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Multiresponsive chromogenic systems operated by light and electrical inputs

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In the framework of supramolecular chemistry, a three component system constituted by Fe^{3+}/Fe^{2+}, crystal violet lactone (CVL) and a spiropyran (SPI) leads to three coloured states, cyan, magenta and yellow, as well as a transparent state, each independently addressable by light and electrical input. The system profits from fine speciation Fe^{3+}/Fe^{2+} complexes with CVL and SPI. Redox stimulus operates the metal, leading to different coloured complexes (ionochromism), while light stimulus operates the SPI component (photochromism).

Introduction

For image production, chromogenic systems responsive to external inputs, such as light (photochromism), electrons (electrochromism) or the addition of ions (ionochromism), are required. A system possessing three coloured states, cyan, magenta and yellow, as well as a transparent state (CMYT), each of which is independently addressable, might be useful for image production. However, this is not an easy task to achieve, since multiresponsive systems usually require a high degree of complexity. Here, we show that the conjugate action of electrons and light input in a three-component system, a spiropyran (SPI), crystal violet lactone (CVL) and a developer Fe(III)/Fe(II), leads to the selective appearance of the four components of the CMYT colour model.

Photochromic systems capable of switching between two colours or more, are well described.[1–3] Spiropyrans are known for their photochromic properties,[4,5] although they also exhibit electrochromism.[6,7] Merocyanine (MERO) species can be obtained electrochemically through the formation of a reduced radical species ($NO_2^{\bullet -}$), followed by a re-oxidation of this radical.[7]

The use of electrochemistry together with light to switch between different states, so-called redox–photochromism, was recently reported,[8–10] in particular for diarylethenes[11–13] and dihydroazulene conjugates.[14–16] In these compounds, while ring opening is driven by light, ring closure is triggered by electrochemical oxidation. Polyoxometalates are another family of compounds possessing photo- and electrochromism.[11] Films consisting of poly(vinyl alcohol), a Dawson-type polyoxometalate and poly(allylamine hydrochloride) were reported to be photochromic and electrochromic from transparent to deep blue.[13] Redox photochromism was also reported for viologen in an organized solid state.[12] In a more applied direction, a photoelectrochromic cell fabricated using a transparent electrode coated with a Ag–TiO_2 nanocomposite, exhibited photochromism when the electrodes were short-circuited, while being substantially suppressed when the cell was open-circuited. The application of a voltage restores the initial state.[17] Patents describing the use of photoelectrochromic materials have also been claimed.[6,18]

In this work, profit is taken from the complexes of Fe(III)/Fe(II) with CVL and SPI. Redox stimuli operate the metal ion, leading to different coloured complexes with CVL and the coloured MERO species (electro-ionochromism), while light stimuli operate the SPI component. The present system arises within the framework of supramolecular chemistry, where the assembly of different molecules can result in properties not present in the individual components. While the SPI is photochromic (pink–colourless), crystal violet lactone ionochromic (blue–colourless) and the developer electrochromic (colourless–pale yellow),† their designed assembly leads to multiple interactions that allow the construction of the CMYT colour model.

Results and discussion

Two of the components of the system interact as shown in eqn (1) and Fig. 1. CVL solubilised in methanol is converted into the open form (CVLO) upon adding Fe(III), giving rise to an absorption spectrum (blue colour) similar to the one obtained for the parent molecule crystal violet (see Fig. 1 solid line). On the contrary, Fe(II) is unable to open the lactone of CVL (Fig. 1 dashed line).

$$\text{CVL} + \text{Fe(III)} \rightleftharpoons \text{CVLO–Fe(III)} \qquad (1)$$

Taking profit from this behaviour, it is possible to switch the mixture reversibly from blue to colourless by the action of an electrochemical input. Cyclic voltammetry shows that CVL is oxidized at potentials higher than those needed to oxidize

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† Fe(II) in water is pale yellow; however, in the concentrations used throughout this work, it is colourless.

