is readily obtained in aqueous media through competitive electron-transfer processes between the helicene and an iridium dye [46]. In the second example, a chiral bispyrene organic constrained polyether macrocycle shows a circularly-polarized ECL (CP-ECL) which displays an ECL dissymmetry factor of about $|8 \times 10^{-3}|$, potentially useful to develop selective CP-ECL reporters for (bio)analytes [47].

Figure 2

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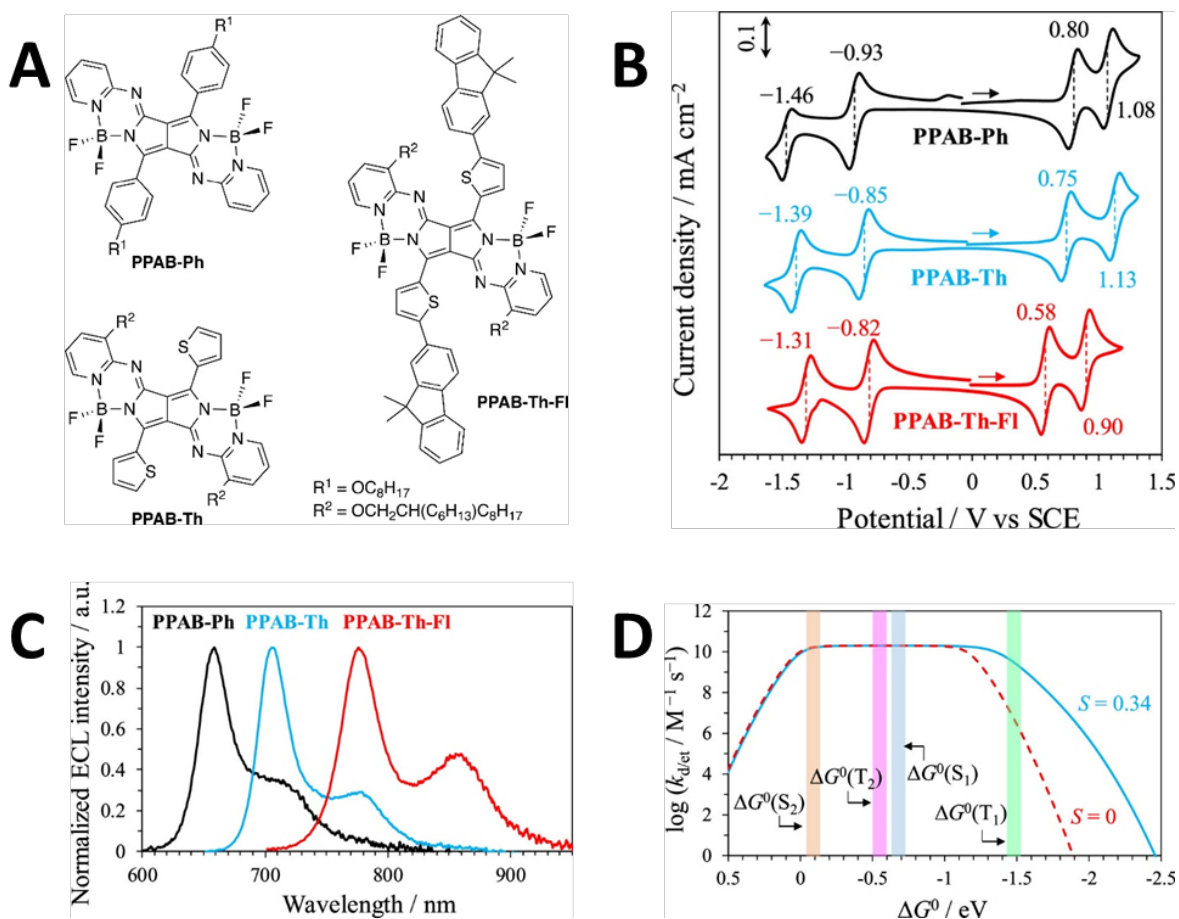
(A) Top: molecular structures of [Ir(ppy)₂(pt-R)]⁺ and the dual helicene [HEL-AMH]⁺; bottom: ECL spectra recorded in a PBS solution containing 10⁻⁴ M [HEL-AMH]⁺ and 10⁻³ M [Ir(ppy)₂(pt-R)]⁺ when applying either 1.1 V (green curve) or 1.3 V (red curve) (adapted from Voci et al [Error. Il segnalibro non è definito.46] with permission from the Royal Society of Chemistry). (B) Top: molecular structure of pyrene-18C6; bottom: CP-ECL of pyrene-18C6, both enantiomers and racemic mixture, measured in acetonitrile (adapted from Zinna et al [Error. Il segnalibro non è definito.47] with permission from the John Wiley and Sons).

