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Review

Electrofluorochromic systems: Molecules and materials exhibiting redox-switchable fluorescence

Hanan Al-Kutubi [a], Hamid Reza Zafarani [b], Liza Rassaei [b], Klaus Mathwig [a],*

[a] Pharmaceutical Analysis, Groningen Research Institute of Pharmacy, University of Groningen, P.O. Box 196, 9700 AD Groningen, The Netherlands
[b] Laboratory of Organic Materials and Interfaces, Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

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ABSTRACT

Electrofluorochromic molecules share the unique property that their fluorescence changes as a function of their oxidation state. This makes them interesting from a fundamental perspective as molecular dyads are designed and synthesized to tune the interplay of electrochemical and luminescent properties of molecules. Electrofluorochromic systems also find applications in sensing because a fluorescent signal can be detected with high sensitivity. Moreover, in the recent years the interest in redox-switchable fluorescent polymers has strongly increased due to their applicability in display devices. Here, we review electrofluorochromic molecules and polymers; we emphasize their structures and functional principles and point to specific applications.

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* Corresponding author.
E-mail address: k.h.mathwig@rug.nl (K. Mathwig).

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1. Introduction

Molecules whose fluorescence can be switched by external stimuli have been garnering attention in the fields of (bio)analytical chemistry, molecular devices, display technology and single molecule detection. While such molecules have been studied for a long time, the term "electrofluorochromism" has only recently been coined for the electrochemical switching of fluorescence [1]. Research is at a relative early state compared to fields in electrochemical manipulation of optical properties such as electrochromism (redox-switchable color) [2] or electrochemical light generation by electrochemiluminescence [3].

Here, we review electrofluorochromic materials with a focus on molecular structures. These materials can be grouped into small molecules and polymers. Small molecules can either be dyads or fluorophores whose emission is electroswitchable. We begin our article with dyads, which consist of separate fluorescent and redox groups. The first of such dyad molecules was synthesized in 1993 [4], but many different classes of dyads with organic as well as metal-containing redox groups have been developed since. These utilize a variety of switching mechanisms, which we briefly review here.

Electroswitchable fluorophores are either dyes or biomolecules, which are responsible for fluorescence in living cells. Due to their intrinsic electrofluorochromism, these molecules often exhibit efficient switching and a higher emission rate. The ability to modulate their fluorescence via electrochemistry allows for fundamental investigations into this behavior [5,6] as well as for single molecule studies of redox processes [7]. Sophisticated instrumentation has been developed for studying electrofluorochromic molecules. Such detection systems have been reviewed by Audebert and Miomandre [1].

Polymers are the newest class of electrofluorochromic materials. The first device consisting of small fluorescent molecules inside a polymer matrix sandwiched between two transparent electrodes was built only in 2006 [8]. However, polymers can also display electrofluorochromism on their own. These systems have since received considerable attention due to their potential applicability as displays. Here we compare their relevant properties towards this goal.

2. Dyads

The general structure of a dyad, shown in Fig. 1, consists of a fluorophore and an electroactive group, bound together by a spacer. Electrofluorochromic dyads have been reviewed previously in 2005 [9]. The fluorophore is responsible for the observed light emission. Altering the redox state of the electroactive group can quench the fluorophore and allows control of emission. Quenching can be done through either an electron transfer-based or energy transfer-based mechanism [10,11].

Quenching based on electron transfer is most often employed and is sometimes referred to as Photo-induced Electron Transfer (PET). This phenomenon is well-known and also has many applications in sensing [12]. The exact quenching mechanism depends on whether the electroactive group can act as an electron donor or acceptor, as shown in Fig. 2. Upon absorption of a photon by the fluorophore, an electron is excited into its LUMO, resulting in a singlet state. If the electroactive group is electron-rich, it can donate an electron into the half empty HOMO of the excited fluorophore, preventing fluorescence emission and quenching the fluorophore. In this case, oxidation of the electroactive group prevents it from donating an electron and hence restores fluorescence. The electroactive group can also act as an electron acceptor. Here, the electron in the LUMO of the excited fluorophore is transferred to the electroactive group, preventing it from returning to its ground state. Reduction of the electroactive group is then needed to revive fluorescence.

Quenching can also occur due to non-radiative energy transfer. In this case, an overlap between the emission spectrum of the excited fluorophore and the electroactive group is required. Generally, energy transfer can occur via either Coulombic interaction or orbital overlap (see Fig. 3). Förster Resonance Energy Transfer (FRET) is the most well-known and often encountered example of Coulombic interaction. It occurs at a long range and based on a dipole–dipole exchange with donor–acceptor distances of up to 100 Å. However, when FRET is forbidden, energy transfer can also occur via orbital overlap. Often referred to as the Dexter mechanism [13], this interaction happens at much shorter range (1–10 Å).

Appropriate matching of the properties of the two dyad moieties is important. A fluorophore with a good stability and a high quantum yield can ensure bright, constant fluorescence. An electroactive group with good stability, uncomplicated kinetics and reversible electrochemistry should provide fast, reliable and durable electroswitching. The groups must also be matched together. By choosing groups with appropriate energy levels, it can be ensured that electrons will flow in the desired direction. Furthermore, avoiding spectral overlap between the emission spectrum of the fluorophore and the absorption spectrum of the electroactive group can reduce unwanted quenching due to energy transfer. And, finally, a spacer with good charge transfer and conformational properties is required. This enhances the efficiency of electroswitchable quenching and prevents quenching through steric effects.

The effects of different fluorophores, electroactive groups and spacers have been researched extensively. To provide an overview, in this review we look at these efforts by dividing them based on the electroactive group used.

2.1. Organic electroactive groups

2.1.1. Quinones

Quinones are the most well-known organic electroactive group used in dyads. The general electrochemistry of quinones in aqueous and protic organic solvents is given in Fig. 4. Benzoquinone can be reduced to hydroquinone, requiring two electrons and two protons.

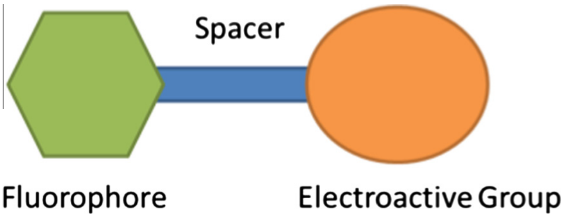

Fig. 1. Schematic of the general molecular structure of a dyad.

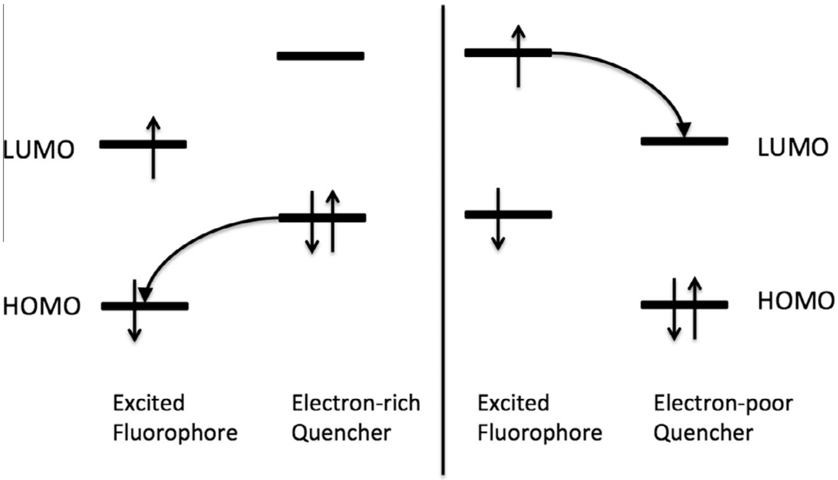

Fig. 2. Electronic state diagram of possible mechanisms for electron transfer-based quenching in Photo-induced Electron Transfer.

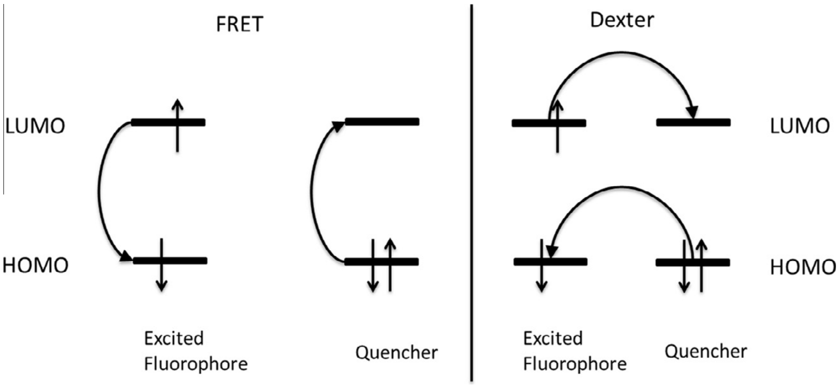

Fig. 3. Electronic state diagram of possible mechanisms for fluorescence quenching by nonradiative energy transfer. Quenching can occur by Förster resonance energy transfer (FRET) or by the Dexter mechanism.

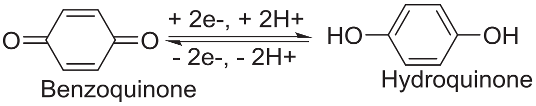

Fig. 4. The general redox reaction of quinones in protic media.

The first electrofluorochromic molecule consisted of a fluorescent Ru(bpy)$_2^{2+}$-moiety attached to a quinone, shown in Fig. 5 [4]. Benzoquinone is known to quench the triplet state of Ru(bpy)$_2^{2+}$ by acting as an electron acceptor. Hence, reduction to the hydroquinone restores fluorescence. Besides Ru(bpy)$_2^{2+}$, other fluorophores have also been used. Examples include ruthenium complexes [14,15], boron-dipyrromethene (BODIPY) [16], N-Dansyl [17] and Rhodamine B [18]. The electrochemistry of

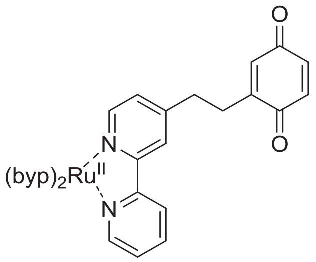

Fig. 5. The first electrofluorochromic molecule, consisting of Ru(bpy)$_2^{2+}$ attached to a quinone-group [4].

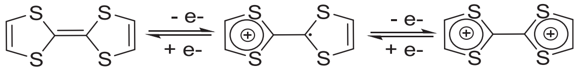

Fig. 6. Electrochemistry of tetrathiafulvalenes.

quinones depends on a variety of factors such as pH, the presence of additional compounds and the solvent used [19]. In an alcoholic solvent, reduced quenching was observed due to incomplete conversion of benzoquinone [20], whereas changes in reversibility were observed upon using a buffered aqueous solution [18]. As biological systems are mostly comprised of water, solubility and reversibility in water are important for the probing of their redox states. Benniston et al. attached BODIPY to a quinone-moiety and were able to see reversible switching in aprotic media [16]. Testing in aqueous media was accomplished by encapsulating the dyads in micelles. A solution containing the fluorescent hydroquinone-form displayed a decrease in fluorescence upon addition of H_2O_2 as chemical reductant. When ascorbic acid was introduced as chemical oxidant to another solution containing the non-fluorescent benzoquinone-form, an increase in fluorescence was observed.

The sensitivity of quinones to their surroundings can also be utilized as shown by the group of Maiya [21,22]. Investigating a dyad consisting of dipyridophenazine (ddpz) and quinone, it was found that both the hydroquinone and benzoquinone form are quenched in aqueous solution. Whereas this quenching can be ascribed to electron transfer for the benzoquinone form, the hydroquinone form was quenched due to proton transfer. Hence, in a more hydrophobic environment, its fluorescence can be restored. Ddpz-complexes are able to bind to DNA, an event that leads to an increase in the hydrophobicity of the dyad environment. Hence, upon binding, the fluorescence of the hydroquinone form was restored, allowing binding to be assessed optically. Furthermore, the presence of the electroactive quinone-group meant that intercalation could be assessed via electrochemical means as well.

Using Rhodamine B, a water-soluble fluorophore, Kierat et al. were able to probe the redox state of the quinone group in aqueous solution using fluorescence [18]. Besides assessment of the effect of copper complexes with different oxidation strengths, the enzyme-catalyzed formation of H_2O_2 was examined in solution.

2.1.2. Tetrathiafulvalenes

Tetrathiafulvalenes constitute another well-known electroactive group. Due to their favourable properties, including stable and reversible electrochemical behavior, they are often employed in molecular and supramolecular switches. The non-aromatic neutral molecule can be oxidized into a radical cation and subsequent dication (see Fig. 6). These cations are stable due to their aromaticity, thus, the redox system is reversible [23].

Despite their electroswitchable behavior, the use of tetrathiafulvalenes in fluorescent switching can result in unwanted effects. Neutral tetrathiafulvalene groups are electron-rich and can act as quenchers through electron donation. However, the cations are electron-poor and can hence quench fluorescence as well by acting as electron acceptors. Hence, oxidizing the neutral molecule does not always restore fluorescence. Furthermore, the radical cation has a very broad absorption spectrum which can result in spectral overlap and lead to energy transfer-based quenching. These two quenching phenomena can occur separately [24,25] or jointly [26]. As the oxidized molecule can exist in two different redox states, Zhang et al. attempted full oxidation to the dication as this shows a much narrower absorption spectrum and could help avoid energy transfer-based quenching [27]. However, instead of fluorescence revival, a further decrease in emission was observed, because the dication was able to quench fluorescence even more by acting as an electron acceptor.