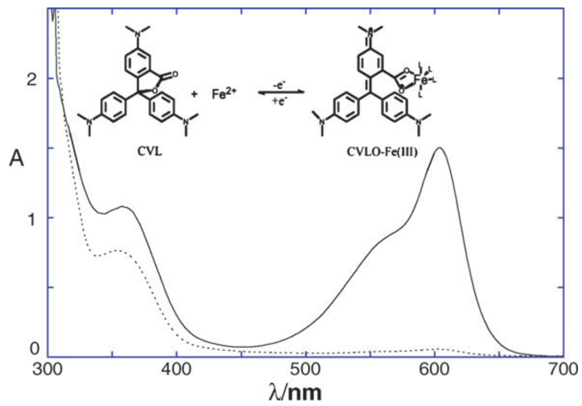


Fig. 1 Absorption spectra of 0.5 mM CVL in the presence of 1 mM Fe(III) (solid line) and 1 mM Fe(II) (dashed line). On the contrary to Fe(II), the oxidized form Fe(III) opens the lactone group of CVL.

Fe(II) to Fe(III), allowing the use of electrochemical inputs to operate only on the metal.[19] In Fig. 2, absorption spectra during reduction (A) and oxidation (B) are shown. Several cycles following the absorbance at 603 nm (C) were recorded. The system exhibits good reversibility and contrast between the two states.

The third component of the present system is the SPI reported in Scheme 1.

At thermal equilibrium in methanol, the SPI and the MERO are the major and minor species, respectively (Fig. 3). The compound used in this work exhibits the usual photochromic properties of its family, switching between transparent (SPI) and pink-red (MERO) by the action of light (eqn (2)). One interesting feature of this compound is its interaction with Fe(III) ions (eqn (3)).[20] The addition of Fe(III) to an equilibrated solution of the compound shifts the equilibrium towards the MERO form, giving rise to a yellow adduct (eqn (3) and Fig. 3). The adduct is also photoactive, and the MERO moiety can be converted to the SPI form upon irradiation at 420 nm with the concomitant releasing of the metal ion (eqn (4) and Fig. 4).

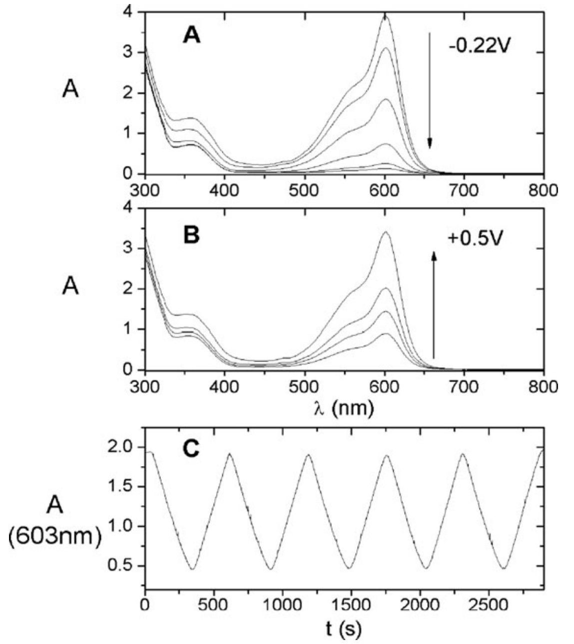
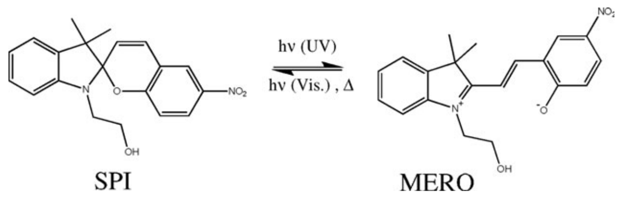


Fig. 2 Spectroelectrochemical data of a 0.1 M methanol solution of TBAP with 300 μM of CVL in the presence of 1 mM of Fe(III). Reduction (A), oxidation (B) and chronoabsorptometry (C) followed at the maximum absorbance of the open form of CVL.