Besides applications as merely ECL emitters, organic molecules offer the opportunity to get insight into the excited state formation and ECL efficiency. Ishimatsu et al provided an experimental-theoretical investigation of three pyrrolopyrrole aza-BODIPYs (PPABs) with ECL wavelength tuning in the near-infrared region (Figure 3). The red-shift was achieved through substituents on the pyrrolopyrrole aza-BODIPYs, where the wavelength emission increases with the series phenyl (Ph) > thiophene (Th) > thiophene-fluorene (Th-FI). Kinetic analysis based on Marcus' theory indicates the direct formation of higher excited states as S₂ and T₂ through electron transfer reaction with the coreactant tri-*n*-propylamine (TPrA) despite the smaller ΔG⁰ compared to S₁ and T₁. In particular, the rate constant of the electron transfer (*k*_{d/et}) to form the S₂ and T₂ reaches the diffusion-limited region (Figure 3D). This highlights the importance to consider the direct formation of higher excited states such as S₂ and T₂ because the energy levels of NIR fluorescent molecules are relatively low. Noteworthy, this has implications on the overall ECL efficiency which can be modulated by changing ΔG⁰ with molecules having different redox potentials [48].

Figure 3

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(A) Molecular structures of PPABs. (B) CVs of 0.5 mM PPABs in DCM at 100 mV s⁻¹; arrows indicate scan direction. (C) ECL spectra of 10 μM PPABs in DCM in the presence of 20 mM TPrA. (D) The rate constant of the electron transfer ($k_{d/et}$) against the Gibbs energy difference (ΔG^0) for PPAB-Th-Fl. The vertical bands indicate the energy gap between $\Delta E_{PPAB1/TPA^*} = (E_{PPAB(Ox1)} - E(TPrA^*))$, where $E(TPrA^*) = -1.7$ V vs SCE, and $E(S_n)$ and $E(T_n)$ of PPAB-Th-Fl. The mixing energy of the initial and final states (H_{if}) is 0.016 eV (adapted from Ishimatsu et al [48] with permission from the American Chemical Society).

ECL TADF

Studies of ECL dyes exhibiting TADF properties have been increasing in the past few years. This interest arises from the theoretical increased ECL efficiency observed in these particular systems due to the exceed of the limitation of spin statistics. Indeed, the annihilation process can give a maximum efficiency equal to 25% of the photoluminescence quantum yield, corresponding to the limit in radiative exciton generation yield. The small energy gap between singlet (S_1) and triplet (T_1) excited states (i.e., ΔE_{ST}) favors the rISC process at room temperature, thus the up-conversion of triplet excitons in singlet excitons, resulting in a hypothetical 100% internal conversion.

Ishimatsu et al. [34] showed that the limit of 25% of efficiency can be overcome using TADF. However, the ECL measurements of TADF systems are affected by the polarity of the solvent and polymerization at the electrode surface, which limits the observation to a single compound over the four reported in the article.

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Huang et al. [49] transferred the concept into the field of polymers, thus studying the heterogeneous ECL (Figure 4). The investigated TADF-polymer showed annihilation ECL in the cathodic region, while it is absent in the anodic region, indicating the higher stability of the radical cations versus radical anions. The authors reported also on the investigation of the co-reactant method in both oxidative-reduction and reductive-oxidation by means of different coreactants. Due to the different stability of radical ions, the oxidative-reduction process with TPrA resulted to be more efficient. The ECL efficiency recorded was below the expected values, which was attributed to the presence of oxygen adsorbed into the polymer during the deposition process onto the electrode surface. This means that the fabrication of devices for heterogeneous TADF-ECL requires particular attention to avoid the adsorption of molecular oxygen onto polymeric structures that can reduce remarkably the efficiency of the up-conversion phenomenon.