Notwithstanding, there are cases in which fluorescence could be recovered upon oxidation. These include cases using porphyrins [28], phthalocyanines [29] and anthracene [30]. Bill et al. inserted a BODIPY unit between the two tetrathiafulvalene rings as shown in Fig. 7 [31]. The electron donating character of the rings as well as the large extent of conjugation allowed the BODIPY fluorescence to be shifted into the NIR-region (peak of emission spectrum λ_{max} = 830 nm), making it the most red-shifted at the time of its publication. Interestingly, fluorescence is only quenched upon the first oxidation, while the second oxidation leads to very weak emission even further into the NIR-region (λ_{max} = 1185 nm).

Finally, Lu et al. incorporated tetrathiafulvalenes in an ion sensing molecule capable of both fluorescent as well as electrochemical sensing (see Fig. 8) [32]. The molecule shows a tenfold increase in fluorescence upon fluoride binding.

The fluoride ion binds to the amide moieties in the arms of the molecule as well as the anthracene units, causing the molecule to become more rigid. The result is a decrease in the efficiency of electron-based quenching. Using cyclic voltammetry, $H_2PO_4^-$ also could be sensed electrochemically. The large size of the $H_2PO_4^-$ ion allows binding to the C=C-group of the TTF-unit and pushes the arms apart. This causes delocalization of the ion's negative charge over the tetrathiafulvalene units and the appearance of a new redox system. The peak height of this new system is proportional to the $H_2PO_4^-$ concentration, opening the possibility of a sensor with dual functionality.

2.1.3. s-Tetrazines

s-Tetrazines (see Fig. 9) are the electron-poorest aromatic system in classical organic chemistry [33]. They can be reversibly reduced to their anionic radical in the absence of acids and in aprotic organic solvents.

Small molecular *s*-tetrazines can be used as electroswitchable fluorophores on their own [8,34]. However, due to their reversible electrochemistry, they can also be used in conjunction with another fluorophore, forming a bichromophore. Unfortunately, very few successful examples of bichromophores containing *s*-tetrazine have been reported. Spectral overlap often results in unwanted quenching due to energy transfer, resulting in complete quenching when, for instance, BODIPY is used [35]. The group of Audebert utilized triphenylamines as electroactive groups and electron donating quenchers, with an *s*-tetrazine as fluorophore, as shown in Fig. 10. Whereas fluorescence could be restored upon oxidation, the quantum yield was low due to spectral overlap [36]. To resolve this issue, triphenylamine moieties with electron-rich groups were investigated [37]. These groups shift the absorption of the cationic triphenylamine radical to a higher wavelength, thus preventing spectral overlap. Despite this, fluorescence was often still quenched. Theoretical calculations showed that the excited tetrazine groups possess a higher energy level than the triphenylamine radicals, resulting in quenching as the triphenylamine radicals act as electron acceptors.

An example incorporating tetrazine into a fluorescent device was given by Seo et al. [38]. By attaching naphthalimide to tetrazine, a dyad consisting of two electroactive fluorophores was created. This dyad is able to exist in three different states. The neutral state showed fluorescence of both fluorophores, whereas the first oxidation should quench only the tetrazine and subsequent oxidation should quench both fluorophores. Incorporating this dyad allowed the creation of a multi-fluorescent device, displaying different fluorescent colors, depending on the potential applied. However, whereas the neutral molecule displayed a yellow fluorescence, fluorescence was completely quenched upon the first reduction as the tetrazine

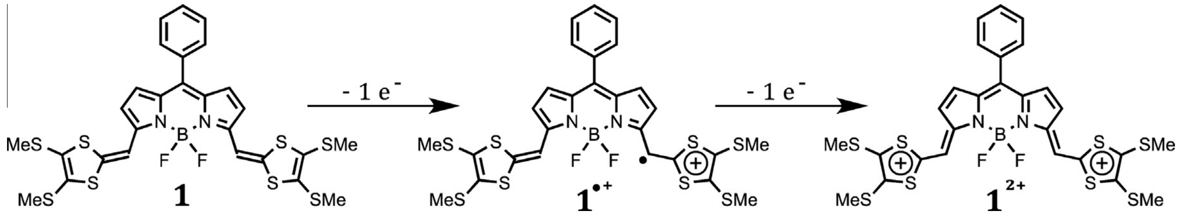

Fig. 7. Insertion of a BODIPY unit within tetrathiafulvalene allows it to have three redox states. The radical cation is non-fluorescent whereas the neutral molecule and dication emit in the NIR-region. Reproduced from Ref. [31] with permission of the Royal Society of Chemistry.

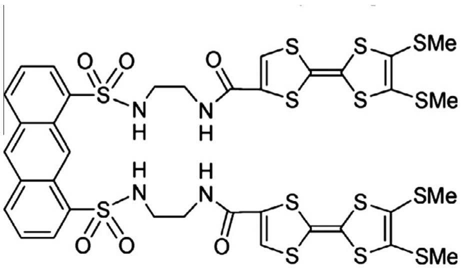

Fig. 8. An electrofluorochromic molecule with dual functionality as a fluorescence and electrochemical sensor. Reprinted with permission from Ref. [32]. Copyright 2005 American Chemical Society.

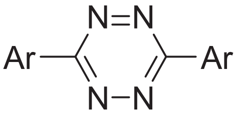

Fig. 9. General structure of *s*-tetrazines.

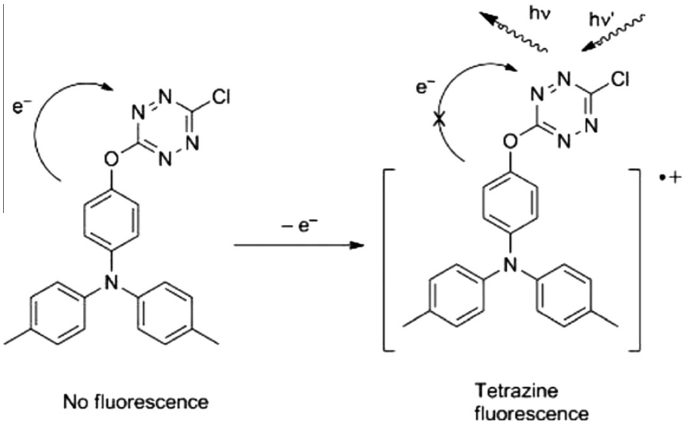

Fig. 10. Combination of triphenylamine and tetrazine and the proposed mechanism of fluorescence switching based on electron transfer. Copyright 2012 Wiley. Used with permission from Ref. [36].

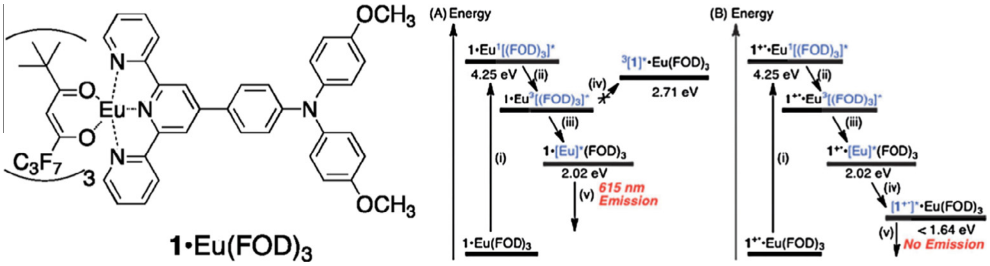

Fig. 11. The addition of an electroactive ligand to form an electroswitchable lanthanide-based complex (left) where quenching is based on altering the ligand energy level (right). Oxidation lowers the energy level of the ligand and allows quenching lanthanide emission through energy transfer. Reproduced from Ref. [40] with permission of the Royal Society of Chemistry.

radicals quenched the naphthalimide fluorescence. Incorporation of additional parent naphthalimide into the device allowed an additional fluorescent source and the attainment of a three-state device.

2.1.4. Other organic electroactive groups

Besides the known organic electroactive groups, other groups can be used as well. Interesting examples include dyads incorporating lanthanide ions. Lanthanides are luminescent due to their electronic [Xe]4f^n configurations [39]. The difference in energy between these levels spans the visible and infrared spectrum allowing excitation by light as well as a sharp and well-defined emission. These 4f-4f transitions are partially forbidden, meaning that the lifetimes of excited states are long. However, the lanthanide ion quantum yield is very low. One way to overcome this problem is through sensitization using 'antennas' – ligands bound to the lanthanide ions. These ligands absorb light more efficiently and can transfer energy or an excited electron to the lanthanide ion, resulting in emission. Yano et al. combined an electroactive triphenylamine-based ligand together with photosensitizing antennas to form a fluorescent lanthanide switch [40]. In its neutral state, the triphenylamine ligand does not participate in the sensitization process as its energy level is simply too high (see Fig. 11). However, upon oxidation, the energy of the ligand is lowered. The energy absorbed by the antennas is then passed on to the ion which can pass it on to the electroactive ligand without emission taking place. A change in ligand energy levels was also utilized by Norel et al. for the sensitization of Ytterbium and Neodymium ions [41]. In this case, a decrease in ligand energy could both prevent sensitization from occurring and cause electrons to flow from the excited ions to the ligand, quenching fluorescence.

The incorporation of biologically derived moieties into dyads is also possible. Yamada et al. used electroactive flavin attached to BODIPY to form a dyad to probe the redox state of the cellular interior [42]. Upon oxidation, a ninefold increase in fluorescence intensity was observed. Cellular studies showed that the dyad was able to permeate HeLa cells, and addition of a reductant and oxidant led to quenching and revival of the BODIPY fluorescence within these cells, respectively. Yan et al. attached nicotinamide adenine dinucleotide to a perylene dye [43]. This dyad showed a very high quantum yield when oxidized and was used for detection of the enzymatic turnover rate of alcohol dehydrogenase. As the dyad is too bulky to be used in the enzyme directly, an indirect method was devised. During the enzymatic reaction, NADH is produced, which can reduce the NAD$^+$ moiety of the dyad, resulting in fluorescence quenching.

Enzymatic activity can also be probed by using the enzyme itself as electroactive group. Introduced first by the group of Canters and Aartsma, this approach allows probing of the activity of oxido-reductases [44]. These enzymes possess an active center with strong, characteristic adsorption in the optical spectrum, depending on its redox state. By covalent attachment of a dye with an emission spectrum overlapping with the enzyme, quenching through FRET can be achieved, depending on the enzyme redox state. Using this approach, the enzymatic activity of both nitride reductase as well as small laccase were investigated. The mechanism and rates of charge transfer could be studied at the single molecule level, providing new insights into the workings of these enzymes [45].

Whereas the fluorophore and electroactive group are often separated by a spacer, this does not have to be the case. Al-Kaysi et al. showed that a Meisenheimer complex can possess electrofluorochromic behavior (see Fig. 12) [46]. Lacking a spacer, the molecule consists of a triazine unit attached to a fluorescent trinitrocyclohexadiene unit. Upon reduction, fluorescence is quenched due to electron transfer from the triazine ring to the fluorophore. Interestingly, switching could also be achieved through protonation as this lowers the HOMO level of triazine, making electron transfer unfavorable. Using fluorescence microscopy, the switching of single molecules was observed upon protonation and deprotonation.

Another interesting example entails two fluorescent Ru-complexs attached together with an azo-bridge [47]. In its neutral state, the azo-bridge acts as a quencher by accepting electrons from the two complexes. However, upon reduction this is no longer the case and the compound behaves as two fluorophores. A similar concept was adopted by Suzuki et al. who used bis(10-methylacridium)s [48]. These molecules are able to undergo reversible bond cleavage upon oxidation. Using a hexaphenylethane derivative, it was shown that the bond results in fluorescence quenching. However, upon bond cleavage, a bis(acridium)-type dye was formed and fluorescence was observed (see Fig. 13). It was also shown that the chirality of the molecule can be preserved upon bond cleavage and formation [49]. This would allow bond formation to be observed using circular dichroism (CD) as well as fluorescence and ultraviolet–visible spectroscopy.

Finally, besides lanthanides and organic dyes, other luminescent moieties can be used as fluorophore. Interesting examples include quantum dots [51,52], silver and gold nanoparticles [53] and titanium dioxide [54].

2.2. Metal-containing electroactive groups

Unlike organic electroactive groups, metals often display one-electron electrochemistry with uncomplicated kinetics. Furthermore, the energetics of metal-based complexes can be tuned by an appropriate choice of ligands or metal [55]. Quenching often occurs through electron transfer. However, in some cases electron exchange can occur, resulting in energy-based transfer through the Dexter mechanism [11].

2.2.1. Macrocycles

Fabbrizzi et al. investigated nickel and copper-based macrocyles as electroactive switches and found that the spacer can affect which quenching mechanism will dominate [13]. Longer, more rigid spacers result in a longer distance between fluorophore and electroactive group. As Dexter energy transfer decreases more strongly with distance, electron transfer-based quenching will dominate. The ligand used can also alter the quenching behavior. It was found that for a nickel-based tetra-azo-macrocycle the ligand undergoes reduction before the metal ion, resulting in a radical anion. This anion

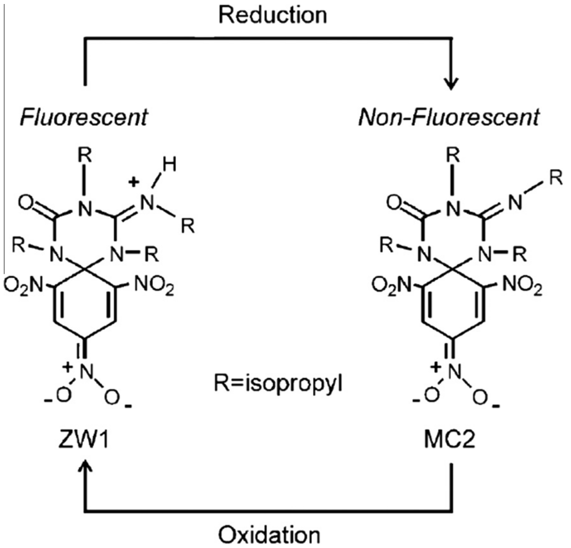

Fig. 12. Electrochemical conversion of a Meisenheimer complex consisting of a triazine and trinitrocyclohexadiene unit. Reduction leads to fluorescence quenching due to electron transfer from the triazine unit. Copyright 2012 Wiley. Used with permission from Ref. [46].