Scheme 1

$$SPI \rightleftharpoons MERO \quad (2)$$

$$MERO + Fe(III) \rightleftharpoons MERO\text{–}Fe(III) \quad (3)$$

$$MERO\text{–}Fe(III) \rightleftharpoons SPI + Fe(III) \quad (4)$$

An analogous behaviour is also observed for the interaction of Fe(II) with the MERO species. In this case, a pink-red colour (496 nm) appears, but this state was not used in the present cycle because it is not fully reversible. The complete set of absorption spectra of the different species involved in the system are shown in Fig. 5. The SPI alone exhibits redox properties, but none of the SPI and MERO species are oxidized in the electrochemical window used in this work to operate the Fe(III)/Fe(II) developer system. On the other hand, the reduction of both species is possible, but at a lower potential than the one used to operate the developer. On this basis, the electrochemistry of the mixture of SPI and iron ions can be operated by changing the oxidation state of the metal without significantly interfering with the electrochemistry of the SPI/MERO component.

Concerning the photochemistry of CVL alone, no spectral changes were observed upon irradiation. However, in the presence of Fe(III), a slow degradation of CVL under UV light takes place, but the reaction is strongly minimized if oxygen is removed from the solution.

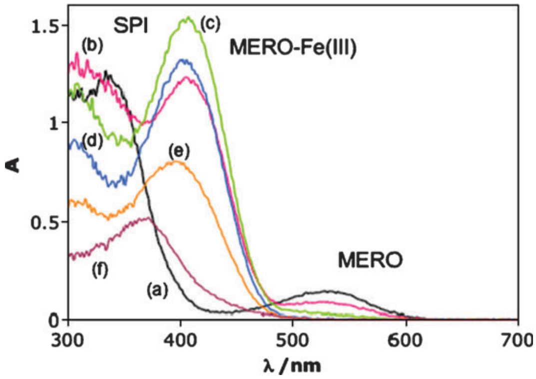


Fig. 3 Absorption spectra of the SPI/MERO compound (150 μM) upon adding FeCl$_3$ in methanol solutions (equilibrated conditions) with different relative Fe(III) molar fractions ($x_{Fe(III)}$ = 0, 0.2, 0.4, 0.6, 0.8 and 1 from (a) to (f)).

