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► **To cite this version:**

Fabien Miomandre. How molecular electrochemistry may shine light by designing electrofluorochromic compounds. *Current Opinion in Electrochemistry*, 2020, 24, pp.56 - 62. 10.1016/j.coelec.2020.07.003 . hal-03491202

HAL Id: hal-03491202

<https://hal.science/hal-03491202>

Submitted on 22 Aug 2022

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How molecular electrochemistry may shine light by designing electrofluorochromic compounds

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Abstract

Luminescence and electrochemistry have been intimately associated for a long time in the framework of electrochemiluminescence where the electrochemical signal triggers light emission through a redox reaction. More recently another aspect of this coupling has been developed in electrofluorochromism, where electrochemistry is used to monitor photoluminescence processes. This review aims to highlight some molecular structures allowing emission properties to be tuned electrochemically through either redox-active luminophores or dyads in which a redox moiety can (de)activate the luminescence of a nearby unit. The working principle and main applications are also briefly discussed.

Introduction

Redox-active molecules with luminescence properties have been the topic of a growing interest during the last decade. The first straightforward reason is the possibility to cumulate two different properties on the same molecular scaffold. The compound of interest can be detected either by an electrode and at the same time be used for imaging purpose. But in some cases, when different emission states are associated to the various redox states of the molecule, a new property appears, called electrofluorochromism, due to the similarity with electrochromism, and displays can be designed according to this concept. When the molecule is non emissive in its starting state and emissive when oxidized or reduced, it is said fluorogenic and can thus be used as a reporter of the presence of other molecules of interest. Luminescence is a technique of choice for imaging, and especially at very small scale (micronic or even submicronic) due to the development of fluorescence microscopy. When coupled to electrochemistry, it is possible to detect redox events through an optical output or to switch this output by changing the redox state electrochemically. These phenomena have been reviewed several times since 2013[1-4] and recent extensions

towards single molecule spectroelectrochemistry[5] or single molecule electrofluorochromism[6] are worth being highlighted.

From the molecular point of view, one can try to extract the main features conferring to a molecular compound redox and luminescence properties. Luminescence can be divided into fluorescence and phosphorescence depending on the spin multiplicity of the emitting state. Fluorescence organic molecules usually possess a rigid aromatic or pi-conjugated backbone because molecular motions like rotation or vibration are well-known non-radiative desexcitation pathways. Fused aromatic rings, possibly incorporating heteroatoms (N, O, S) are often parts of the molecular structure of organic fluorophores. In some cases, the fluorophore may have redox properties as well, for example due to the presence of electron withdrawing or electron donating groups. This constitutes the first class of electrofluorochromic (EFC) compounds showing direct conversion. The second class comprises molecular systems made of a fluorophore electronically or energetically connected to a redox unit. A large variety of molecular structures can be imagined by combining luminescent and redox-active subunits in the forms of dyads or triads. Finally, polymers are also well suited for EFC especially because a variety of combination of redox active, luminescent and color tuning subunits can be assembled in the macromolecular backbone and therefore can be considered as a third class of EFC molecular systems.

In this review, we will give some striking examples of these different categories of redox-active luminescent molecules (see chart 1), as well as some frameworks for their utilization, in fundamental studies or in devices.