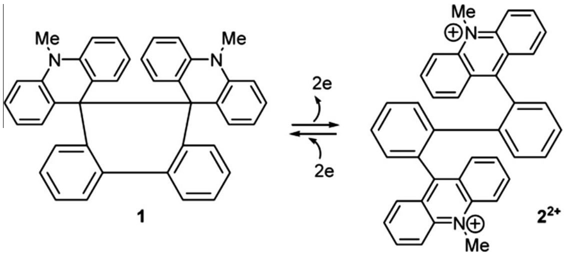

Fig. 13. Bond cleavage of a hexaphenylethane derivative of bis(10-methylacridium) results in the formation of a dye and restores fluorescence emission. Reprinted from Ref. [50], Copyright (2003), with permission from Elsevier.

can form a complex with the metal, and due to the folded geometry of the dyad, electron transfer is possible from the radical into the fluorophore, resulting in quenching as shown in Fig. 14.

The coordination of the ligand around the metals can also be affected. It is known that copper displays different coordination geometries based on its redox state, with Cu(I) preferring tetrahedral and Cu(II) preferring a hexagonal geometry. Amendola et al. used this difference to investigate the coordination of copper using fluorescence [57]. A fluorophore was added which could be quenched upon coordination with copper. Due to the difference in geometry and the ligands used, this was only possible in a tetrahedral conformation, as shown in Fig. 15. Hence the fluorescence intensity could be used as an indicator of copper coordination. A similar principle was used by Yilmaz who investigated the complex formation of copper and manganese-based compounds using fluorescence [58,59].

2.2.2. Ferrocenes

Ferrocene is the most popular and well-known metal-containing electroactive group. Known for its stability and good redox properties, this compound is often incorporated into dyads. The most obvious choice is the combination with established fluorophores. Martínez et al. investigated the use of pyrene [60], whereas Zhang et al. looked at perylene diimide [61] and the effect of spacers on the efficiency of perylene diimide quenching [62]. BODIPY was used by attachment of ferrocene either to its two side-rings [63] or the boron atom [64], as shown in Fig. 16. It was found that attachment to boron promoted intersystem crossing from singlet to triplet state, a phenomena often associated with the presence of heavy atoms. This crossing allowed the excited state lifetime of the dyad to be extended by three orders of magnitude.

Attachment of ferrocene to non-established fluorophores is also possible. Zhou et al. attached zinc porphyrin to ferrocene and investigated the effects of spacers, finding that both electronic communication as well as steric effects are important [65]. Rochford et al. investigated the effect of two additional groups on the fluorescence quenching efficiency in a zinc porphirin-based system and found that extending the delocalization of excited-state electrons caused a reduction in quenching efficiency [66].

Finally, it was shown that the fluorescence of lanthanides could be modulated by attaching a ferrocene-based ligand that can act both as sensitizer and quencher, depending on the ferrocene redox state [67].

3. Electroswitchable fluorophores

Not all electroswitchable molecules possess a dyad-structure. Molecules that lose or gain fluorescence upon electrochemical modulation are called electroswitchable fluorophores. These include commercially available dyes and biologically active molecules as well as other molecules which have been synthesized with this property in mind. The mechanism for fluorescence loss and gain is often complex and many factors can contribute, depending on the type of molecule.

3.1. Non-radical fluorophores

In biological cells, most fluorescence is due to Dihydronicotinamide adenine dinucleotide (reduced: NADH, oxidized: NAD^+) and flavins [68,69]. NADH is an essential cofactor for redox reactions and metabolism in living cells [70,71]. Its reduced form is highly fluorescent with absorption and emission maxima at 340 nm and 460 nm, respectively. The fluorescent group is the reduced nicotinamide ring with a lifetime of about 0.4 ns in aqueous buffer [72]. The oxidized form is nonfluorescent.

Flavins are valuable biochemical compounds which take part in reactions as coenzymes and photoreceptors. Their structure and electrochemistry are shown in Fig. 17. They are found in both plants and animals [73]. Riboflavin (Vitamin B2) is the precursor of all flavins found in nature; however, only a small portion of flavins in tissues is present as free riboflavin. The majority is in the form of cofactors called flavocoenzymes, mostly as flavin adenine dinucleotide (FAD) and in lesser amounts as flavin mononucleotide (FMN) [74,75]. Enzymes using flavins are involved in various metabolic redox processes in living organisms due to their ability to biologically catalyzing electron transfer reactions [76,77]. In the oxidized state, flavins are fluorescent with emission in the green spectrum whereas in the reduced state they are hardly fluorescent [76]. When bound

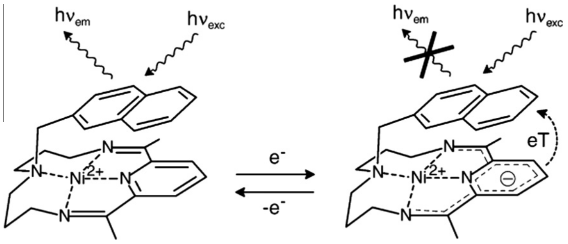

Fig. 14. Quenching upon energy transfer from a ligand radical-metal complex to the fluorophore. Reproduced from Ref. [56] with permission of the Royal Society of Chemistry.

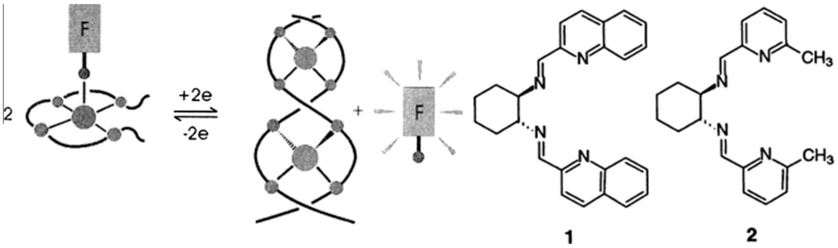

Fig. 15. Fluorescence quenching based on coordination of copper (left) and the chemical structure of the ligands used (right). Reprinted with permission from Ref. [57]. Copyright 2003 American Chemical Society.

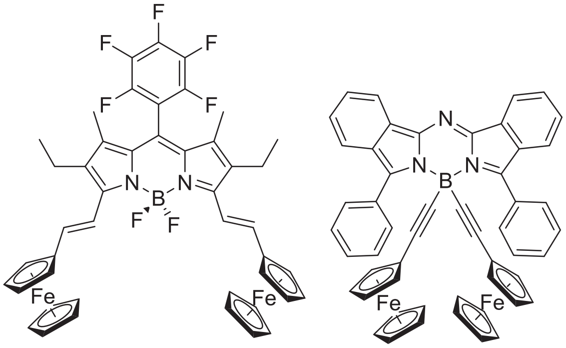

Fig. 16. The chemical structure of boron-dipyrromethene (BODIPY) with ferrocene units attached to the two side-rings (left) and the boron atom (right). Refs. [63,64].

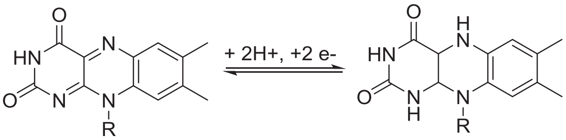

Fig. 17. The general structure and electrochemistry of flavins.

to proteins, flavins exhibit only weak fluorescence or no fluorescence. This is in contrast to NADH, which is highly fluorescent when bound to proteins [78].

Due to their electrochromic and redox properties phenazine cation dyes have been widely used in diverse applications such as electrode transfer mediators in catalyzing biological reactions as well as in biosensor development [79,80]. Cresyl violet (see Fig. 18) as a phenoxazine dye shows fluorescence in the oxidized state and has a reduced non-fluorescent state [81]. Cresyl violet can be used as an electron transfer mediator to explore interfacial electron transfer mechanisms of chemical or biological redox reactions as well as biosensor development [79].

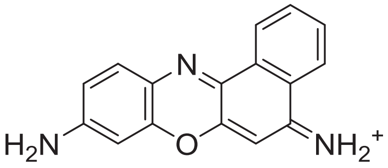

Fig. 18. The chemical structure of cresyl violet.

Due to their highly intense fluorescence, redox-switchable fluorophores have been employed in single-molecule studies. Both NADH and FAD were used as sensors for unraveling enzyme kinetics at the single-molecule level [82,83]; and recently microfabricated nanofluidic devices were used to detect fluorescent switching of individual flavin mononucleotide molecules confined in nano-cavities [84,85]. Also the electrofluorochromic behavior of cresyl violet was explored in a pioneering spectroelectrochemical single-molecule experiment [81].

Redox-sensitive green fluorescent proteins (GFP) allow the visualization of the redox state in cells [86]. Properties such as efficient fluorescence and stability throughout a wide range of pH and solvent conditions make GFP a suitable indicator of intracellular concentrations of H^+, Ca^{2+} and halide ions. Introducing redox active groups into GPF allows the modification of the fluorescent properties [87,88].

Resazurin, also called Alamar Blue, is a blue non-fluorescent redox dye [89,90]. Upon reduction, resorufin is formed (see Fig. 19). This results in strong fluorescence with a change in color (to red) and a shift in its fluorescence which can be quantified fluorimetrically [90]. Resazurin is non-toxic to cells and stable in culture medium without cells, however it is reduced in the presence of living cells [91]. These properties present resazurin reduction as an indicator of chemical cytotoxicity in cultured cells and provides a convenient index of cell proliferation [90,92] by measuring the changes in dye fluorescence. Resazurin is added to the cells and is subsequently converted to resorufin by mitochondrial enzyme activity [93]. As shown in Fig. 19, reduction of resazurin consists of two stages; in the first stage, blue colored resazurin is reduced to red colored resorufin by loss of one oxygen atom. This reaction is not reversible by atmospheric oxygen. Next, the red colored resorufin is further reduced to a colorless hydroresorufin. This reaction is however reversible by atmospheric oxygen [94].

Porphyrins are fluorophores, naturally exhibiting intense luminescence in the range of 630–690 nm, and can be used in luminescence diagnostics [96–98]. They have a tetrapyrrolic macrocycle with side substituents, and they can coordinate metal atoms firmly to form metalloporphyrins [99]. Porphyrins can be found in hemoglobin, urine and in erythrocytes [97]. Due to their fluorescence and ability to accumulate in many types of cancer cells, they are used in cancer diagnostics [100].

Browne et al. showed that conformational changes in a synthetic molecules, brought on by electrochemical means, can also result in changes in fluorescence [101]. A molecule with reversible switching between red fluorescence and a quenched state was synthesized, as shown in Fig. 20.

3.2. Radicals

Using electrochemistry, it is possible to inject a single unpaired electron into an organic molecule, creating a radical. Whereas some radicals show fluorescence on their own, they are often difficult to obtain and short-lived [1]. Exceptions include chloromethoxy-*s*-tetrazine and a BODIPY derivative [102]. Kanazawa et al. have shown that the dye Yellow-1 can show electrofluorochromism due to the cleavage of a bond upon oxidation, forming a radical [103]. While the dye is non-fluorescent in its neutral state, bond cleavage causes extension of conjugation throughout the system, resulting in fluorescence, as shown in Fig. 21. By placing a mixture of the dye and benzoquinone between two ITO plates, an electrofluorochromic device was fabricated [104].

Radical stabilization can be achieved through a combination of conjugation and steric hindrance. Seo et al. used these principles to form an electroswitchable device based on a polymethine dye [105]. Extended electron delocalization and steric

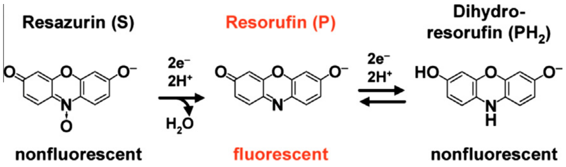

Fig. 19. Redox chemistry of resazurin in aqueous solutions. Reprinted with permission from Ref. [95]. Copyright 2009 American Chemical Society.

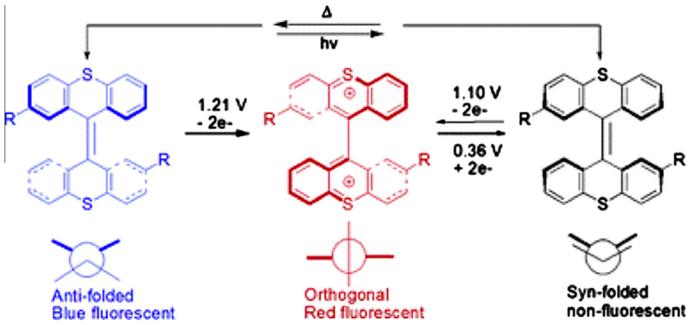

Fig. 20. Schematic showing fluorescence modulation upon conformational change. Electrochemical switching between a red fluorescent state and a non-fluorescent state is possible. Reprinted with permission from Ref. [101]. Copyright 2006 American Chemical Society.

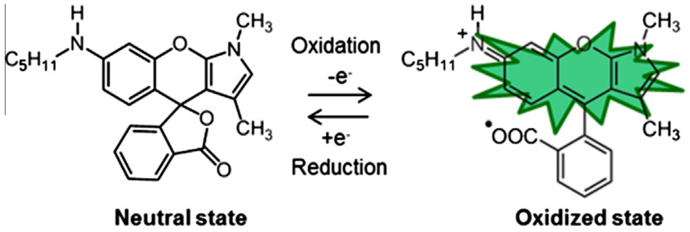

Fig. 21. Fluorescence switching upon bond cleavage/radical formation. Reprinted with permission from Ref. [103]. Copyright 2014 American Chemical Society.