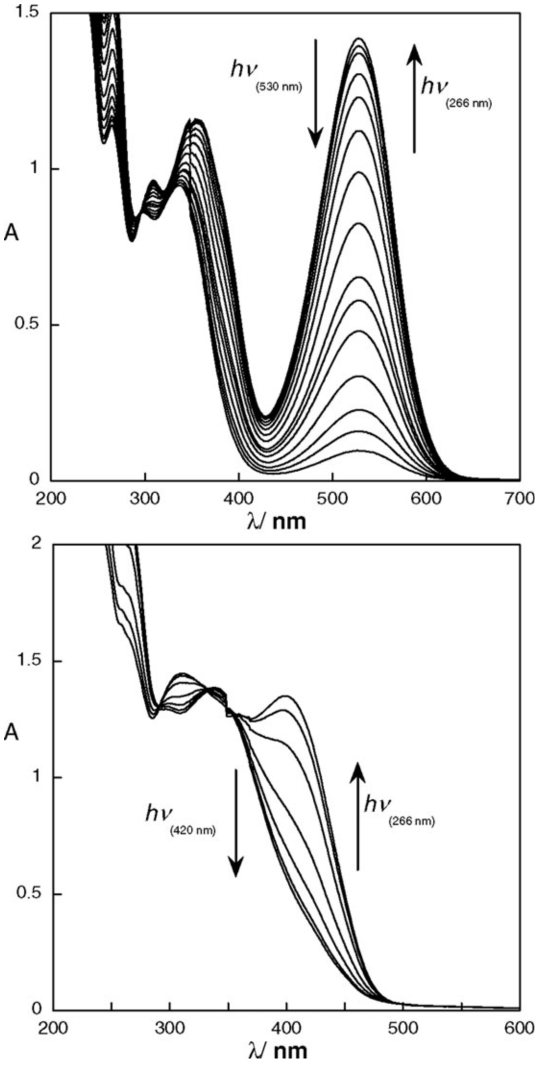


Fig. 4 Top: Irradiation of the SPI (0.1 mM) in methanol solution and 0.1 M TBAP. Bottom: The same in the presence of Fe(III) in 2-fold excess (0.2 mM).

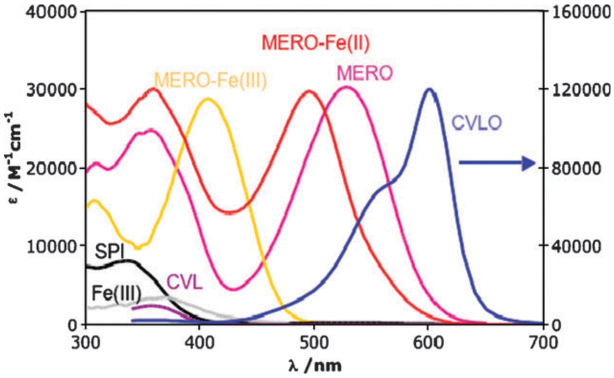


Fig. 5 Molar absorption spectra of all the molecular species involved in the photoelectrochromic system in methanol.

When equimolar concentrations of CVL and Fe(II) (0.035 mM) and a 25-fold excess of SPI are mixed (in a total volume of 10 ml) under visible light and electric stimulus (cathodic, −0.1 V), the solution is colourless (Fig. 6, state 1). Under these conditions, no coloured complexes are formed, the predominant species being the leuco CVL form, Fe(II) and SPI. Blue state 2 is reached by re-oxidation of the metal at +0.7 V for 20 min. The formation of Fe(III) opens the CVL form to yield the CVLO–Fe(III) complex, as shown previously in Fig. 1. Yellow state 3 is obtained upon controlled irradiation of state 2 with UV light for about 2 min. The SPI form opens to give the MERO coloured species, which competes more efficiently than CVLO for the Fe(III) ion (log $K_{\text{MERO–Fe(III)}}$ = 5.8, log $K_{\text{(MERO)}_2\text{–Fe(III)}}$ = 6.2; log $K_{\text{CVLO–Fe(III)}}$ = 3.0, log $K_{\text{(CVLO)}_2\text{–Fe(III)}}$ = 3.5 at 21 °C in MeOH), decreasing substantially the blue colour and forming the yellow MERO–Fe(III) complex. When all the Fe(III) has been sequestered by the MERO species (SPI is in excess), further irradiation for about 15 min converts the remaining SPI form into the red MERO species, giving rise to state 4. It is worth noting that the system can reverse back from state 4 to state 3 by selective irradiation at 530 nm (3 min) of the MERO species (eqn (2)). In the same way, irradiation of the MERO–Fe(III) complex at 420 nm (2 min) permits a change back from state 3 to state 2. In this case, the released Fe(III) (eqn (4)) becomes available to open the CLV to give back the blue colour (eqn (1)). Finally, the system can return to state 1 by cathodic electrolysis (9 min) of Fe(III) ions to Fe(II) ions. From this point onwards, the cycle can be repeated.‡