The same group reported an interesting approach to reduce the impact of oxygen in TADF systems, thus allowing the study of TADF-ECL in an aqueous environment[28]. By following a similar strategy already applied for Ir complexes [50], the TADF dye has been encapsulated in nanoparticles shielded by an amphiphilic polymer.

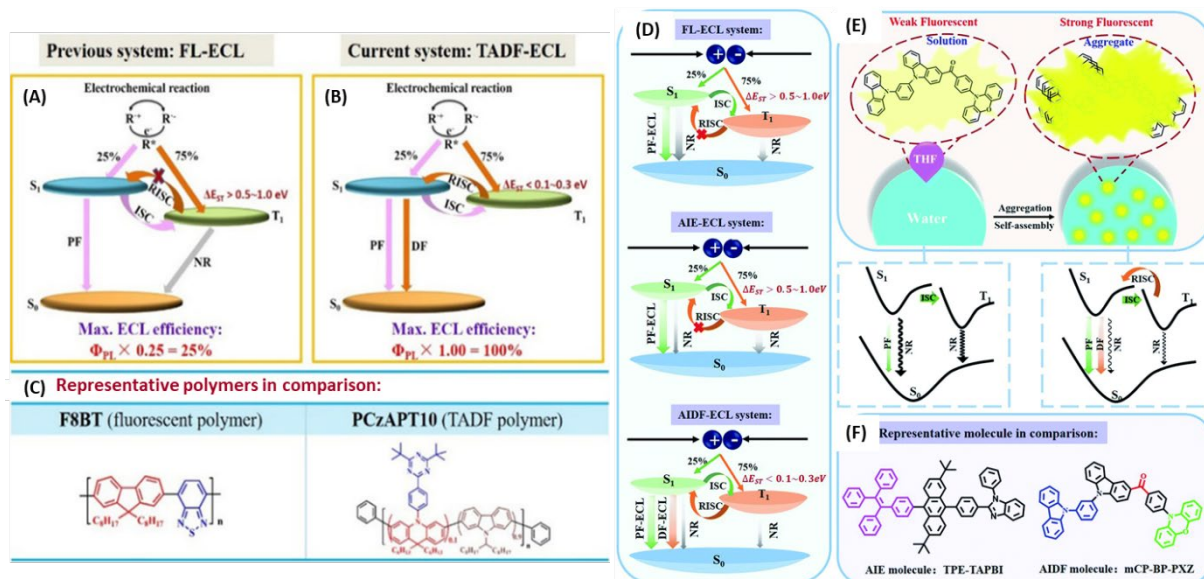
By modulating the nature of the dye, it is possible to combine the feature of the delayed fluorescence (DF) with the aggregation-induced emission (AIE). This particular system (called AIDF) has been also investigated for ECL in aqueous solutions [Errone. Il segnalibro non è definito.27] (Figure 4). The resulting experimental conditions are very similar to the above-mentioned (nanoparticles) due to the precipitation method employed to induce the aggregation of aromatic dyes in water. The comparison between ECL properties of pure AIE dye with the AIDF system indicates the importance of the up-conversion phenomenon for the enhancement of the ECL efficiency also in this configuration.

Kumar et al developed a TADF compound based on the sky-blue emitter 4,5-dicarbazolyphthalonitrile (2CzPN) with the addition of a strong electron-withdrawing group such as phosphine-chalcogenide onto the carbazole donor that stabilized the HOMO level relative to the pristine compound and promoted a blue-shift in the emission by increasing the HOMO-LUMO gap. Selected 2CzPN derivatives showed an unprecedented delayed onset of the ECL, primarily emitting *via* organic long-persistent luminescence [51] and that the delay in the onset times correlated with the ΔE_{ST} of the emitters [52].

Figure 4

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Schematic illustrations of two types of ECL mechanisms: (A) fluorescent-ECL and (B) thermally activated delayed fluorescent (TADF)-ECL, and (C) respective chemical structures (adapted from Huang et al [49] with permission from the John Wiley and Sons). (D) Schematic illustration of the fluorescent-type ECL (FL-ECL), aggregation-induced emission-type ECL (AIE-ECL) and aggregation-induced delayed fluorescence (AIDF)-type ECL (AIDF-ECL) and their mechanisms, in which S_1 , T_1 , S_0 , PF-ECL, DF-ECL, IS, RISC, and NR respectively represent the lowest singlet state, the lowest triplet state, the ground singlet state, prompt fluorescent ECL, delayed fluorescent ECL, intersystem crossing, reverse intersystem crossing, and non-radiative deactivation; (E) preparation of the AIDF aggregated luminogens by self-assembly in a mixed solvent. Inside the dashed box are the schematic diagrams of photophysical transitions in the molecular state in a THF solution or the aggregated solid state in a THF/H₂O mixed solvent; (F) chemical structures of AIE (left) and AIDF (right) molecules (adapted from Zhang et al [Error. Il segnalibro non è definito.27] with permission from the Royal Society of Chemistry).