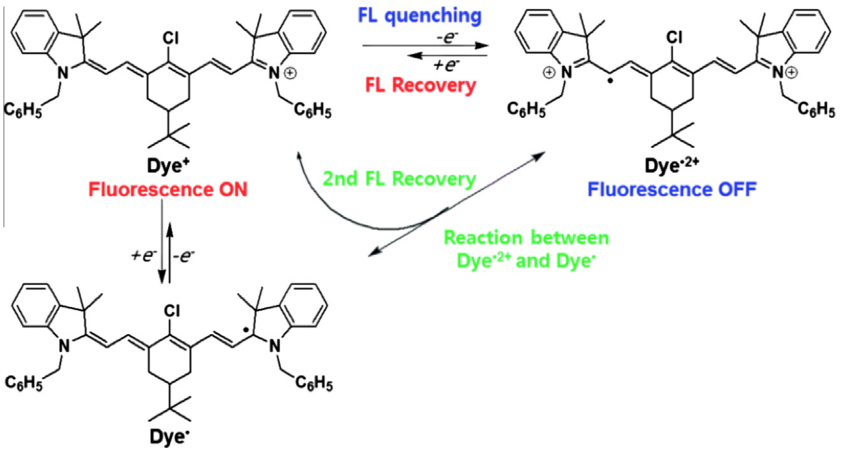

Fig. 22. The redox chemistry of a polymethine dye, showing different processes of dye regeneration. Besides electrochemistry, reactions between the dye radical and dication radical also regenerate the cation. Reproduced from Ref. [105] with permission of the Royal Society of Chemistry.

hindrance through the presence of bulky groups protected the radical molecule from degradation reactions and contributed to its reversible switching ability, shown in Fig. 22. An additional reaction between the radical and dication radical of the dye also resulted in regeneration of the cation molecule, facilitating reversibility. The extended electron delocalization also allowed absorption and fluorescence in the NIR-region, being the first electrofluorochromic device to do so.

Certain molecules are known to form stable cation radicals. Triphenylamines have been used in conjunction with tetrazines in bichromophoric dyads. However, their ability to form a stable cation radical and their interesting optical properties warrant their investigation as electroswitchable fluorophores on their own. Quinton et al. showed that the attachment of different groups to the phenyl groups of triphenylamine could allow tuning of the fluorescent emission as well as alteration of the switching efficiency [106]. Additional groups can also be used to stabilize multiple redox states. A triphenylamine with two additional amine groups was shown to exhibit four different redox states as shown in Fig. 23 [107]. Interestingly, whereas the neutral molecule was fluorescent, the monocation and trication were not. The dication showed weak fluorescence.

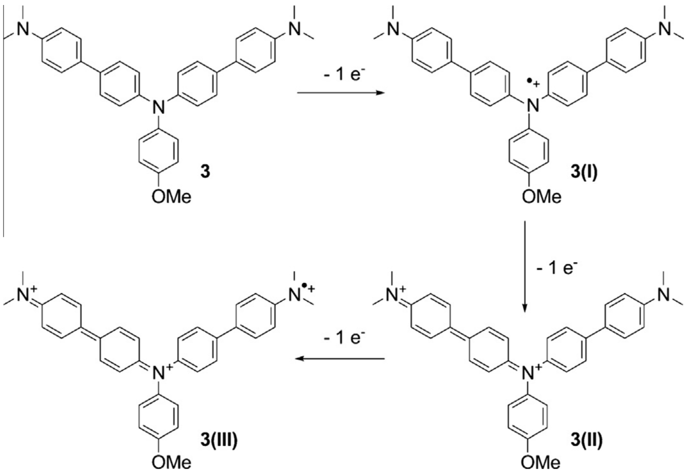

Fig. 23. Adding of additional amine groups allows the existence of multiple stable redox states within a triphenylamine derivative. The neutral molecule shows fluorescence, whereas the cation and trication do not. The dication is only weakly fluorescent. Copyright 2015 Wiley. Used with permission from Ref. [107].

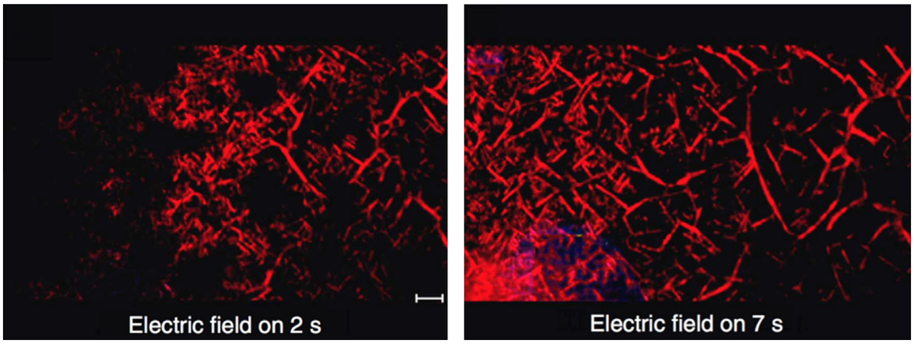

Fig. 24. Polarized optical microscope images showing the transition from an isotropic to an ordered phase upon reduction of an electrofluorochromic liquid crystal system based on the thioviologens (scale bar: 40 μm). Reprinted by permission from Macmillan Publishers Ltd.: Nature Communications (Ref. [108]), copyright (2014).

Thienoviologens have also been shown to exhibit electrofluorochromism. This property was first demonstrated by Beneduci et al. who succeeded in forming an ionic liquid crystal with electrofluorochromic properties [108]. Besides an unordered isotropic phase, two ordered phases could be formed (columnar and calamitic). Fluorescence was observed upon reduction as the radical is formed. Interestingly, for the isotropic phase this increase in fluorescence is accompanied by a redshift in emission, attributed to the isotropic phase converting into an ordered phase upon reduction, as can be seen in Fig. 24. However, whereas liquid crystals possess interesting properties such as the ability to self-heal [109], they require high temperatures to be formed. Another possibility is the incorporation of these compounds in a gel matrix [110]. Drop-casting a gel containing thienoviologens and ferrocene between two ITO plates afforded the formation of an electrofluorochromic device. It is the dication that is fluorescent in this case, with the monocation causing quenching due to energy transfer.

4. Polymers

Polymers can offer many advantages over small molecules. The ability to mold, cast and pattern polymers makes them suited for use in solid-state electroswitchable devices.

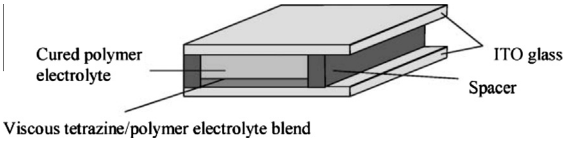

Fig. 25. Schematic of a typical structure of an electrofluorochromic device. Reproduced from Ref. [34] with permission of the Royal Society of Chemistry.

Table 1

Comparison of electrofluorochromic polymers used in electrofluorochromic devices.

Polymer	Applied potentials (V)	Reference electrode	Contrast ratio	Scanrate (mV/s)	Cycles (#)	Intensity loss (%)	Quantum yield	Comments
Tetrazine molecules inside matrix [8]	+2 to −2	None	n.a.	2000	120	n.a.	n.a.	Scan rate estimated
s-triazine bridged p-phenylene vinylene [121]	+2 to −2	None	~2	1000	1500	<20%	0.14	Contrast ratio around the value given. Iodine used as quencher
s-triazine bridged p-phenylene vinylene [122]	+2 to −2	None	1.3	1000	19	n.a.	0.44	Contrast ratio estimated. Iodine used as quencher. Quantum yield defined in solution
9-methylanthracene polymer [123]	+2 to −2	None	3.86	1000	1000	Minor	n.a.	Iodine used as quencher/dopant
s-triazine bridged p-phenylene vinylene [124]	+1.5 to −1.5	None	n.a	300	50	n.a	0.57	Quantum yield defined in solution. Amount of cycles estimated
Poly(1,3,4-oxadiazole) [125]	+1.8 to −1.8	Ag/Ag$^+$	1.2	360	1000	Very minor	0.13	
Poly(N-alkyl-2,7-di(2-thienyl)carbazoles) [126]	−0.2 to 0.6	Ag/Ag$^+$	~100	100	24	n.a.	0.3	All experiments conducted using a three-electrode setup in solution
Copolymers of fluorene, triphenylamine and 1,3-diphenylimidazolidin-2-one [127]	0 to 0.9	None	16.3	300	25	10%	0.73	All experiments conducted using a three-electrode setup in solution
			n.a.	200	40	40%		In device; 20% loss after first cycle
Cyanotriphenylamine-based polymers [128]	0 to 1.6	Ag/AgCl	152	13.3	10	>50%	0.65	Experiments conducted in solution. Contrast ratio not defined during switching
Copolymers of fluorene, triphenylamine, benzo(2,1,3)thiadiazole and 1,3-diphenylimidazolidin-2-one (1) [129]	−1.0 to 1.0	None	21.4	50	10	<10%	0.17	Switching of potential done consecutively for the different scan rates, starting with the lowest value
			6.2	400	50	5%		
			6.7	400	50	10%		
Polymethine dyes [105]	−0.5 to 1.1	Ag/Ag$^+$	1.5	53.3	100	30%	n.a.	
Poly(4-Cyanotriphenylamine) [130]	−1.5 to 1.9	None	242	9.4	300	1%	0.22	Durability tested at a scanspeed of 110 mV/s
			44	340				
Polyamides with fluorene-based triphenylamine units [119]	0 to 0.8	Ag/AgCl	12.7	26.7	10	Minor	0.47	Measurement in solution, scanspeed for contrast ratio determination not given

By embedding them inside a polymer matrix, devices can be fabricated based on small electrofluorochromic molecules [8,38,104,105,110]. Kim et al. used this approach for the fabrication of the first electrofluorochromic device (see Fig. 25) and found that the formation of a thin layer of active material allowed fast switching and can prevent side reactions [8]. The use of a polymer matrix also allows for the incorporation of compounds such as charge balancing mediators [104], additional fluorophores [38], internal references [104,110] and oxidizers [110]. However, polymers can also display electrofluorochromic behavior on their own.

We compare the contrast ratio, stability and scan rates of electrofluorochromic polymers in Table 1. An important characteristic of electrofluorochromic molecules and devices is their contrast ratio. It is defined as the ratio of fluorescence intensity in the 'on'-state and 'off'-state. An indication of the overall brightness of the device is given by the quantum yield of the material, defined as the amount of fluorescent photons emitted per amount of photons absorbed. The quantum yield for a polymer can be measured when the polymer is in solution or when it is in solid form. In solution, the quantum yield is often much higher. The stability of the device is often tested by switching the applied voltage to turn the fluorescence on and off for many consecutive cycles. The loss in intensity during this switching is a measure of the durability of the material. Here, the speed at which this happens is of importance as a lower speed allows the reaction to run to completion, resulting in higher contrast ratios during switching. However, as switching is often done at higher speeds, the contrast ratios observed when testing the durability are lower than those given when the optical properties of the material are examined. Finally, these polymers are often tested using a solid state device. However, in some cases testing is done by coating the polymer onto an electrode and placing it inside a solution. Whereas this allows the use of a reference electrode, and hence more control over the applied potential, care must be taken when comparing these results to those obtained in a solid state device.

Conjugated polymers are able to display intrinsic fluorescence. The first polymer-based light emitting device was reported in 1990 and was based on poly(*p*-phenylene vinylene) (PPV) [111]. Since then, many more groups have been developed [112] of which fluorene is one of the most well known. A small selection of the groups featured in this review is given in Fig. 26. Fluorescence in polymers occurs via a mechanism similar to that of small molecules. However, due to their extended conjugation, polymers possess a bandgap instead of discrete energy levels. Therefore the polymers can have semiconducting or insulating properties and their conductivity can be tuned by doping [113]. Unlike semiconductors, polymers can be doped by oxidation or reduction of groups within the polymer matrix. Here, n-doping is achieved by addition of electrons into the system by reduction, and p-doping is accomplished by electron removal via oxidation. Upon removal, electron-deficient holes are formed. As a photon is absorbed by the polymer, an exciton (i.e., an electron-hole pair) is created. Quenching occurs when the exciton decays nonradiatively (e.g., by combination with a hole) and, thus, fluoresence emission is prevented [114].

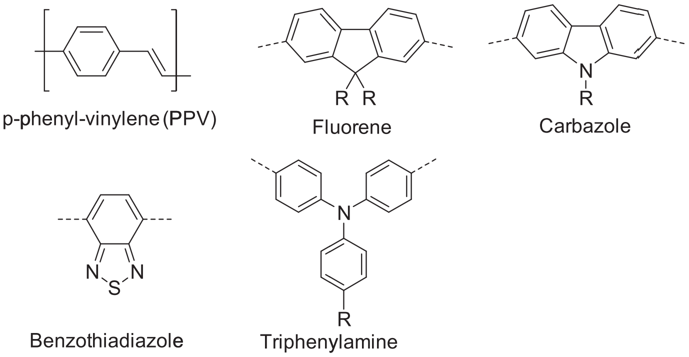

Fig. 26. Besides poly(p-phenylene vinylene), many groups have been developed to endow the polymer with fluorescence and electrochemical stability.

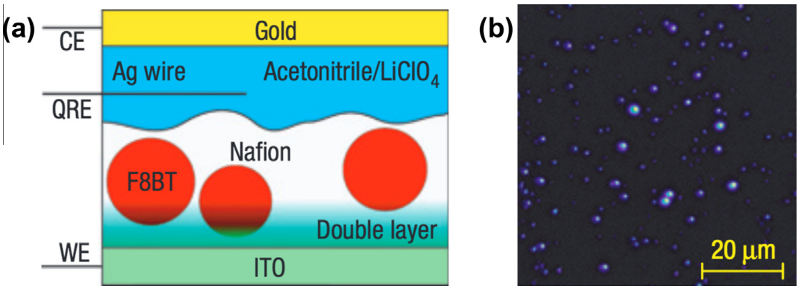

Fig. 27. Schematic of the electrode setup used by Palacios et al. (a), and a microscopy image of single polymer particles (b). Reprinted by permission from Macmillan Publishers Ltd.: Nature Materials (Ref. [116]), copyright (2007).