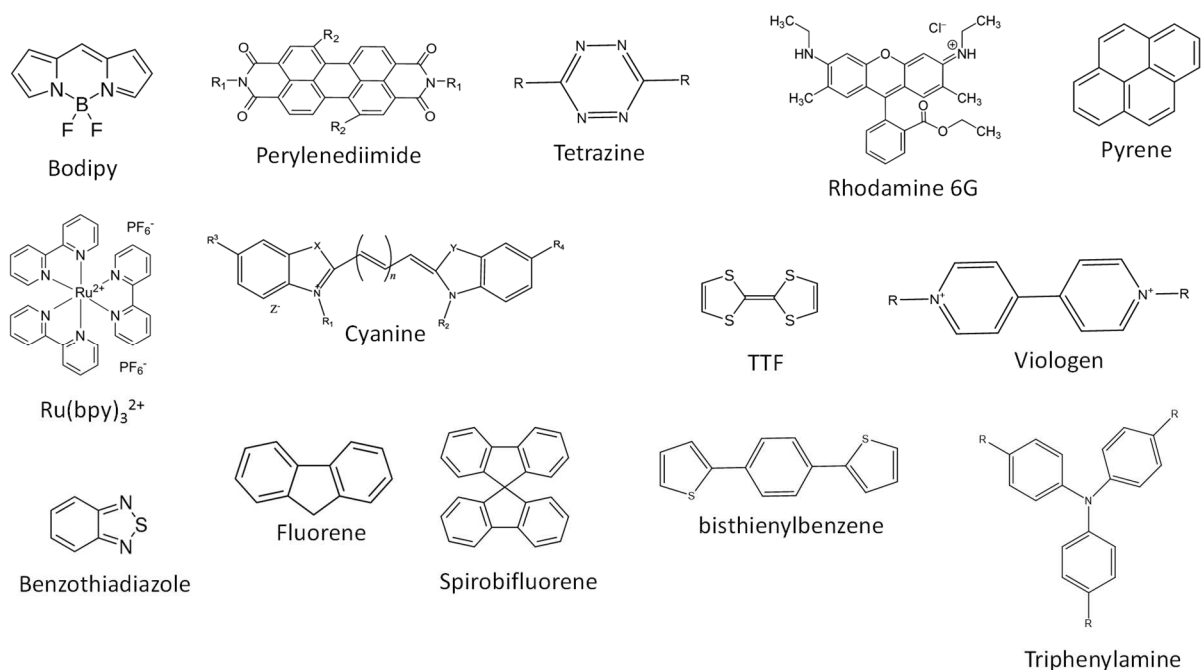


Chart 1: Main molecular backbones used as electrofluorochromic units

1. Direct conversion dyes

A direct conversion may be observed when the fluorophore is also redox-active. We can consider separately the case of organic dyes on one hand and of organometallic compounds on the other because the possibilities offered are a little bit different.

Organic dyes

Classical fluorescent dyes, like rhodamine 6G or rhodamine 101, both popular standards for quantum yield determination, have been considered very early[7] or more recently[8] as electrofluorochromic probes. Perylenediimide (PDI) stands also among the first compounds to have been investigated in this framework because it emits in the visible with high yield and can be reduced at moderate potential values[9]. (1,2,4,5)-Tetrazines are also good candidates although having a much lower absorption coefficient and were used to design the first electrofluorochromic window[10]. As PDI tetrazines can be cathodically converted into a non-emissive form.

On the other hand, boron dipyrromethene (BODIPY) derivatives are also highly emissive compounds[11] that can be reversibly oxidized into a non-emissive cation radical[12, 13]. Substituting carbon by nitrogen between the two pyrrolic units shifts the emission in the NIR

range and aza-BODIPYs are nice examples of NIR emissive EFC compounds[14], like some polymethine dyes called cyanines [15].

EFC molecules can also display electrochromic (EC) properties as reported recently for carbazole-dibenzofuran derivatives[16**]. In that case, the neutral compounds are usually colorless but emissive, while they become colored and non-emissive in their reduced form. This combination of properties allows to design dual mode displays working either in reflective or emissive mode.