Conclusion

Organic emitters have been shown to possess a wide range of fascinating properties that can be exploited in ECL. From aggregation-induced emission and thermally-activated delayed fluorescence to polymeric nanoparticles and surface functionalization for a renovated interest in organic molecules: here, we summarised these new concepts applied in ECL organic emitters.

Conflict of interest

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

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References

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
- of outstanding interest

1. Richter MM: **Electrochemiluminescence (ECL)**. *Chem Rev* 2004, **104**:3003-3036.
2. Miao W: **Electrogenerated Chemiluminescence and Its Biorelated Applications**. *Chem Rev* 2008, **108**:2506-2553.
3. Zanut A, Fiorani A, Canola S, Saito T, Ziebart N, Rapino S, Rebecani S, Barbon A, Irie T, Josel H-P, Negri F, Marcaccio M, Windfuhr M, Imai K, Valenti G, Paolucci F: **Insights into the mechanism of coreactant electrochemiluminescence facilitating enhanced bioanalytical performance**. *Nat Commun* 2020, **11**:2668.
4. Zanut A, Fiorani A, Rebecani S, Kesarkar S, Valenti G: **Electrochemiluminescence as emerging microscopy techniques**. *Anal Bioanal Chem* 2019, **411**:4375-4382.
5. Rebecani S, Zanut A, Santo CI, Valenti G, Paolucci F: **A Guide Inside Electrochemiluminescent Microscopy Mechanisms for Analytical Performance Improvement**. *Anal Chem* 2022, **94**:336-348.
6. Hiramoto K, Villani E, Iwama T, Komatsu K, Inagi S, Inoue KY, Nashimoto Y, Ino K, Shiku H: **Recent Advances in Electrochemiluminescence-Based Systems for Mammalian Cell Analysis**. *Micromachines* 2020, **11**:530.
7. Villani E, Inagi S: **Mapping the Distribution of Potential Gradient in Bipolar Electrochemical Systems through Luminol Electrochemiluminescence Imaging**. *Anal Chem* 2021, **93**:8152-8160.
8. Villani E, Shida N, Inagi S: **Electrogenerated chemiluminescence of luminol on wireless conducting polymer films**. *Electrochim Acta* 2021, **389**:138718.
9. Valenti G, Fiorani A, Li H, Sojic N, Paolucci F: **Essential Role of Electrode Materials in Electrochemiluminescence Applications**. *ChemElectroChem* 2016, **3**:1990-1997.
10. Fiorani A, Eßmann V, Santos CS, Schuhmann W: **Enhancing Electrogenerated Chemiluminescence on Platinum Electrodes through Surface Modification**. *ChemElectroChem* 2020, **7**:1256-1260.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