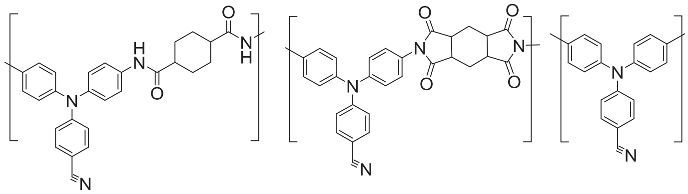

Fig. 28. The chemical structure of cyanotriphenylamines with the polyamide and polyimide form (left and center), respectively [128], and highly conjugated form (right) [130].

The coupling of electrochemical processes and fluorescence can be used to study kinetics of charge transfer and quenching inside polymers. Gesquiere et al. coupled electrochemistry to fluorescence spectroscopy to study single nanoparticles of a fluorescent PPV-derivative, poly[2-methoxy, 5-(2′-ethylhexyloxy)-*p*-phenylenevinylene] (MEH−PPV) [114]. The energetics and charge transfer mechanics of quenching upon potential modulation were examined. It was shown that injected holes are able to quench the excited state of the polymer due to electron transfer as well as energy transfer. Single fluorene-based F8BT particles were also studied. The investigation of single particles allowed the discrimination of subpopulations of particles that behave differently towards an applied potential. Using this technique, reversible and irreversible quenching as well as hole injection and removal were examined (see Fig. 27) [115,116]. Montilla et al. studied PPV and Poly-[2,7-(fluorene)-1,4-(phenylene)] polymer films and examined charge transfer kinetics and quenching due to swelling and other processes [117,118].

Often, electrofluorochromic polymers are copolymers consisting of different constituents. By appropriate choice of constituents the solubility, bandgap, morphology and HOMO and LUMO energy levels can be tuned [112]. Sun et al. synthesized a triphenylamine-based polymer and used fluorene groups to protect the para-position from degradation as well as increase solubility and processability [119]. In some cases, a reduction in solubility can also be achieved. Montilla et al. attached perylene diimide (PDI) fluorophores to a fluorescent poly(fluorene-alt-phenylene) backbone [120]. It was shown that the PDI-groups aggregate, causing their fluorescence to be quenched and their electron accepting ability to be enhanced. Attachment of the appropriate amount of PDI units and matching of energy levels increased the efficiency of electron transfer-based quenching. The neutral polymer displayed a low quantum yield due to this electron transfer-based quenching. Upon reduction, electrons were injected into the aggregates and electron transfer-based quenching was inhibited. After reduction of aggregates, the free PDI units were reduced, quenching their fluorescence. Application of more negative potentials resulted in the formation of PDI dianions and quenching of the backbone due to energy transfer to these dianions.

Aggregation can also enhance fluorescence, as was shown for cyanotriphenylamines, displaying a much higher quantum yield in solid state than in solution [131]. Oxidation of the triphenylamine-groups resulted in both fluorescence quenching and the appearance of color [128]. Comparison between the polyamide and polyimide form, shown in Fig. 28, showed better performance by the polyamide. This polyamide was later compared to a highly conjugated cyanotriphenylamine by Wu et al. also shown in Fig. 28 [130]. Conjugation afforded faster switching as well as one of the highest contrast ratios seen, attributed to the fast charge transport.

Kuo et al. combined three different polymer constituents to obtain a copolymer with their combined properties [127]. Blue fluorescent fluorene and redox-active triphenylamine groups were combined with urea, whose polymers possess a high mechanical and thermal stability, a high quantum yield and good conductivity. The result was an electroactive polymer with blue fluorescence and enhanced redox stability as the dipolar urea groups stabilized the triphenylamine radicals. Further addition of an electron-deficient benzothiazole group, as shown in Fig. 29a allowed the emitted color to be tuned and shifted to the yellow spectrum, depending on the amount incorporated into the copolymer. By blending the blue and yellow emitting copolymers, a device with white emission could be realized [129]. Alternatively, separation of the two polymers into two separate layers, each attached to an electrode, allows them to be individually addressed, creating a multifluorescent device [132], shown in Fig. 29b. The device emitted white fluorescent light when both polymers were in their neutral state. Upon oxidation of one layer only the emission of the other layer could be detected.

Such a bilayer device was also fabricated by Kim et al. using an electrofluorochromic anthracene film and an electrochromic poly(3,4-ethylenedioxythiophene) (PEDOT) film [133]. As the anthracene layer is quenched upon oxidation and the PEDOT layer only displays color when reduced, switching between the blue fluorescence of the anthracene and the yellow color of the PEDOT was possible. In this case, iodine was used as dopant for PEDOT and quencher for anthracene to enhance the contrast ratio and switching time.

Similar to molecular dyads, ions can quench the fluorescence of polymers due to electron or energy transfer. This effect can be used to introduce electrochemical switching in fluorescent polymers which cannot be reversibly oxidized. The group of Kim was able to modulate the fluorescence of triazine-bridged PPV polymers using iodine [122,124]. It was found that the quenching efficiency depended on the redox state of iodide, increasing in the order $I^- < I_2 < I_3^-$. Iodine was also used as a quencher for the methylene-bridged anthracene polymer mentioned above [123]. Unlike PPV-based polymers, anthracene-based polymers can exhibit electrofluorochromism without the addition of iodine. However, iodide was found to improve the contrast ratio.

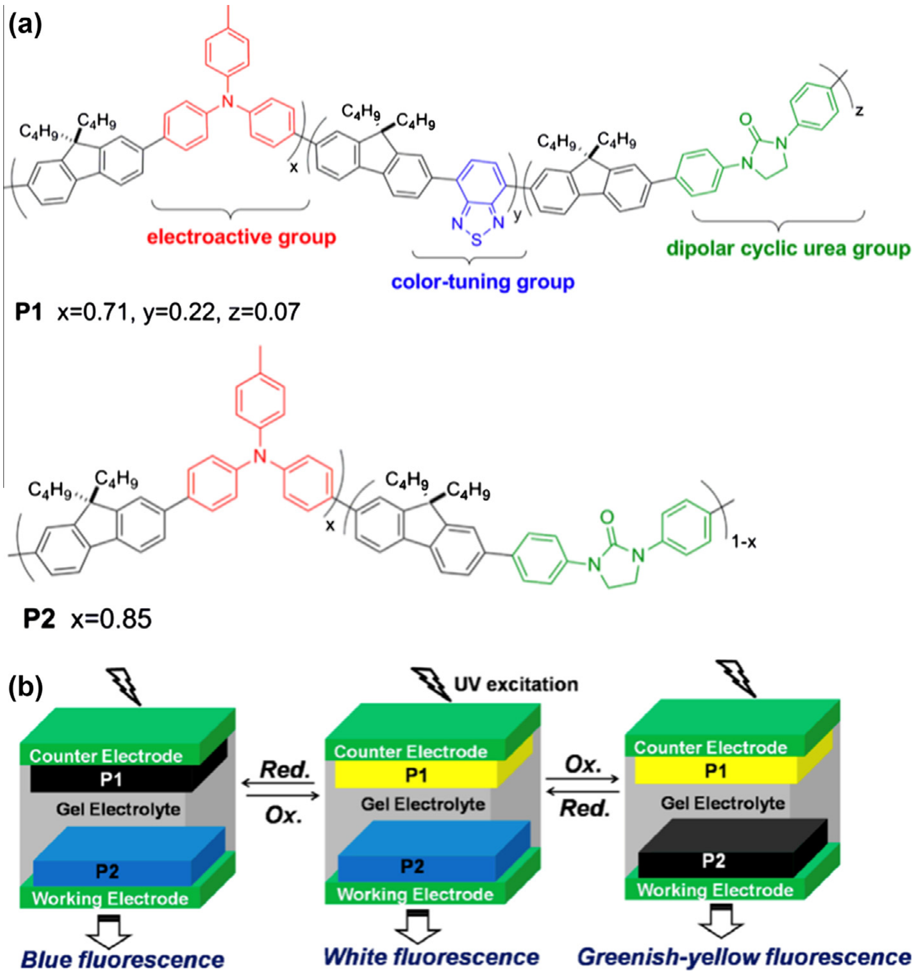

Fig. 29. (a) Two copolymers containing fluorescent fluorene, electroactive triphenylamine and stabilizing cyclic urea groups with and without color-tuning benzothiazole groups, and (b) a two layer device from these copolymers with three possible emission states. Reprinted with permission from Ref. [132]). Copyright 2014 American Chemical Society.

The ability of ions to quench polymer fluorescence can also be used for sensing. For this application, the possibility of multiple recognition sites combined with a high conductivity can result in a high sensitivity [134]. Ding et al. utilized an electrofluorochromic polymer as a selective cyanide sensor [135]. Electron-poor benzothiazole groups were used as binding sites for the electron-rich cyanide, whereas carbazole served as electroactive group and fluorophore, and hexylthiophene was used as separator. Upon oxidation, the polymer was quenched. The addition of cyanide reduced the degree of quenching, restoring fluorescence depending on the amount of cyanide. This interaction was proven to be very selective when compared to other ions and nucleophiles. However, as cyanide is often present in aqueous solution, hydrophobicity of the polymer becomes a problem. To overcome this, a nanostructured polymer film was synthesized with the aim of reducing the diffusive distance of the cyanide ion inside the film as well as increasing the contact area between polymer and electrolyte [135]. Electropolymerization was used to attain a film consisting of polymeric nanogranules. Upon testing, it was observed that an increase in the water content caused an increase in the oxidation potential needed for fluorescence quenching to occur. In a fully aqueous solution, the potential reached a level where degradation of the polymer was likely to occur. However, an electrolyte with 67% water could still be used. Theoretical calculations showed that upon binding, cyanide donates electrons to the oxidized polymer, partially reducing it again and restoring fluorescence. Electropolymerization can also be used to obtain polymeric fibers as shown by Kawabata et al. [126]. The electrofluorochromic fibers were shown to give fluorescence emission perpendicular to the fiber axis, as is shown in Fig. 30.

Structural assembly is important for both the charge transport as well as the optical properties of polymers. Yang et al. were able to control the structural assembly of a polymer as well as to modify its chiral properties electrochemically [136]. The polymer backbone consisted of 3,4-propylenedioxythiophene (ProDOT), a monomer with a chiral alkyl chain. Phenylene groups were added to obtain a higher degree of rotational freedom around the polymer chain. Circular dichroism indicated a helical packing of the polymer. Oxidation was accompanied by a quenching of the fluorescence and a change in color as well

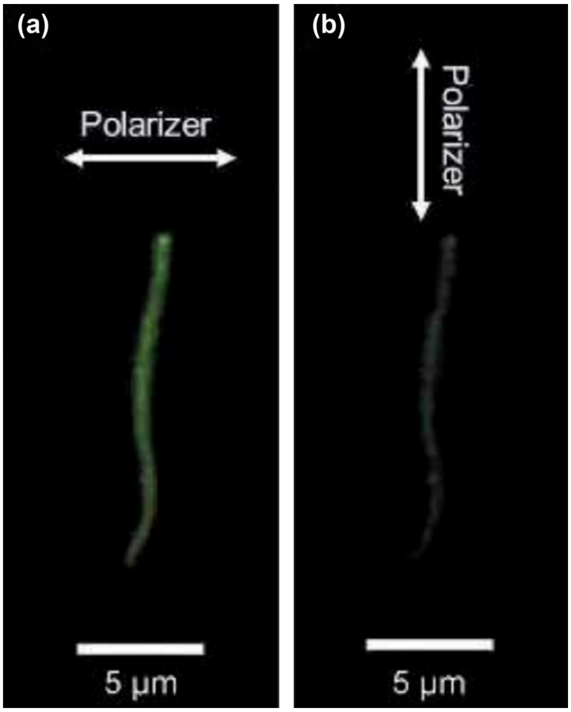

Fig. 30. Scanning electron microscopy images of nanofibers with polarized emission. Copyright 2015 Wiley. Used with permission from Ref. [126].

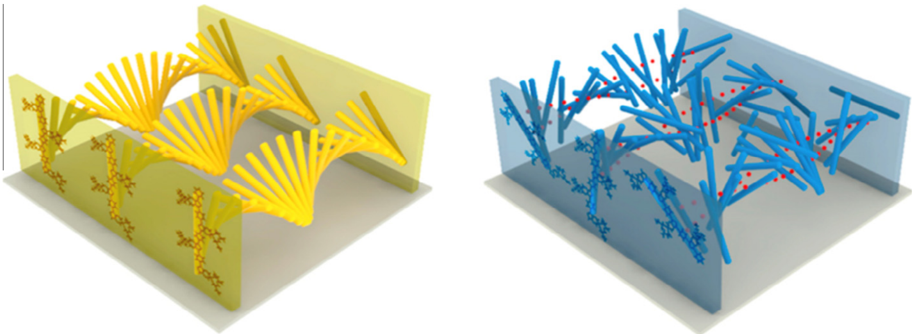

Fig. 31. Schematic showing the helical packing (left) and unwinding upon oxidation (right) of the chiral polymer. Reprinted with permission from Ref. [136]. Copyright 2014 American Chemical Society.

as a conformation change. To maintain charge neutrality, injection of a charge into the polymer is accompanied by anion diffusion from the electrolyte. As shown in Fig. 31, this diffusion results in swelling and loosening of the coiled helical packing. This changed the CD-spectra of the polymer, allowing changes in electrochemistry to be seen using CD.

Structuring of polymers at bulk level is also possible. Whereas this is usually done using spin coating, photopatterning is also possible [125]. Using the photosensitive oxadiazole group, a poly(1,3,4-oxadiazole) thin film was synthesized. Interestingly, quenching occurred upon reduction instead of oxidation.

