

# 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,  $\pi$ - $\pi$  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 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.

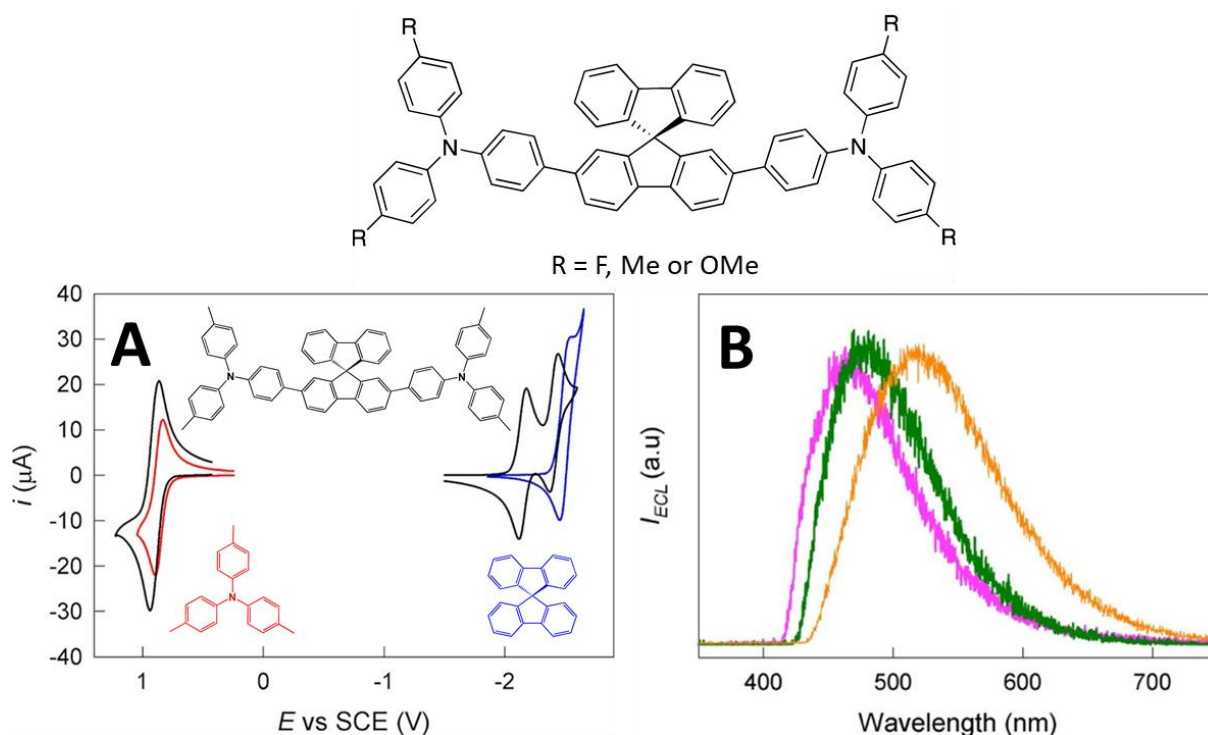
The synthesis of these compounds often requires a precise molecular design in order to obtain the desired properties such as the fine-tuning of the ECL emission [22] (Figure 1) or the binding of the dye to the electrode surface [23]. In particular, red-shifted ECL curves have been obtained by enhancing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

A general approach involves the functionalization of a  $\pi$ -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  $\pi$ -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-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<sup>-1</sup>. (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  $\pi$ - $\pi$  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].

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].