11. Sakanoue K, Fiorani A, Irkham, Einaga Y: **Effect of Boron-Doping Level and Surface Termination in Diamond on Electrogenerated Chemiluminescence.** *ACS Appl Electron Mater* 2021, **3**:4180-4188.
12. Yuan Y, Han S, Hu L, Parveen S, Xu G: **Coreactants of tris(2,2'-bipyridyl)ruthenium(II) Electrogenerated Chemiluminescence.** *Electrochim Acta* 2012, **82**:484-492.
13. Fiorani A, Valenti G, Irkham, Paolucci F, Einaga Y: **Quantification of electrogenerated chemiluminescence from tris(bipyridine)ruthenium(II) and hydroxyl ions.** *Phys Chem Chem Phys* 2020, **22**:15413-15417.
14. Fiorani A, Valenti G, Iurlo M, Marcaccio M, Paolucci F: **Electrogenerated chemiluminescence: A molecular electrochemistry point of view.** *Curr Opin Electrochem* 2018, **8**:31-38.
15. Haghghatbin MA, Laird SE, Hogan CF: **Electrochemiluminescence of cyclometalated iridium (III) complexes.** *Curr Opin Electrochem* 2018, **7**:216-223.
16. Nikolaou P, Valenti G, Paolucci F: **Nano-structured materials for the electrochemiluminescence signal enhancement.** *Electrochim Acta* 2021, **388**:138586.
17. Fiorani A, Merino JP, Zanut A, Criado A, Valenti G, Prato M, Paolucci F: **Advanced carbon nanomaterials for electrochemiluminescent biosensor applications.** *Curr Opin Electrochem* 2019, **16**:66-74.
18. Bertonecello P, Ugo P: **Recent Advances in Electrochemiluminescence with Quantum Dots and Arrays of Nanoelectrodes.** *ChemElectroChem* 2017, **4**:1663-1676.
19. Valenti G, Rampazzo E, Kesarkar S, Genovese D, Fiorani A, Zanut A, Palomba F, Marcaccio M, Paolucci F, Prodi L: **Electrogenerated chemiluminescence from metal complexes-based nanoparticles for highly sensitive sensors applications.** *Coord Chem Rev* 2018, **367**:65-81.
20. Imai K, Valenti G, Villani E, Rapino S, Rampazzo E, Marcaccio M, Prodi L, Paolucci F: **Numerical Simulation of Doped Silica Nanoparticle Electrochemiluminescence.** *J Phys Chem C* 2015, **119**:26111-26118.
21. Kesarkar S, Rampazzo R, Zanut A, Palomba F, Marcaccio M, Valenti G, Prodi L, Paolucci F: **Dye-doped nanomaterials: Strategic design and role in electrochemiluminescence.** *Curr Opin Electrochem* 2018, **7**:130-137.
22. Rizzo F, Polo F, Bottaro G, Fantacci S, Antonello S, Armelao L, Quici S, Maran F: **From Blue to Green: Fine-Tuning of Photoluminescence and Electrochemiluminescence in Bifunctional Organic Dyes.** *J Am Chem Soc* 2017, **139**:2060-2069.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

23. Kudruk S, Villani E, Polo F, Lamping S, Körsgen M, Arlinghaus HF, Paolucci F, Ravoo BJ, Valenti G, Rizzo F: **Solid state electrochemiluminescence from homogeneous and patterned monolayers of bifunctional spirobifluorene.** *Chem Commun* 2018, **54**:4999-5002.
- First study on heterogenous ECL generated by homogeneous and patterned monolayers of PAH covalently bound onto electrode surface.
24. Qi H, Chen Y-H, Cheng C-H, Bard AJ: **Electrochemistry and Electrogenerated Chemiluminescence of Three Phenanthrene Derivatives, Enhancement of Radical Stability, and Electrogenerated Chemiluminescence Efficiency by Substituent Groups.** *J Am Chem Soc* 2013, **135**:9041-9049.
25. Lee YO, Pradhan T, Choi K, Choi DH, Lee JH, Kim JS: **Electrogenerated chemiluminescence of N,N-dimethylamino functionalized tetrakis(phenylethynyl)pyrenes.** *Tetrahedron* 2013, **69**:5908-5912.
26. Wei X, Zhu M-J, Yan H, Lu C, Xu J-J: **Recent Advances in Aggregation-Induced Electrochemiluminescence.** *Chem Eur J* 2019, **25**:12671-12683.
27. Zhang B, Kong Y, Liu H, Chen B, Zhao B, Luo Y, Chen L, Zhang Y, Han D, Zhao Z, Zhong B, Niu L: **Aggregation-induced delayed fluorescence luminogens: the innovation of purely organic emitters for aqueous electrochemiluminescence.** *Chem Sci* 2021, **12**:13283-13291.
- ECL based on aggregation-induced delayed fluorescence (AIDF) luminogens, compared with the previous organic aggregation-induced emission (AIE) luminogens, integrate the superiorities of both AIE and the utilization of dark triplets via thermal-activated spin up-conversion properties which are capable of close-to-unity exciton utilization for ECL.
28. Zeng Z, Huang P, Kong Y, Tong L, Zhang B, Luo Y, Chen L, Zhang Y, Han D, Niu L: **Nanoencapsulation strategy: enabling electrochemiluminescence of thermally activated delayed fluorescence (TADF) emitters in aqueous media.** *Chem Commun* 2021, **57**:5262-5265.
29. Polo F, Rizzo F, Veiga-Gutierrez M, De Cola L, Quici S: **Efficient Greenish Blue Electrochemiluminescence from Fluorene and Spirobifluorene Derivatives.** *J Am Chem Soc* 2012, **134**:15402-15409.
30. Rashidnadimi S, Hung TH, Wong K-T, Bard AJ: **Electrochemistry and Electrogenerated Chemiluminescence of 3,6-Di(spirobifluorene)-N-phenylcarbazole.** *J Am Chem Soc* 2008, **130**:634-639.