5. Summary and outlook

Out of the different classes of electrofluorochromic molecules, synthetic dyads are the most diverse. The possible choice of the redox group and attached fluorophore allows a wide variation of different organic or inorganic structures. A potential application of the dyads resides in the field of functional building blocks for molecular electronics. However, an implementation in a real-world application does not lie foreseeably in the near future; much more research in the integration of molecules in devices is necessary.

Applications in sensing are established, with a diverse range of analytes such as cyanide [135], $H_2PO_4^-$ ions [32] or (metal) ions [12] in general. We believe that the trend of the development of new practical sensors for novel analytes will continue.

Finally, the field of electrofluorochromic display devices is most recent with an increasing number of materials, mostly polymers, being developed in the past years. Electrofluorochromic devices rely on the straightforward fabrication of sandwiching gels or polymers between transparent electrodes. Here, more advanced fabrication methods (such as microfabrication) could yield improvements in the future. Whether redox-switchable fluorescent materials will be able to compete with established display technologies in real-word illumination will ultimately depend on their lifetime, switching time, quantum yield, contrast ratio and cost.

References

[1] P. Audebert, F. Miomandre, Electrofluorochromism: from molecular systems to set-up and display, Chem. Sci. 4 (2013) 575, http://dx.doi.org/10.1039/c2sc21503a.

[2] P.M.S. Monk, R.J. Mortimer, D.R. Rosseinsky, Electrochromism: Fundamentals and Applications, John Wiley & Sons, 2008.

[3] L. Hu, G. Xu, Applications and trends in electrochemiluminescence, Chem. Soc. Rev. 39 (2010) 3275–3304, http://dx.doi.org/10.1039/b923679c.

[4] V. Goulle, A. Harriman, J.-M. Lehn, An electro-photoswitch: redox switching of the luminescence of a bipyridine metal complex, J. Chem. Soc. Chem. Commun. (1993) 1034–1063, http://dx.doi.org/10.1039/c39930001034.

[5] R.G. Compton, R.G. Wellington, Spectrofluorimetric hydrodynamic voltammetry: the investigation of electrode reaction mechanisms, J. Phys. Chem. 98 (1994) 270–273, http://dx.doi.org/10.1021/j100052a045.

[6] R.G. Compton, J. Winkler, D.J. Riley, S.D. Bearpark, Spectrofluorimetric hydrodynamic voltammetry: investigation of reactions at solid/liquid interfaces, J. Phys. Chem. 98 (1994) 6818–6825, http://dx.doi.org/10.1021/j100078a026.

[7] K. Mathwig, T.J. Aartsma, G.W. Canters, S.G. Lemay, Nanoscale methods for single-molecule electrochemistry, Annu. Rev. Anal. Chem. 7 (2014) 383–404, http://dx.doi.org/10.1146/annurev-anchem-062012-092557.

[8] Y. Kim, E. Kim, G. Clavier, P. Audebert, New tetrazine-based fluoroelectrochromic window; modulation of the fluorescence through applied potential, Chem. Commun. (Camb) (2006) 3612–3614, http://dx.doi.org/10.1039/b608312a.

[9] U. Resch-Genger, G. Hennrich, Fluorescent redox-switchable devices, Top. Fluoresc. Spectrosc. 9 (2005) 189–218.

[10] C.D. Geddes, J.R. Lakowicz (Eds.), Topics in Fluorescence Spectroscopy, Springer, US, Boston, MA, 2005, http://dx.doi.org/10.1007/b101259.

[11] B. Valeur, M.N. Berberan-Santos, Molecular Fluorescence: Principles and Applications, John Wiley & Sons, 2012.

[12] A.P. de Silva, T.S. Moody, G.D. Wright, Fluorescent PET (photoinduced electron transfer) sensors as potent analytical tools, Analyst 134 (2009) 2385–2393, http://dx.doi.org/10.1039/b912527m.

[13] L. Fabbrizzi, M. Licchelli, G. De Santis, N. Sardone, A.H. Velders, Fluorescence redox switching systems operating through metal centres: the NiIII/NiII couple, Chem. – A Eur. J. 2 (1996) 1243–1250, http://dx.doi.org/10.1002/chem.19960021010.

[14] Y.-X. Yuan, Y. Chen, Y.-C. Wang, C.-Y. Su, S.-M. Liang, H. Chao, et al, Redox responsive luminescent switch based on a ruthenium(II) complex [Ru(bpy)2 (PAIDH)]2+, Inorg. Chem. Commun. 11 (2008) 1048–1050, http://dx.doi.org/10.1016/j.inoche.2008.05.026.

[15] F. Miomandre, R.B. Pansu, J.F. Audibert, A. Guerlin, C.R. Mayer, Electrofluorochromism of a ruthenium complex investigated by time resolved TIRF microscopy coupled to an electrochemical cell, Electrochem. Commun. 20 (2012) 83–87, http://dx.doi.org/10.1016/j.elecom.2012.03.030.

[16] A.C. Benniston, G. Copley, K.J. Elliott, R.W. Harrington, W. Clegg, Redox-controlled fluorescence modulation in a BODIPY-quinone dyad, Eur. J. Org. Chem. (2008) 2705–2713, http://dx.doi.org/10.1002/ejoc.200800191.

[17] R.A. Illos, D. Shamir, L.J.W. Shimon, I. Zilbermann, S. Bittner, N-Dansyl-carbazoloquinone; a chemical and electrochemical fluorescent switch, Tetrahedron Lett. 47 (2006) 5543–5546, http://dx.doi.org/10.1016/j.tetlet.2006.05.139.

[18] R.M. Kierat, B.M.B. Thaler, R. Krämer, A fluorescent redox sensor with tuneable oxidation potential, Bioorg. Med. Chem. Lett. 20 (2010) 1457–1459, http://dx.doi.org/10.1016/j.bmcl.2009.03.171.

[19] P.S. Guin, S. Das, P.C. Mandal, Electrochemical reduction of quinones in different media: a review, Int. J. Electrochem. 2011 (2011) 1–22, http://dx.doi.org/10.4061/2011/816202.

[20] P. Ravichandiran, S. Vasanthkumar, Synthesis of heterocyclic naphthoquinone derivatives as potent organic fluorescent switching molecules, J. Taibah Univ. Sci. 9 (2015) 538–547, http://dx.doi.org/10.1016/j.jtusci.2014.12.003.

[21] S. Arounaguiri, B.G. Maiya, "Electro-Photo Switch" and "Molecular Light Switch" devices based on Ruthenium(II) complexes of modified dipyridophenazine ligands: modulation of the photochemical function through ligand design, Inorg. Chem. 38 (1999) 842–843, http://dx.doi.org/10.1021/ic981109z.

[22] A. Ambroise, B.G. Maiya, Ruthenium(II) complexes of redox-related, modified dipyridophenazine ligands: synthesis, characterization, and dna interaction, Inorg. Chem. 39 (2000) 4256–4263, http://dx.doi.org/10.1021/ic991468+.

[23] D. Canevet, M. Sallé, G. Zhang, D. Zhang, D. Zhu, Tetrathiafulvalene (TTF) derivatives: key building-blocks for switchable processes, Chem. Commun. (2009) 2245–2269, http://dx.doi.org/10.1039/b818607n.

[24] C. Farren, C.A. Christensen, S. FitzGerald, M.R. Bryce, A. Beeby, Synthesis of novel phthalocyanine−tetrathiafulvalene hybrids; intramolecular fluorescence quenching related to molecular geometry, J. Org. Chem. 67 (2002) 9130–9139, http://dx.doi.org/10.1021/jo020340y.

[25] X. Guo, D. Zhang, H. Zhang, Q. Fan, W. Xu, X. Ai, et al, Donor–acceptor–donor triads incorporating tetrathiafulvalene and perylene diimide units: synthesis, electrochemical and spectroscopic studies, Tetrahedron 59 (2003) 4843–4850, http://dx.doi.org/10.1016/S0040-4020(03)00700-2.

[26] S. Leroy-Lhez, J. Baffreau, L. Perrin, E. Levillain, M. Allain, M.-J. Blesa, et al, Tetrathiafulvalene in a perylene-3,4:9,10-bis(dicarboximide)-based dyad: a new reversible fluorescence-redox dependent molecular system, J. Org. Chem. 70 (2005) 6313–6320, http://dx.doi.org/10.1021/jo050766n.

[27] Y. Zhang, Z. Xu, H. Qiu, G. Lai, Y. Shen, Synthesis, spectroscopic and electrochemical properties of the perylene–tetrathiafulvalene dyads, J. Photochem. Photobiol. A Chem. 204 (2009) 32–38, http://dx.doi.org/10.1016/j.jphotochem.2009.02.016.

[28] H. Li, J.O. Jeppesen, E. Levillain, J. Becher, A mono-TTF-annulated porphyrin as a fluorescence switch, Chem. Commun. (2003) 846–847, http://dx.doi.org/10.1039/b212456d.

[29] C. Loosli, C. Jia, S.-X. Liu, M. Haas, M. Dias, E. Levillain, A. Neels, G. Labat, A. Hauser, S. Decurtins, Synthesis and electrochemical and photophysical studies of tetrathiafulvalene-annulated phthalocyanines, J. Org. Chem. 70 (2005) 4988–4992, http://dx.doi.org/10.1021/jo0501801.

[30] G. Zhang, D. Zhang, X. Guo, D. Zhu, A new redox-fluorescence switch based on a triad with tetrathiafulvalene and anthracene units, Org. Lett. 6 (2004) 1209–1212, http://dx.doi.org/10.1021/ol036511i.

[31] N.L. Bill, J.M. Lim, C.M. Davis, S. Bähring, J.O. Jeppesen, D. Kim, et al, Π-Extended tetrathiafulvalene BODIPY (ex-TTF-BODIPY): a redox switched "on-off-on" electrochromic system with two near-infrared fluorescent outputs, Chem. Commun. (Camb) 50 (2014) 6758–6761, http://dx.doi.org/10.1039/c4cc02567a.

[32] H. Lu, W. Xu, D. Zhang, C. Chen, D. Zhu, A novel multisignaling optical-electrochemical chemosensor for anions based on tetrathiafulvalene, Org. Lett. 7 (2005) 4629–4632, http://dx.doi.org/10.1021/ol051735h.

[33] G. Clavier, P. Audebert, S-Tetrazines as building blocks for new functional molecules and molecular materials, Chem. Rev. 110 (2010) 3299–3314, http://dx.doi.org/10.1021/cr900357e.

[34] Y. Kim, J. Do, E. Kim, G. Clavier, L. Galmiche, P. Audebert, Tetrazine-based electrofluorochromic windows: modulation of the fluorescence through applied potential, J. Electroanal. Chem. 632 (2009) 201–205, http://dx.doi.org/10.1016/j.jelechem.2008.07.022.

[35] C. Dumas-Verdes, F. Miomandre, E. Lépicier, O. Galangau, T.T. Vu, G. Clavier, et al, BODIPY-tetrazine multichromophoric derivatives, Eur. J. Org. Chem. 2010 (2010) 2525–2535, http://dx.doi.org/10.1002/ejoc.200900874.

[36] C. Quinton, V. Alain-Rizzo, C. Dumas-Verdes, G. Clavier, F. Miomandre, P. Audebert, Design of new tetrazine–triphenylamine bichromophores – fluorescent switching by chemical oxidation, Eur. J. Org. Chem. 2012 (2012) 1394–1403, http://dx.doi.org/10.1002/ejoc.201101584.

[37] C. Quinton, V. Alain-Rizzo, C. Dumas-Verdes, F. Miomandre, P. Audebert, Tetrazine–triphenylamine dyads: influence of the nature of the linker on their properties, Electrochim. Acta 110 (2013) 693–701, http://dx.doi.org/10.1016/j.electacta.2013.02.113.

[38] S. Seo, Y. Kim, Q. Zhou, G. Clavier, P. Audebert, E. Kim, White electrofluorescence switching from electrochemically convertible yellow fluorescent dyad, Adv. Funct. Mater. 22 (2012) 3556–3561, http://dx.doi.org/10.1002/adfm.201102153.

[39] S.V. Eliseeva, J.-C.G. Bunzli, Lanthanide luminescence for functional materials and bio-sciences, Chem. Soc. Rev. 39 (2010) 189–227, http://dx.doi.org/10.1039/B905604C.

[40] M. Yano, K. Matsuhira, M. Tatsumi, Y. Kashiwagi, M. Nakamoto, M. Oyama, et al, "ON-OFF" switching of europium complex luminescence coupled with a ligand redox process, Chem. Commun. (Camb) 48 (2012) 4082–4084, http://dx.doi.org/10.1039/c2cc31078c.

[41] L. Norel, E. Di Piazza, M. Feng, A. Vacher, X. He, T. Roisnel, et al, Lanthanide sensitization with ruthenium carbon-rich complexes and redox commutation of near-IR luminescence, Organometallics 33 (2014) 4824–4835, http://dx.doi.org/10.1021/om500059d.

[42] Y. Yamada, Y. Tomiyama, A. Morita, M. Ikekita, S. Aoki, BODIPY-based fluorescent redox potential sensors that utilize reversible redox properties of flavin, ChemBioChem 9 (2008) 853–856, http://dx.doi.org/10.1002/cbic.200700718.

[43] P. Yan, M.W. Holman, P. Robustelli, A. Chowdhury, F.I. Ishak, D.M. Adams, Molecular switch based on a biologically important redox reaction, J. Phys. Chem. B 109 (2005) 130–137, http://dx.doi.org/10.1021/jp045793g.

[44] J.J. Davis, H. Burgess, G. Zauner, S. Kuznetsova, J. Salverda, T. Aartsma, et al, Monitoring interfacial bioelectrochemistry using a FRET switch, J. Phys. Chem. B 110 (2006) 20649–20654, http://dx.doi.org/10.1021/jp0630525.