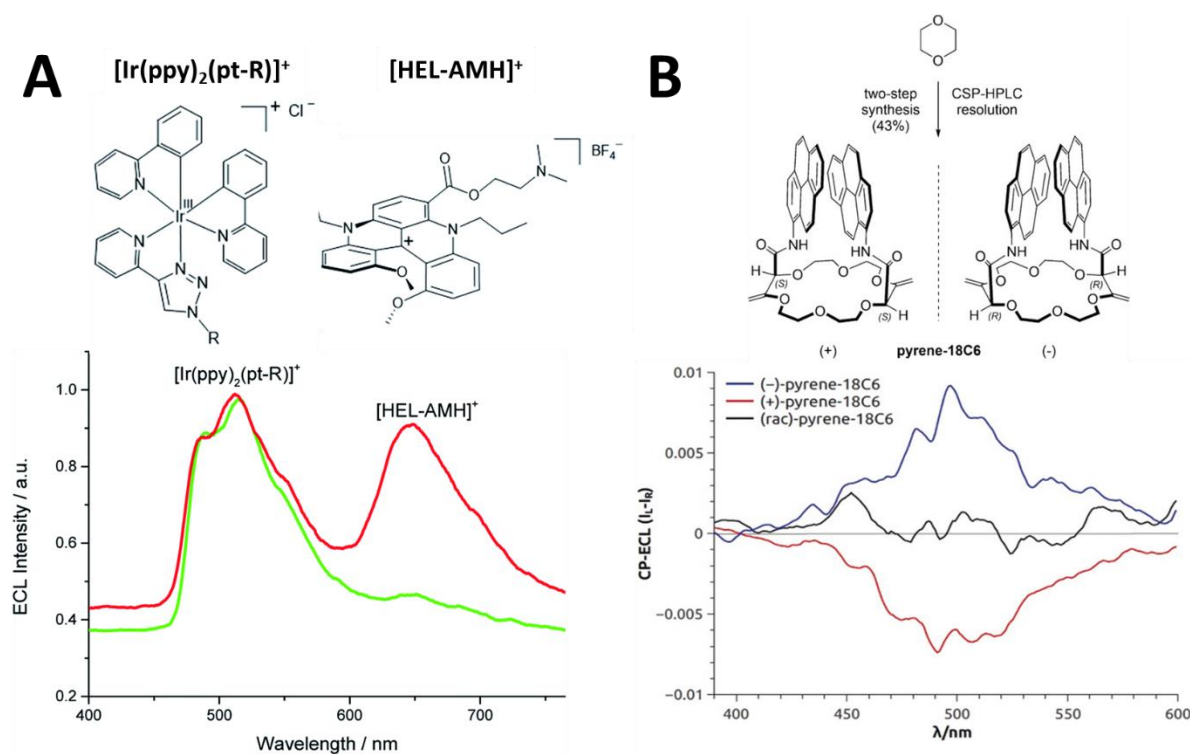
The transposition of Aggregation-Induced Emission (AIE) in the ECL field opened a new range of applications for organic dyes which had been precluded previously. Tetraphenylethylene units [40], thiophene [41], 1,1-disubstituted 2,3,4,5-tetraphenylsiloles [42], and carboranyl carbazoles [43] are examples 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  $\pi$ - $\pi$  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- $\alpha$ ]pyrimidine derivatives, where the presence of the aromatic chain rings provides a high possibility for  $\pi$  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**