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When citing, please refer to the published version.

31. Voci S, Verlhac JB, Polo F, Clermont G, Daniel J, Castet F, Blanchard-Desce M, Sojic N: **Photophysics, Electrochemistry and Efficient Electrochemiluminescence of Trigonal Truxene-Core Dyes.** *Chem Eur J* 2020, **26**:8407-8416.
32. Rizzo F, Cucinotta F: **Recent Developments in AIEgens for Non-doped and TADF OLEDs.** *Isr J Chem* 2018, **58**:874-888.
33. Uoyama H, Goushi K, Shizu K, Nomura H, Adachi C: **Highly efficient organic light-emitting diodes from delayed fluorescence.** *Nature* 2012, **492**:234-238.
34. Ishimatsu R, Matsunami S, Kasahara T, Mizuno J, Edura T, Adachi C, Nakano K, Imato T: **Electrogenerated Chemiluminescence of Donor–Acceptor Molecules with Thermally Activated Delayed Fluorescence.** *Angew Chem Int Ed* 2014, **53**:6993-6996.
- TADF molecules exhibit green to red ECL. Remarkably, spin up-conversion through thermal activation shows that the ECL from TADF molecules could reach an efficiency which is comparable to its photo-luminescence quantum yield.
35. Kapturkiewicz A, Herbich J, Nowacki J: **Highly efficient electrochemical generation of fluorescent intramolecular charge-transfer states.** *Chem Phys Lett* 1997, **275**:355-362.
- This is the first study on ECL D-A systems with TADF features.
36. Luo R, Lv H, Liao Q, Wang N, Yang J, Li Y, Xi K, Wu X, Ju H, Lei J: **Intrareticular charge transfer regulated electrochemiluminescence of donor–acceptor covalent organic frameworks.** *Nat Commun* 2021, **12**:6808.
37. Luo Q-X, Cui W-R, Li Y-J, Cai Y-J, Mao X-L, Liang R-P, Qiu JD: **Construction of sp² Carbon-Conjugated Covalent Organic Frameworks for Framework-Induced Electrochemiluminescence.** *ACS Appl Electron Mater* 2021, **3**:4490-4497.
38. Yang L, Koo D, Wu J, Wong JM, Day T, Zhang R, Kolongoda H, Liu K, Wang J, Ding Z, Pagenkopf BL: **Benzosiloles with Crystallization-Induced Emission Enhancement of Electrochemiluminescence: Synthesis, Electrochemistry, and Crystallography.** *Chem Eur J* 2020, **26**:11715-11721.
39. Han Z, Yang Z, Sun H, Xu Y, Ma X, Shan D, Chen J, Huo S, Zhang Z, Du P, Lu X: **Electrochemiluminescence Platforms Based on Small Water-Insoluble Organic Molecules for Ultrasensitive Aqueous-Phase Detection.** *Angew Chem Int Ed* 2019, **58**:5915-5919.