[45] L.C. Tabares, A. Gupta, T.J. Aartsma, G.W. Canters, Tracking electrons in biological macromolecules: from ensemble to single molecule, Molecules 19 (2014) 11660–11678, http://dx.doi.org/10.3390/molecules190811660.

[46] R.O. Al-Kaysi, J.L. Bourdelande, I. Gallardo, G. Guirado, J. Hernando, Investigation of an acid–base and redox molecular switch: from bulk to the single-molecule level, Chem. – A Eur. J. 13 (2007) 7066–7074, http://dx.doi.org/10.1002/chem.200700236.

[47] J. Otsuki, K. Sato, M. Tsujino, N. Okuda, K. Araki, M. Seno, Ruthenium complexes containing an azobipyridine ligand as redox-responsive molecular switches, Chem. Lett. (1996) 847–848, http://dx.doi.org/10.1246/cl.1996.847.

[48] T. Suzuki, T. Takeda, E. Ohta, K. Wada, R. Katoono, H. Kawai, et al, Bis(10-methylacridinium)s as a versatile platform for redox-active functionalized dyes and novel structures, Chem. Rec. 15 (2015) 280–294, http://dx.doi.org/10.1002/tcr.201402073.

[49] T. Suzuki, Y. Kuroda, K. Wada, Y. Sakano, R. Katoono, K. Fujiwara, et al, Oxidative protonolysis of the expanded central C–C bond in a Di(spiroacridan)-type Hexaphenylethane derivative accompanied by UV-vis, FL, and CD spectral changes, Chem. Lett. 1 (2014) 887–889, http://dx.doi.org/10.1246/cl.140192.

[50] T. Suzuki, A. Migita, H. Higuchi, H. Kawai, K. Fujiwara, T. Tsuji, A novel redox switch for fluorescence: drastic UV–vis and fluorescence spectral changes upon electrolysis of a hexaphenylethane derivative of 10,10′-dimethylbiacridan, Tetrahedron Lett. 44 (2003) 6837–6840, http://dx.doi.org/10.1016/S0040-4039(03)01717-9.

[51] W. Ma, L.-X. Qin, F.-T. Liu, Z. Gu, J. Wang, Z.G. Pan, et al, Ubiquinone-quantum dot bioconjugates for in vitro and intracellular complex I sensing, Sci. Rep. 3 (2013) 1537, http://dx.doi.org/10.1038/srep01537.

[52] L. Jin, Y. Fang, D. Wen, L. Wang, E. Wang, S. Dong, Reversibly electroswitched quantum dot luminescence in aqueous solution, ACS Nano 5 (2011) 5249–5253, http://dx.doi.org/10.1021/nn201455a.

[53] F. Miomandre, S. Stancheva, J.-F. Audibert, A. Brosseau, R.B. Pansu, M. Lepeltier, et al, Gold and silver nanoparticles functionalized by luminescent iridium complexes: synthesis and photophysical and electrofluorochromic properties, J. Phys. Chem. C 117 (2013) 12806–12814, http://dx.doi.org/10.1021/jp312625x.

[54] S. Seo, C. Allain, J. Na, S. Kim, X. Yang, C. Park, et al, Electrofluorescence switching of tetrazine-modified TiO_2 nanoparticles, Nanoscale 5 (2013) 7321–7327, http://dx.doi.org/10.1039/c3nr01648j.

[55] J. Otsuki, T. Akasaka, K. Araki, Molecular switches for electron and energy transfer processes based on metal complexes, Coord. Chem. Rev. 252 (2008) 32–56, http://dx.doi.org/10.1016/j.ccr.2007.03.005.

[56] M. Di Casa, L. Fabbrizzi, M. Licchelli, A. Poggi, D. Sacchi, M. Zema, A novel fluorescence redox switch based on the formal NiII/NiI couple, J. Chem. Soc. Dalton Trans. (2001) 1671–1675, http://dx.doi.org/10.1039/b101310f.

[57] V. Amendola, L. Fabbrizzi, P. Pallavicini, E. Sartirana, A. Taglietti, Monitoring the redox-driven assembly/disassembly of a dicopper(I) helicate with an auxiliary fluorescent probe, Inorg. Chem. 42 (2003) 1632–1636, http://dx.doi.org/10.1021/ic026061a.

[58] I. Yilmaz, In situ monitoring of metallation of metal-free phthalocyaninevia UV–Vis and steady-state fluorescence techniques. Thin-layer UV–Vis and fluorescence spectroelectrochemistry of a new non-aggregating and electrochromic manganese(3+) phthalocyanine, New J. Chem. 32 (2008) 37–46, http://dx.doi.org/10.1039/B709520A.

[59] I. Yilmaz, Synthesis, electrochemistry, thin-layer UV–vis and fluorescence spectroelectrochemistry of a new salicylaldimine ligand and its copper complex, Transition Met. Chem. 33 (2007) 259–265, http://dx.doi.org/10.1007/s11243-007-9039-6.

[60] R. Martínez, I. Ratera, A. Tárraga, P. Molina, J. Veciana, A simple and robust reversible redox-fluorescence molecular switch based on a 1,4-disubstituted azine with ferrocene and pyrene units, Chem. Commun. (2006) 3809–3811, http://dx.doi.org/10.1039/b608264e.

[61] R. Zhang, Z. Wang, Y. Wu, H. Fu, J. Yao, A novel redox-fluorescence switch based on a triad containing ferrocene and perylene diimide units, Org. Lett. 10 (2008) 3065–3068, http://dx.doi.org/10.1021/ol801053t.

[62] R. Zhang, Y. Wu, Z. Wang, W. Xue, H. Fu, J. Yao, Effects of photoinduced electron transfer on the rational design of molecular fluorescence switch, J. Phys. Chem. C 113 (2009) 2594–2602, http://dx.doi.org/10.1021/jp809135j.

[63] O. Galangau, I. Fabre-Francke, S. Munteanu, C. Dumas-Verdes, G. Clavier, R. Méallet-Renault, et al, Electrochromic and electrofluorochromic properties of a new boron dipyrromethene–ferrocene conjugate, Electrochim. Acta 87 (2013) 809–815, http://dx.doi.org/10.1016/j.electacta.2012.09.048.

[64] E. Maligaspe, T.J. Pundsack, L.M. Albert, Y.V. Zatsikha, P.V. Solntsev, D.A. Blank, et al, Synthesis and charge-transfer dynamics in a ferrocene-containing organoboryl aza-BODIPY donor–acceptor triad with boron as the hub, Inorg. Chem. 54 (2015) 4167–4174, http://dx.doi.org/10.1021/acs.inorgchem.5b00494.

[65] Y. Zhou, K.T. Ngo, B. Zhang, Y. Feng, J. Rochford, Synthesis, electronic and photophysical characterization of π-conjugated meso-ferrocenyl-porphyrin fluorescent redox switches, Organometallics 33 (2014) 7078–7090, http://dx.doi.org/10.1021/om500697g.

[66] J. Rochford, A.D. Rooney, M.T. Pryce, Redox control of meso-zinc(II) ferrocenylporphyrin based fluorescence switches, Inorg. Chem. 46 (2007) 7247–7249, http://dx.doi.org/10.1021/ic0703326.

[67] M. Tropiano, N.L. Kilah, M. Morten, H. Rahman, J.J. Davis, P.D. Beer, et al, Reversible luminescence switching of a redox-active ferrocene-europium dyad, J. Am. Chem. Soc. 133 (2011) 11847–11849, http://dx.doi.org/10.1021/ja203069s.

[68] R.C. Benson, R.A. Meyer, M.E. Zaruba, G.M. McKhann, Cellular autofluorescence – is it due to flavins?, J Histochem. Cytochem. 27 (1979) 44–48, http://dx.doi.org/10.1177/27.1.438504.

[69] S. Huang, A.A. Heikal, W.W. Webb, Two-photon fluorescence spectroscopy and microscopy of NAD(P)H and flavoprotein, Biophys. J. 82 (2002) 2811–2825, http://dx.doi.org/10.1016/S0006-3495(02)75621-X.

[70] J.V. Rocheleau, W.S. Head, D.W. Piston, Quantitative NAD(P)H/flavoprotein autofluorescence imaging reveals metabolic mechanisms of pancreatic islet pyruvate response, J. Biol. Chem. 279 (2004) 31780–31787, http://dx.doi.org/10.1074/jbc.M314005200.

[71] A.A. Heikal, Intracellular coenzymes as natural biomarkers for metabolic activities and mitochondrial anomalies, Biomarkers Med. 4 (2010) 241–263. <http://www.futuremedicine.com/doi/abs/10.2217/bmm.10.1> (accessed November 29, 2015)..

[72] S.F. Velick, Fluorescence spectra and polarization of glyceraldehyde-3-phosphate and lactic dehydrogenase coenzyme complexes, J. Biol. Chem. 233 (1958) 1455–1467. <http://www.ncbi.nlm.nih.gov/pubmed/13610856> (accessed November 24, 2015)..

[73] R.D. Braun, An electrochemical study of flavin adenine dinucleotide, J. Electrochem. Soc. 124 (1977) 1342–1347, http://dx.doi.org/10.1149/1.2133651.

[74] S. Webers, E. Schleicher, Flavins and Flavoproteins, Springer, New York, NY, 2014, http://dx.doi.org/10.1007/978-1-4939-0452-5.

[75] V.I. Birss, H. Elzanowska, R.A. Turner, The electrochemical behavior of flavin adenine dinucleotide in neutral solutions, Can. J. Chem. 66 (1988) 86–96, http://dx.doi.org/10.1139/v88-013.

[76] P.A. van den Berg, J. Widengren, M.A. Hink, R. Rigler, A.J.W. Visser, Fluorescence correlation spectroscopy of flavins and flavoenzymes: photochemical and photophysical aspects, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 57 (2001) 2135–2144, http://dx.doi.org/10.1016/S1386-1425(01)00494-2.

[77] V. Joosten, W.J.H. van Berkel, Flavoenzymes, Curr. Opin. Chem. Biol. 11 (2007) 195–202, http://dx.doi.org/10.1016/j.cbpa.2007.01.010.

[78] C.C. Fjeld, W.T. Birdsong, R.H. Goodman, Differential binding of NAD+ and NADH allows the transcriptional corepressor carboxyl-terminal binding protein to serve as a metabolic sensor, Proc. Natl. Acad. Sci. USA 100 (2003) 9202–9207, http://dx.doi.org/10.1073/pnas.1633591100.

[79] C. Lei, J. Deng, Hydrogen peroxide sensor based on coimmobilized methylene green and horseradish peroxidase in the same montmorillonite-modified bovine serum albumin–glutaraldehyde matrix on a glassy carbon electrode surface, Anal. Chem. 68 (1996) 3344–3349, http://dx.doi.org/10.1021/ac960291n.

[80] C. Lei, D. Hu, E. Ackerman, Clay nanoparticle-supported single-molecule fluorescence spectroelectrochemistry, Nano Letters 9 (2009) 655–658, http://dx.doi.org/10.1021/nl802998e.

[81] C. Lei, D. Hu, E.J. Ackerman, Single-molecule fluorescence spectroelectrochemistry of cresyl violet, Chem. Commun. (Camb) 7345 (2008) 5490–5492, http://dx.doi.org/10.1039/b812161c.

[82] H.P. Lu, L. Xun, X.S. Xie, Single-molecule enzymatic dynamics, Science 282 (1998) 1877–1882, http://dx.doi.org/10.1126/science.282.5395.1877.

[83] Q. Xue, E.S. Yeung, Differences in the chemical reactivity of individual molecules of an enzyme, Nature 373 (1995) 681–683, http://dx.doi.org/10.1038/373681a0.

[84] K. Mathwig, Q. Chi, S.G. Lemay, L. Rassaei, Handling and sensing of single enzyme molecules: from fluorescence detection towards nanoscale electrical measurements, ChemPhysChem 17 (2016) 452–457, http://dx.doi.org/10.1002/cphc.201500686.

[85] L.P. Zaino, D.A. Grismer, D. Han, G.M. Crouch, P.W. Bohn, Single occupancy spectroelectrochemistry of freely diffusing flavin mononucleotide in zero-dimensional nanophotonic structures, Faraday Discuss. (2015), http://dx.doi.org/10.1039/C5FD00072F.

[86] C.T. Dooley, T.M. Dore, G.T. Hanson, W.C. Jackson, S.J. Remington, R.Y. Tsien, Imaging dynamic redox changes in mammalian cells with green fluorescent protein indicators, J. Biol. Chem. 279 (2004) 22284–22293, http://dx.doi.org/10.1074/jbc.M312847200.

[87] G.T. Hanson, R. Aggeler, D. Oglesbee, M. Cannon, R.A. Capaldi, R.Y. Tsien, et al, Investigating mitochondrial redox potential with redox-sensitive green fluorescent protein indicators, J. Biol. Chem. 279 (2004) 13044–13053, http://dx.doi.org/10.1074/jbc.M312846200.

[88] K. Jiang, C. Schwarzer, E. Lally, S. Zhang, S. Ruzin, T. Machen, et al, Expression and characterization of a redox-sensing green fluorescent protein (reduction–oxidation-sensitive green fluorescent protein) in Arabidopsis, Plant Physiol. 141 (2006) 397–403, http://dx.doi.org/10.1104/pp.106.078246.

[89] S. Munshi, R.C. Twining, R. Dahl, Alamar blue reagent interacts with cell-culture media giving different fluorescence over time: potential for false positives, J. Pharmacol. Toxicol. Methods 70 (2014) 195–198, http://dx.doi.org/10.1016/j.vascn.2014.06.005.

[90] M.M. Nociari, A. Shalev, P. Benias, C. Russo, A novel one-step, highly sensitive fluorometric assay to evaluate cell-mediated cytotoxicity, J. Immunol. Methods 213 (1998) 157–167, http://dx.doi.org/10.1016/S0022-1759(98)00028-3.