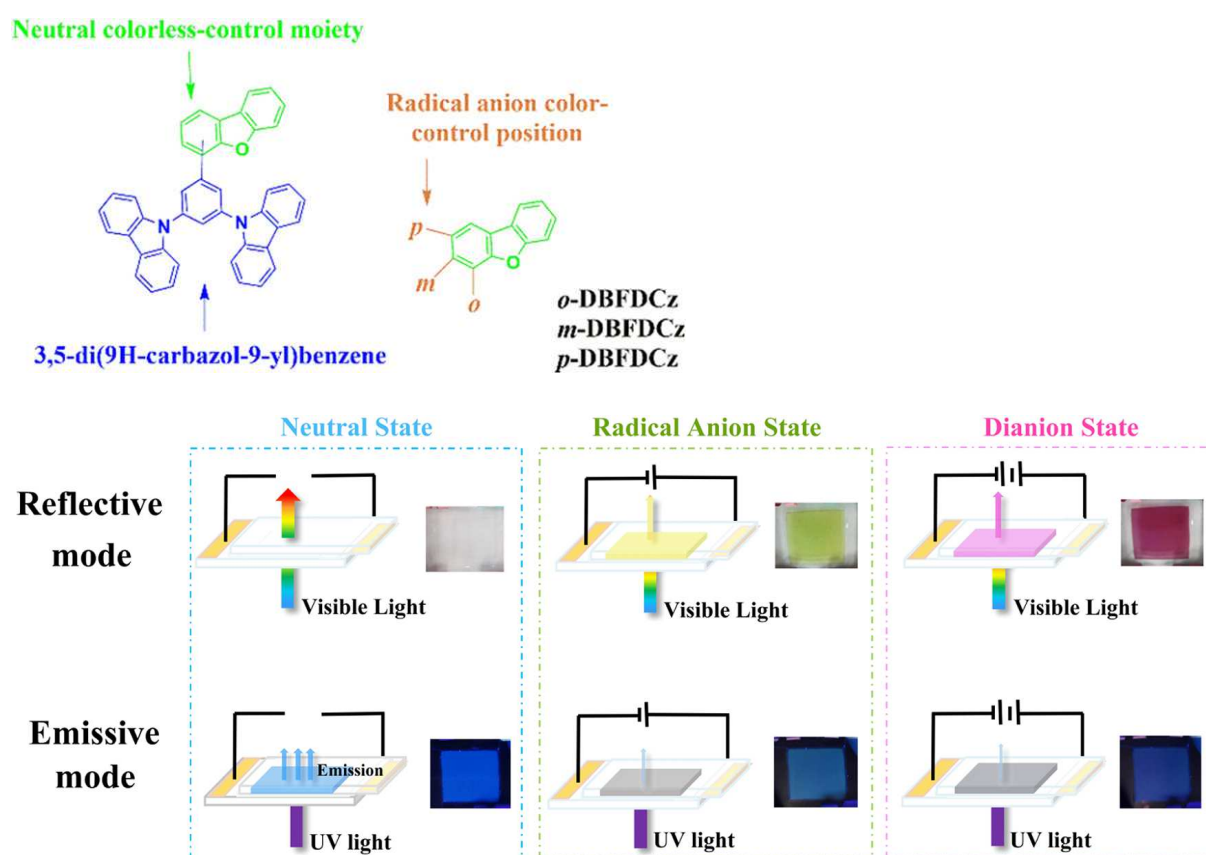


Figure 1: Illustration of EC (reflective mode) and EFC (emissive mode) properties of *m*-DBFDCz (adapted from ref. [16**]).

EFC compounds can possess additional interesting properties when smartly designed. Thus thienoviologens substituted by long alkyl chains have been shown to display liquid crystal properties in addition to electrofluorochromism[17].

Organometallics

Transition metal complexes fulfill also the requirements for electroluminochromism due to their long-live luminescence and the multiple metal or ligand centered redox states. The topic has been recently reviewed[18]. Ruthenium polypyridines have been extensively studied for electrochemiluminescence (ECL) and naturally for electrofluorochromism as well[19, 20]. More recently cyclometallated iridium complexes which have the advantage of seeing their emission wavelength tuned according to the nature of ligands were also investigated as EFC dyes[21].

One of the great advantages of organometallic complexes in the EFC framework is the possibility to modify the ligand composition to incorporate redox active units. One of the first example was proposed by Lehn et al. in 1993 with a ruthenium complex incorporating a quinone unit[22]. A similar example with a TTF redox unit can also be found in the more recent literature[23].

2. Dyads

Beyond the direct conversion of redox-active fluorophores, another important class of EFC compounds rely on molecules where a redox unit is covalently connected to a fluorophore. The main difference with the previous category is that these dyads are generally non-emissive due to photoinduced electron or energy transfer. Oxidation or reduction may cancel this transfer either by a direct change of the redox state for photoinduced electron transfer or indirectly by a shift in the absorption features in the case of energy transfer. Therefore, these systems behave as OFF-ON switches, instead of ON-OFF in the direct conversion cases.

One of the first examples reported of organic dyads of this kind associates tetrathiafulvalene (TTF) and pyrene as redox unit and fluorophore respectively[24]. Later on TTF and BODIPY were also associated in an EFC dyad[25]. Reversible redox units are privileged and thus it is not surprising to find besides the already mentioned TTF, ferrocene[26-32] or para substituted triphenylamine (TPA) [33] for oxidative systems and quinone[34,35] for reductive systems. Alternatively, ruthenium acetylide complexes can also play the role of the redox switch with a zinc porphyrin as the fluorophore[36,37].

A further step in the design of EFC dyads is to reach multi-state systems. For that, TTF is especially suited because of its two successive reversible oxidation steps leading to the cation radical and dication. Associated with BODIPY in a pi-extended backbone leads to an ON-OFF-ON switch since the cation radical compound is non-emissive while the neutral and dication forms are emissive at two different wavelengths in the NIR[38].

EFC dyads based on energy transfer quenching are of interest as well because they usually associate EC and EFC units. The basic concept is to quench the emission of a luminophore when the EC unit is one state and not in the other, simply because a spectral overlap occurs between EC absorption and EFC emission in only one redox state. According to this principle, Kobayashi designed EC-EFC dual displays that can work either as a pure EC device under ambient light or as an EFC device under UV [39]. The EC unit is made of a viologen switching between a transparent and an intense blue state upon reduction, while the luminophore is an europium complex emitting red light. One can deduce as a general principle that the EC and luminophore must have complementary absorption and emission colors in one state and the EC unit ideally not to absorb at all in the visible in the other state.