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40. Ji S-Y, Zhao W, Gao H, Pan J-B, Xu C-H, Quan Y-W, Xu J-J, Chen HY: **Highly Efficient Aggregation-Induced Electrochemiluminescence of Polyfluorene Derivative Nanoparticles Containing Tetraphenylethylene.** *iScience* 2020, **23**:100774.
41. Cui L, Zhou J, Li C-C, Deng S, Gao W, Zhang X, Luo X, Wang X, Zhang CY: **Bipolar Aggregation-Induced Electrochemiluminescence of Thiophene-Fused Conjugated Microporous Polymers.** *ACS Appl Mater Interfaces* 2021, **13**:28782-28789.
42. Han Z, Yang Z, Sun H, Xu Y, Ma X, Shan D, Chen J, Huo S, Zhang Z, Du P, Lu X: **Electrochemiluminescence Platforms Based on Small Water-Insoluble Organic Molecules for Ultrasensitive Aqueous-Phase Detection.** *Angew Chem Int Ed* 2019, **58**:5915-5919.
43. Wei X, Zhu M-J, Cheng Z, Lee M, Yan H, Lu C, Xu JJ: **Aggregation-Induced Electrochemiluminescence of Carboranyl Carbazoles in Aqueous Media.** *Angew Chem Int Ed* 2019, **58**:3162-3166.
44. Yang L, Hendsbee AD, Xue Q, He S, De-Jager CR, Xie G, Welch GC, Ding Z: **Atomic Precision Graphene Model Compound for Bright Electrochemiluminescence and Organic Light-Emitting Diodes.** *ACS Appl Mater Interfaces* 2020, **12**:51736-51743.
45. Zhang R, Cheng J, Yang L, Wong JM, Adsetts JR, Wang R, Liu J, Ding Z, Wang H-B: **Optimizing the Electrochemiluminescence of Readily Accessible Pyrido[1,2- α]pyrimidines through “Green” Substituent Regulation.** *ChemElectroChem* 2021, **8**:547-557.
46. Voci S, Duwald R, Grass S, Hayne DJ, Bouffier L, Francis PS, Lacour J, Sojic N: **Self-enhanced multicolour electrochemiluminescence by competitive electron-transfer processes.** *Chem Sci* 2020, **11**:4508-4515.
- Multicolor ECL emission from red to blue is obtained in aqueous media through competitive electron-transfer processes between a self-enhanced organic ECL dye (i.e., it contains both luminophore and coreactant functions) and a ruthenium or iridium dye by potential selection.
47. Zinna F, Voci S, Arrico L, Brun E, Homberg A, Bouffier L, Funaioli T, Lacour J, Sojic N, Di Bari L: **Circularly-Polarized Electrochemiluminescence from a Chiral Bispyrene Organic Macrocycle.** *Angew Chem Int Ed* 2019, **58**:6952-6956.

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●● This is the first observation of circular polarization of ECL from a purely organic derivative. The compound displays an ECL dissymmetry factor which is in good agreement with the corresponding photoluminescence value. This provides an extra dimension to the ECL phenomenon and opens the way to chiral detection and discrimination.

48. Ishimatsu R, Shintaku H, Kage Y, Kamioka M, Shimizu S, Nakano K, Furuta H, Imato T: **Efficient Electrogenerated Chemiluminescence of Pyrrolopyrrole Aza-BODIPYs in the Near-Infrared Region with Tripropylamine: Involving Formation of S₂ and T₂ States.** *J Am Chem Soc* 2019, **141**:11791-11795.

●● Kinetic analysis based on Marcus theory helps to rationalize the ECL efficiency based on the formation of higher excited states such as S₂ and T₂ for NIR fluorescent molecules.

49. Huang P, Zhang B, Hu Q, Zhao B, Zhu Y, Zhang Y, Kong Y, Zeng Z, Bao Y, Wang W, Cheng Y, Niu L: **Polymer Electrochemiluminescence Featuring Thermally Activated Delayed Fluorescence.** *ChemPhysChem* 2021, **22**:726-732.

50. Zanarini S, Rampazzo E, Bonacchi S, Juris R, Marcaccio M, Montalti M, Paolucci F, Prodi L: **Iridium Doped Silica-PEG Nanoparticles: Enabling Electrochemiluminescence of Neutral Complexes in Aqueous Media.** *J Am Chem Soc* 2009, **131**:14208-14209.

51. Kabe R, Adachi C: **Organic long persistent luminescence.** *Nature* 2017, **550**:384-387.

52. Kumar S, Tourneur P, Adsetts JR, Wong MY, Rajamalli P, Chen D, Lazzaroni R, Viville P, Cordes DB, Slawin AMZ, Olivier Y, Cornil J, Ding Z, Zysman-Colman E: **Photoluminescence and Electrochemiluminescence of Thermally Activated Delayed Fluorescence (TADF) Emitters Containing Diphenylphosphine Chalcogenide-Substituted Carbazole Donors.** DOI:10.26434/chemrxiv-2021-2270g, 2022.

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