[91] A. Mariscal, R.M. Lopez-Gigosos, M. Carnero-Varo, J. Fernandez-Crehuet, Fluorescent assay based on resazurin for detection of activity of disinfectants against bacterial biofilm, Appl. Microbiol. Biotechnol. 82 (2009) 773–783, http://dx.doi.org/10.1007/s00253-009-1879-x.

[92] S. Karuppusamy, K.M. Rajasekaran, High throughput antibacterial screening of plant extracts by resazurin redox with special reference to medicinal plants of Western Ghats, Glob. J. Pharmacol. 3 (2009) 63–68. <http://www.idosi.org/gjp/3(2)09/2.pdf>.

[93] F. Bonnier, M.E. Keating, T.P. Wróbel, K. Majzner, M. Baranska, A. Garcia-Munoz, et al, Cell viability assessment using the Alamar blue assay: a comparison of 2D and 3D cell culture models, Toxicol. In Vitro 29 (2015) 124–131, http://dx.doi.org/10.1016/j.tiv.2014.09.014.

[94] T. Elavarasan, S.K. Chhina, M. Parameswaran (Ash), K. Sankaran, Resazurin reduction based colorimetric antibiogram in microfluidic plastic chip, Sens. Actuators B Chem. 176 (2013) 174–180, http://dx.doi.org/10.1016/j.snb.2012.10.011.

[95] W. Xu, H. Shen, Y.J. Kim, X. Zhou, G. Liu, J. Park, et al, Single-molecule electrocatalysis by single-walled carbon nanotubes, Nano Letters 9 (2009) 3968–3973, http://dx.doi.org/10.1021/nl900988f.

[96] T.B. Norsten, N.R. Branda, Photoregulation of fluorescence in a porphyrinic dithienylethene photochrome, J. Am. Chem. Soc. 123 (2001) 1784–1785, http://dx.doi.org/10.1021/ja005639h.

[97] R. Alfano, D. Tata, J. Cordero, P. Tomashefsky, F. Longo, M. Alfano, Laser induced fluorescence spectroscopy from native cancerous and normal tissue, IEEE J. Quantum Electron. 20 (1984) 1507–1511, http://dx.doi.org/10.1109/JQE.1984.1072322.

[98] M.I. Gaiduk, V.V. Grigoryants, A.F. Mironov, V.D. Rumyantseva, V.I. Chissov, G.M. Sukhin, Fibre-laser IR luminescence diagnostics of malignant tumours using rare earth porphyrins, J. Photochem. Photobiol. B Biol. 7 (1990) 15–20, http://dx.doi.org/10.1016/1011-1344(90)85139-N.

[99] D.B. Papkovsky, Luminescent porphyrins as probes for optical (bio)sensors, Sens. Actuators B Chem. 11 (1993) 293–300, http://dx.doi.org/10.1016/0925-4005(93)85267-E.

[100] R. Wiglusz, J. Legendziewicz, A. Graczyk, S. Radzki, P. Gawryszewska, J. Sokolnicki, Spectroscopic properties of porphyrins and effect of lanthanide ions on their luminescence efficiency, J. Alloys Compd. 380 (2004) 396–404, http://dx.doi.org/10.1016/j.jallcom.2004.03.065.

[101] W.R. Browne, M.M. Pollard, B. de Lange, A. Meetsma, B.L. Feringa, Reversible three-state switching of luminescence: a new twist to electro- and photochromic behavior, J. Am. Chem. Soc. 128 (2006) 12412–12413, http://dx.doi.org/10.1021/ja064423y.

[102] F. Miomandre, C. Allain, G. Clavier, J.F. Audibert, R.B. Pansu, P. Audebert, et al, Coupling thin layer electrochemistry with epifluorescence microscopy: an expedient way of investigating electrofluorochromism of organic dyes, Electrochem. Commun. 13 (2011) 574–577, http://dx.doi.org/10.1016/j.elecom.2011.03.013.

[103] K. Kanazawa, K. Nakamura, N. Kobayashi, High-contrast electroswitching of emission and coloration based on single-molecular fluoran derivatives, J. Phys. Chem. A 118 (2014) 6026–6033, http://dx.doi.org/10.1021/jp5060588.

[104] K. Kanazawa, K. Nakamura, N. Kobayashi, Electroswitchable optical device enabling both luminescence and coloration control consisted of fluoran dye and 1,4-benzoquinone, Sol. Energy Mater. Sol. Cells (2015), http://dx.doi.org/10.1016/j.solmat.2015.06.061.

[105] S. Seo, S. Pascal, C. Park, K. Shin, X. Yang, O. Maury, et al, NIR electrochemical fluorescence switching from polymethine dyes, Chem. Sci. 5 (2014) 1538, http://dx.doi.org/10.1039/c3sc53161a.

[106] C. Quinton, V. Alain-Rizzo, C. Dumas-Verdes, F. Miomandre, G. Clavier, P. Audebert, Redox-controlled fluorescence modulation (electrofluorochromism) in triphenylamine derivatives, RSC Adv. 4 (2014) 34332, http://dx.doi.org/10.1039/C4RA02675F.

[107] C. Quinton, V. Alain-Rizzo, C. Dumas-Verdes, F. Miomandre, G. Clavier, P. Audebert, Redox- and protonation-induced fluorescence switch in a new triphenylamine with six stable active or non-active forms, Chemistry 21 (2015) 2230–2240, http://dx.doi.org/10.1002/chem.201404622.

[108] A. Beneduci, S. Cospito, M. La Deda, L. Veltri, G. Chidichimo, Electrofluorochromism in π-conjugated ionic liquid crystals, Nat. Commun. 5 (2014) 3105, http://dx.doi.org/10.1038/ncomms4105.

[109] S. Cospito, A. Beneduci, L. Veltri, M. Salamonczyk, G. Chidichimo, Mesomorphism and electrochemistry of thienoviologen liquid crystals, Phys. Chem. Chem. Phys. 17 (2015) 17670–17678, http://dx.doi.org/10.1039/c5cp02350e.

[110] A. Beneduci, S. Cospito, M. La Deda, G. Chidichimo, Highly fluorescent thienoviologen-based polymer gels for single layer electrofluorochromic devices, Adv. Funct. Mater. 25 (2015) 1240–1247, http://dx.doi.org/10.1002/adfm.201403611.

[111] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, et al, Light-emitting diodes based on conjugated polymers, Nature 347 (1990) 539–541, http://dx.doi.org/10.1038/347539a0.

[112] X. Guo, M. Baumgarten, K. Müllen, Designing π-conjugated polymers for organic electronics, Progr. Polym. Sci. 38 (2013) 1832–1908, http://dx.doi.org/10.1016/j.progpolymsci.2013.09.005.

[113] D.T. McQuade, A.E. Pullen, T.M. Swager, Conjugated polymer-based chemical sensors, Chem. Rev. 100 (2000) 2537–2574, http://dx.doi.org/10.1021/cr9801014.

[114] A.J. Gesquiere, S.-J. Park, P.F. Barbara, F-V/SMS: a new technique for studying the structure and dynamics of single molecules and nanoparticles, J. Phys. Chem. B 108 (2004) 10301–10308, http://dx.doi.org/10.1021/jp049583f.

[115] R.E. Palacios, F.-R.F. Fan, A.J. Bard, P.F. Barbara, Single-Molecule Spectroelectrochemistry (SMS-EC), J. Am. Chem. Soc. 128 (2006) 9028–9029, http://dx.doi.org/10.1021/ja062848e.

[116] R.E. Palacios, F.-R.F. Fan, J.K. Grey, J. Suk, A.J. Bard, P.F. Barbara, Charging and discharging of single conjugated-polymer nanoparticles, Nat. Mater. 6 (2007) 680–685, http://dx.doi.org/10.1038/nmat1959.

[117] F. Montilla, R. Mallavia, In situ electrochemical fluorescence studies of PPV, J. Phys. Chem. B 110 (2006) 25791–25796, http://dx.doi.org/10.1021/jp065070s.

[118] F. Montilla, I. Pastor, C.R. Mateo, E. Morallón, R. Mallavia, Charge transport in luminescent polymers studied by in situ fluorescence spectroscopy, J. Phys. Chem. B 110 (2006) 5914–5919, http://dx.doi.org/10.1021/jp054118j.

[119] N. Sun, F. Feng, D. Wang, Z. Zhou, Y. Guan, G. Dang, et al, Novel polyamides with fluorene-based triphenylamine: electrofluorescence and electrochromic properties, RSC Adv. 5 (2015) 88181–88190, http://dx.doi.org/10.1039/C5RA16730B.

[120] F. Montilla, R. Esquembre, R. Gómez, R. Blanco, J.L. Segura, Spectroelectrochemical study of electron and energy transfer in poly(fluorene-alt-phenylene) with perylenediimide pendant groups, J. Phys. Chem. C 112 (2008) 16668–16674, http://dx.doi.org/10.1021/jp8046533.

[121] J. Yoo, T. Kwon, B.D. Sarwade, Y. Kim, E. Kim, Multistate fluorescence switching of s-triazine-bridged p-phenylene vinylene polymers, Appl. Phys. Lett. 91 (2007) 241107, http://dx.doi.org/10.1063/1.2821308.

[122] T. Kwon, B.D. Sarwade, Y. Kim, J. Yoo, E. Kim, A *p*-phenylene vinylene polymer bridged by a triazine for electro-fluorescence switching, Mol. Cryst. Liq. Cryst. 486 (2008) 101/[1143]–109/[1151], http://dx.doi.org/10.1080/15421400801917833.

[123] J. You, Y. Kim, E. Kim, Electrochemical fluorescence switching from anthracene polymer films, Mol. Cryst. Liq. Cryst. 520 (2010) 128/[404]–135/[411], http://dx.doi.org/10.1080/15421400903584226.

[124] J. Yoo, P. Jadhav, E. Kim, Fluorescence switching of a copolymer of s-triazine and p-phenylene vinylene by redox reaction of iodide ions, Mol. Cryst. Liq. Cryst. 491 (2008) 114–121, http://dx.doi.org/10.1080/15421400802329491.

[125] S. Seo, Y. Kim, J. You, B.D. Sarwade, P.P. Wadgaonkar, S.K. Menon, et al, Electrochemical fluorescence switching from a patternable poly(1,3,4-oxadiazole) thin film, Macromol. Rapid Commun. 32 (2011) 637–643, http://dx.doi.org/10.1002/marc.201000791.

[126] K. Kawabata, H. Goto, Dynamically controllable emission of polymer nanofibers: electrofluorescence chromism and polarized emission of polycarbazole derivatives, Chemistry 18 (2012) 15065–15072, http://dx.doi.org/10.1002/chem.201201471.

[127] C.-P. Kuo, Y.-S. Lin, M. Leung, Electrochemical fluorescence switching properties of conjugated polymers composed of triphenylamine, fluorene, and cyclic urea moieties, J. Polym. Sci. Part A Polym. Chem. 50 (2012) 5068–5078, http://dx.doi.org/10.1002/pola.26354.

[128] H.-J. Yen, G.-S. Liou, Flexible electrofluorochromic devices with the highest contrast ratio based on aggregation-enhanced emission (AEE)-active cyanotriphenylamine-based polymers, Chem. Commun. 49 (2013) 9797, http://dx.doi.org/10.1039/c3cc45838e.

[129] C.-P. Kuo, C.-N. Chuang, C.-L. Chang, M. Leung, H.-Y. Lian, K. Chia-Wen Wu, White-light electrofluorescence switching from electrochemically convertible yellow and blue fluorescent conjugated polymers, J. Mater. Chem. C 1 (2013) 2121, http://dx.doi.org/10.1039/c3tc00876b.

[130] J.-H. Wu, G.-S. Liou, High-performance electrofluorochromic devices based on electrochromism and photoluminescence-active novel poly(4-cyanotriphenylamine), Adv. Funct. Mater. 24 (2014) 6422–6429, http://dx.doi.org/10.1002/adfm.201401608.

[131] H.-J. Yen, C.-J. Chen, G.-S. Liou, Novel high-efficiency PL polyimide nanofiber containing aggregation-induced emission (AIE)-active cyanotriphenylamine luminogen, Chem. Commun. (Camb) 49 (2013) 630–632, http://dx.doi.org/10.1039/c2cc37857d.

[132] C. Kuo, C. Chang, C. Hu, C. Chuang, K. Ho, M. Leung, Tunable electrofluorochromic device from electrochemically controlled complementary fluorescent conjugated polymer films, ACS Appl. Mater. Interfaces 6 (2014) 17402–17409, http://dx.doi.org/10.1021/am505539g.

[133] Y. Kim, J. Kim, J. You, E. Kim, Electrochemical modulation of color and fluorescence in one cell using conducting polymers, Mol. Cryst. Liq. Cryst. 538 (2011) 39–44, http://dx.doi.org/10.1080/15421406.2011.563628.

[134] H.N. Kim, Z. Guo, W. Zhu, J. Yoon, H. Tian, Recent progress on polymer-based fluorescent and colorimetric chemosensors, Chem. Soc. Rev. 40 (2011) 79–93, http://dx.doi.org/10.1039/c0cs00058b.

[135] G. Ding, T. Lin, R. Zhou, Y. Dong, J. Xu, X. Lu, Electrofluorochromic detection of cyanide anions using a nanoporous polymer electrode and the detection mechanism, Chem. – A Eur. J. 20 (2014) 13226–13233, http://dx.doi.org/10.1002/chem.201403133.

[136] X. Yang, S. Seo, C. Park, E. Kim, Electrical chiral assembly switching of soluble conjugated polymers from propylenedioxythiophene–phenylene copolymers, Macromolecules 47 (2014) 7043–7051, http://dx.doi.org/10.1021/ma501059z.