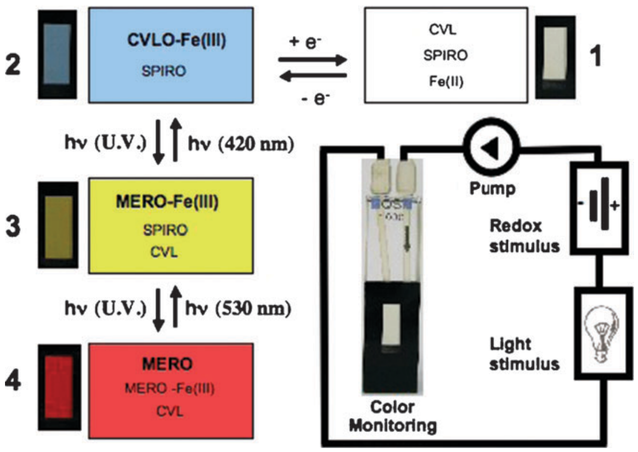


Fig. 6 Operation of the CMYT colour model based on the three component system: SPI (1 mM), CVL (35 mM) and Fe(III) (35 mM); methanol, 0.1 M TBAP.

Conclusion

We have illustrated the concept of a CMYT image device (cyan, magenta, yellow and transparent) operated by light and electrical input. The present system arises from the framework of supramolecular chemistry, where the assembly of different molecules can produce properties not present in the individual components. While the SPI is photochromic (pink–colourless), the crystal violet lactone ionochromic (blue–colourless) and the developer electrochromic (colourless–pale yellow), their

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‡ The performance of the cycle was tested by comparing the initial and final absorptions of state 1.

designed assembly leads to multiple interactions that allow the construction of the CMYT colour model.

Experimental section

N-(2-Hydroxyethyl)-3′,3′-dimethyl-6-nitro-spiro[2*H*-1-benzopyran-2,2′-indoline] (SPI) was synthesized as described elsewhere.[21] Crystal violet lactone (Aldrich, 97%), iron(III) chloride hexahydrate (Aldrich), iron(II) sulfate heptahydrate (Merck, 99.5%), anhydrous iron(III) chloride (Riedel, 98%) and tetrabutylammonium perchlorate (TBAP, Fluka) were certified analytical grade and used without further purification. Absolute ethanol (Panreac, 99.5%), methanol (Aldrich, 99.9%) and all other solvents were purchased from Sigma-Aldrich, were of HPLC grade and used without further purification.

Optical spectroscopic measurements

Absorption spectra were recorded on a Shimadzu UV-2100 spectrometer.

Electrochemical measurements

Cyclic voltammetry was performed in a conventional three-electrode cell under an argon atmosphere at 21 °C using a potentiostat–galvanostat Model 20 Autolab from Eco Chemie BV (Utrecht, The Netherlands). The collection of data was controlled by GPES version 4.9 Eco Chemie BV software. The working electrode was a vitreous carbon microelectrode, the auxiliary electrode was a platinum wire and the reference electrode was Ag/AgCl (RE-5B from BAS).

Spectroelectrochemistry

Electrolysis was performed using a two electrochemical half-cell configuration. The first half-cell was composed of the chromogenic solution, a platinum net as a working electrode and a reference electrode (saturated calomel electrode, ref. 921 from Radiometer Analytical). In the second half-cell, a counter-electrode was immersed in the electrolyte solution. Both cells were ionically connected by a liquid electrolyte diaphragm using Vycor® glass rods to avoid solution migration between the half-cells. Colour monitoring of bulk electrolysis was accomplished using a spectrophotometric flow-through cell (Hellma), where the chromogenic solution was pumped from the electrolysis cell through the spectrophotometric cell using a peristaltic pump. The solution was looped between the electrolysis cell and the spectrophotometric cell under an argon atmosphere during cathodic and anodic electrolysis.

Photochemistry

Photochemical reactions were performed using monochromatic irradiation with an irradiation setup from Spex with a Xenon lamp of 450 W and a monochromator from Jobin Yvon Horiba (model H10 UV). Sample volumes of 3 to 8 ml were used.

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