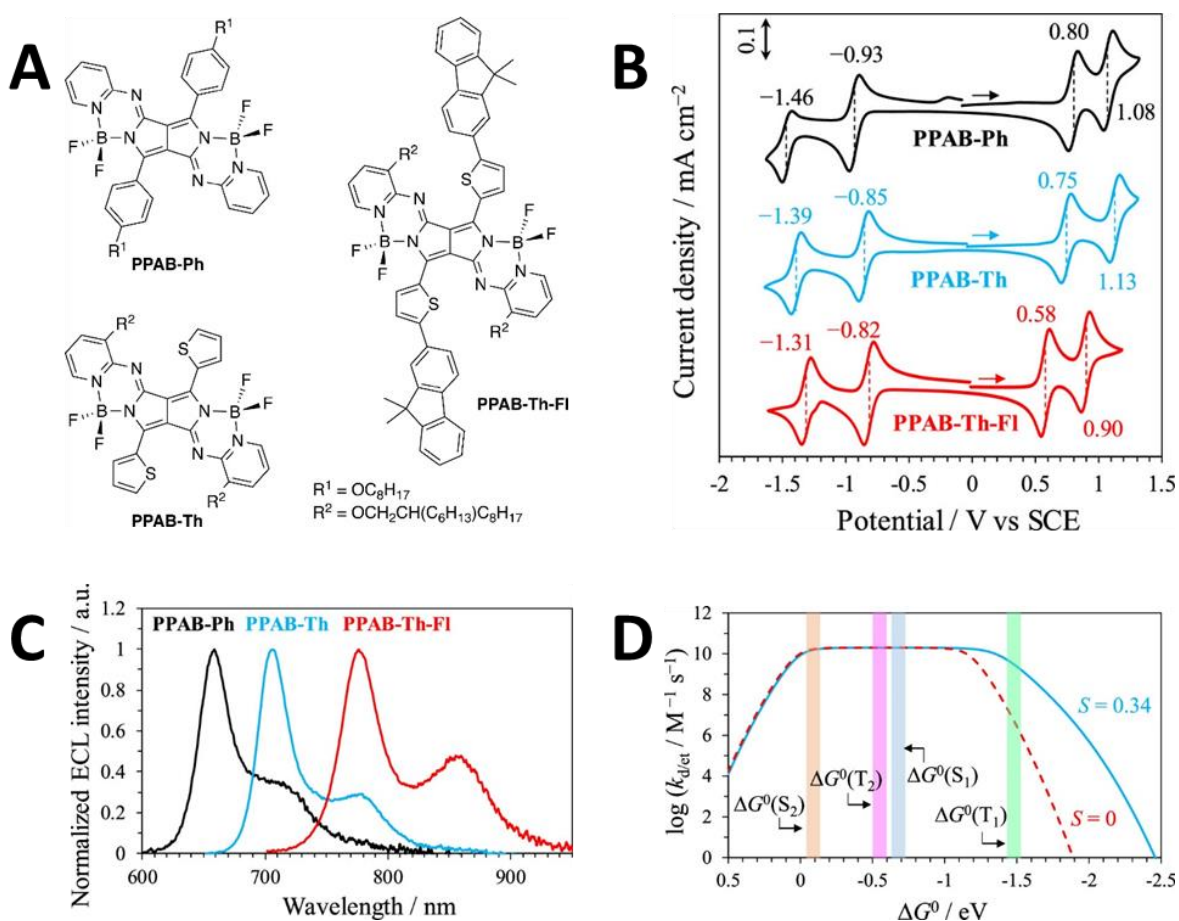


(A) Top: molecular structures of [Ir(ppy)<sub>2</sub>(pt-R)]<sup>+</sup> and the dual helicene [HELAMH]<sup>+</sup>; bottom: ECL spectra recorded in a PBS solution containing 10<sup>-4</sup> M [HEL-AMH]<sup>+</sup> and 10<sup>-3</sup> M [Ir(ppy)<sub>2</sub>(pt-R)]<sup>+</sup> when applying either 1.1 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  $S_2$  and  $T_2$  through electron transfer reaction with the coreactant tri-*n*-propylamine (TPrA) despite the smaller  $\Delta G^0$  compared to  $S_1$  and  $T_1$ . In particular, the rate constant of the electron transfer ( $k_{d/et}$ ) to form the  $S_2$  and  $T_2$  reaches the diffusion-limited region (Figure 3D). This highlights the importance to consider the direct formation of higher excited states such as  $S_2$  and  $T_2$  because the energy levels of NIR fluorescent molecules are relatively low. Noteworthy, this has implication on the overall ECL efficiency which can be modulated by changing  $\Delta G^0$  with molecules having different redox potentials [48].

Figure 3



(A) Molecular structures of PPABs. (B) CVs of 0.5 mM PPABs in DCM at 100 mV s<sup>-1</sup>; 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 ( $\Delta G^0$ ) for PPAB-Th-FI. The vertical bands indicate the energy gap between  $\Delta E_{PPAB/TPrA^*} = (E_{PPAB(Ox1)} - E(TPrA^*))$ , where  $E(TPrA^*) = -1.7$  V vs SCE, and  $E(S_n)$  and  $E(T_n)$  of PPAB-Th-FI. 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.,  $\Delta E_{ST}$ ) 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.

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.

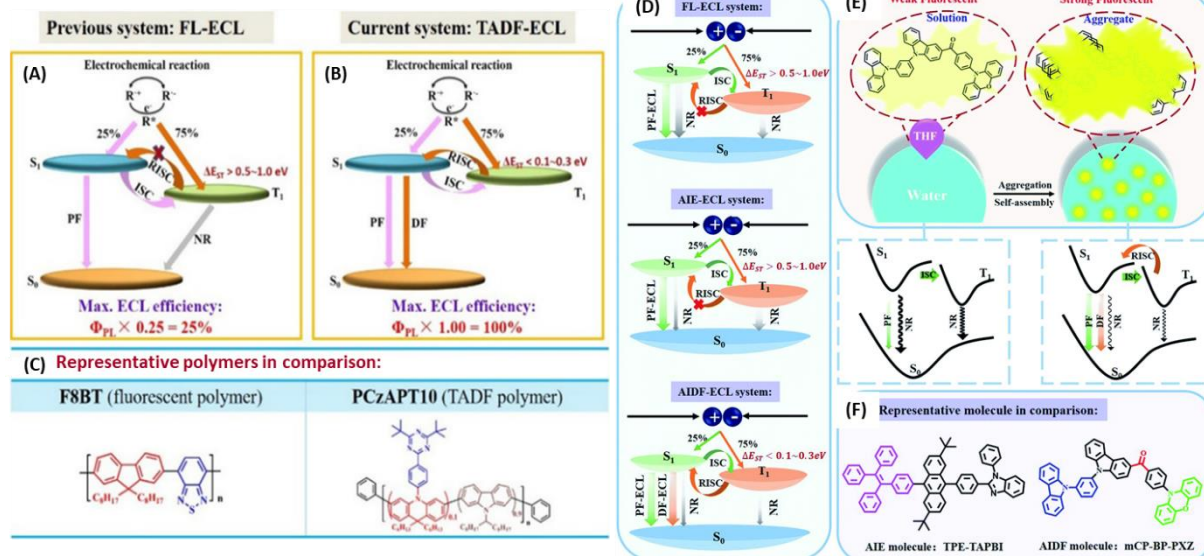
The same group reported an interesting approach to reduce the impact of oxygen in TADF systems, thus allowing the study of TADF-ECL in an aqueous environment[28]. By following a similar strategy already applied for Ir **complexes** [50], the TADF dye has been encapsulated in nanoparticles shielded by 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 [**Errore. 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  $\Delta E_{ST}$  of the emitters [52].

**Figure 4**





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/H<sub>2</sub>O 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.

## Acknowledgments

This work is supported by the Italian Ministero dell'Istruzione, Università e Ricerca (PRIN-2017FJCPEX and PRIN-2017PBXP4), University of Bologna for the "Proof of Concept d'Ateneo" (PoC UniBo) and Fondazione CarisBo (project #18668). F.R. thanks the Deutsche Forschungsgemeinschaft (grant n. RI 2635/6-1) and Westfälische Wilhelms-Universität Münster for financial support.

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