Other systems of interest are made by inserting between two similar redox active units a fluorescent linker. Most of the recent examples of EFC triads of this kind use diphenyl or triphenylamine redox centers and a luminescent bridge made of indolocarbazole[40**], fluorene[41*, 42] or pyrene[42*]. Upon oxidation, a mixed valence state is obtained, possibly stabilized by the presence of the conjugated linker and providing interesting optoelectronic properties to these systems.

Another valuable combination of properties is the one of EFC with photochromism. Adequate molecular compounds may undergo an emission switch either by changing the redox state electrochemically or by photoisomerization. One of the first examples is provided by Tian with a dithienylmaleimide conjugated with ferrocene units[32]. Very recently Rigaut et al. proposed multifunctional molecular scaffolds where both light and electrochemistry can tune the luminescence of a lanthanide complex in the NIR when conjugated with a dithienylethene as the photochromic unit and a ruthenium acetylide as the redox switch[43**].

3. Polymers

EFC polymers are very attractive because most applications (displays, sensors...) are based on solid state devices. Although it is possible to incorporate EFC molecules into a polymer matrix while keeping the desired properties, it is more convenient to use directly polymers as EFC thin films. The first idea was to consider conjugated polymers, because they are known for a long time to be electroactive and some are highly emissive in the visible range (polyfluorenes (PF), polyparaphenylenevinylene (PPV)). Pioneering works by Montilla have demonstrated by emission spectroelectrochemistry how the luminescence of PPV or PF derivatives can be tuned according to the redox state of the polymer chain[44, 45]. Later on polyoxadiazoles were also used as EFC thin films on electrodes by E. Kim[46]. When using conjugated polymers, generally EFC properties are coupled with electrochromism as the bandgap changes dramatically with the redox state of the polymer. A third property like circular dichroism can be monitored as well when chirality is introduced in the macromolecular backbone as smartly illustrated by E. Kim[47]. Polyparatriphenylamines are also EFC polymers with high contrast ratio, especially when the counter electrode material is well chosen to optimize the colorimetric properties while minimizing the working voltage[48].

Another specific interest of polymers over small molecules is the possibility to observe Aggregation Induced Emission (AIE) or Aggregation Enhanced Emission (AEE), that is a high enhancement of the emission intensity when moving from solution to solid state (thin film or powder). To observe that, restrictions in the intramolecular rotational motions should take place in the solid state. Recent examples of polyamides bearing various TPA derived units can be found and they all exhibit EC and EFC properties[49-52**]. TPA-tetraphenylethylene (TPE) units are especially designed to generate AIE because the torsion angle between TPA and TPE limits the pi-stacking interactions usually observed in conjugated polymers and may limit the emission quantum yield in the solid state.

An illustration of an efficient AIE and EFC association is shown in figure 2:

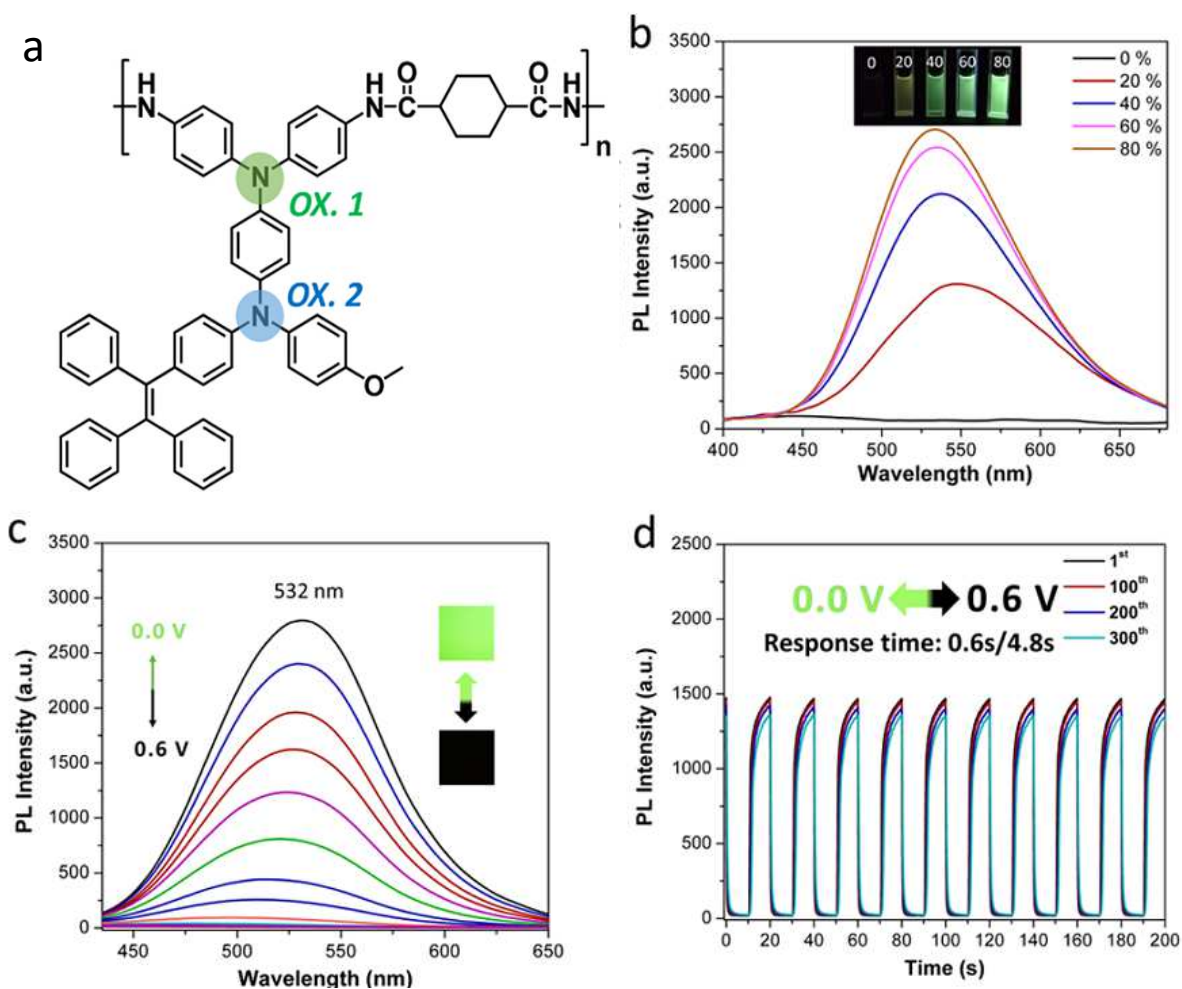


Figure 2: (a) TPE-PDA-PA and (b) its fluorescence spectra in NMP –water mixtures with different water contents (inset: fluorescence images in NMP –water mixtures). (c) Fluorescence spectra of a TPE-PDA-PA film at different applied potentials. (d) Fluorescence switching response under applied potentials between 0.0 and 0.6 V at the cycling time of 20 s for 300 cycles (on/off: 0.6/4.8 s); (adapted from ref. [52**])

Another smart idea consists in incorporating separate redox moieties and fluorophores in the main macromolecular backbone, which is an adaptation of the dyad strategy to the polymer framework. A proof of principle is provided by Kuo et al. who associated a fluorene to a triphenylamine as the redox group and benzothiadiazole (BTD) as a color tuning group[53**]. Removing BTD changes the emission color and this way a white emitting polymer can be obtained by simply mixing the two polymers in a blend. The emission can be switched off as well upon oxidation as does the emission of each component.

Another design consists in having a fluorescent bridge separating two redox moieties in the repetition unit, a way of extending to polymers the same concept already reported above for molecules. A recent paper describes polyamides containing a pyrene or spirobifluorene bridge separating diphenylamine units[42]. In such systems, changing the fluorescent bridge can tune the coupling between the two redox units and thus the absorption and emission colors.

Finally, instead of incorporating the EFC moiety in the repetition unit of the polymer, another possibility is to graft it as a pendant group on a conjugated polymer backbone. As the conjugated polymer might be itself electrofluorochromic, this results in a structure associating two EFC units possibly cross-talking. In such a structure, one may expect the redox state of the polymer to influence the luminescence of the grafted EFC unit, but also reversely the redox state of the EFC unit to tune the luminescence of the polymer. This was nicely demonstrated by Audebert et al. with a bithienylbenzene (TBT) bearing a tetrazine substituent[54]. The tetrazine luminescence can be reversibly switched off and on, upon polymer reduction and oxidation respectively. The process is unfortunately not reversible when considering the TBT luminescence switch with the redox state of the tetrazine.

Conclusion

We have reported in this review some strategies recently used to design redox-active luminescent molecular and macromolecular compounds. The topic is still in rapid evolution and more sophisticated systems might appear in the near future to enrich the panel of properties likely to be monitored electrochemically in addition to luminescence.

Declaration of interest: none

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