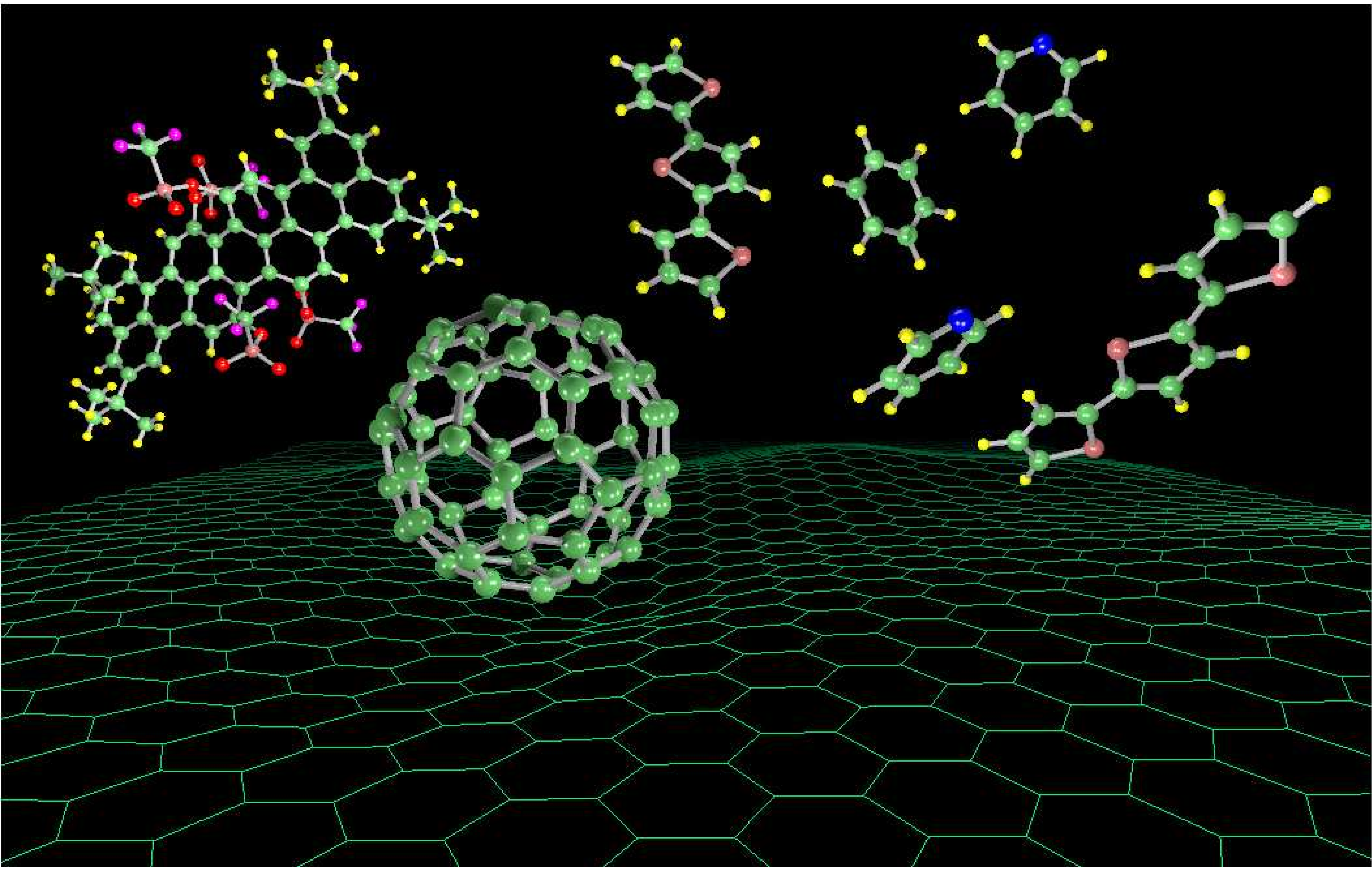
INFUSION

Engineering optoelectronic interfaces: a global action intersecting fundamental concepts and technology implementation of self-organized organic materials

D4.4 Information brochure (December 2019)



European Union
Marie Skłodowska-Curie Actions
Research and Innovation Staff Exchange (RISE)
Call H2020-MSCA-RISE-2016
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MSCA RISE SCHEME[1]

Under the Marie Skłodowska-Curie Actions (MSCA) of the EU H2020 research programme, the RISE scheme promotes international and inter-sector collaboration through research and innovation staff exchanges, and sharing of knowledge and ideas from research to market (and vice-versa). The scheme fosters a shared culture of research and innovation that welcomes and rewards creativity and entrepreneurship and helps to turn creative ideas into innovative products, services or processes.

RISE projects are expected to strengthen existing– and build new – networks of international and/or intersectoral cooperation, as well as to significantly improve interaction between organisations in the academic and non-academic sectors in the EU member states, associated countries, and non-associated third countries.

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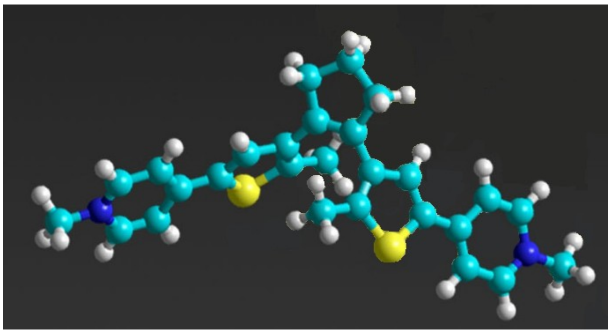
1 "GUIDE FOR APPLICANTS Marie Skłodowska-Curie Actions", (Research and Innovation Staff Exchange (RISE) H2020-MSCA-RISE-2016, EU, Brussels, December 8, 2015).

2 https://tatdaros.wixsite.com/infusion/

INFUSION PROJECT FRAMEWORK

Investing in energy efficiency and saving is crucial to support energy accessibility and environmental protection, and it is the world's best interest to share and implement forms of energy efficiency. This implies a stronger and effective transnational policy to promote and disseminate know-how about new technologies both at the market and R&D level. In this respect, development of projects centred on energy efficient technologies based on nanostructured organic materials certainly is a strategic field. The progresses in mastering organic matter by self-assembly and self-organization to form ordered soft-materials revolutionized the field opening new frontiers for both fundamental and applied research.

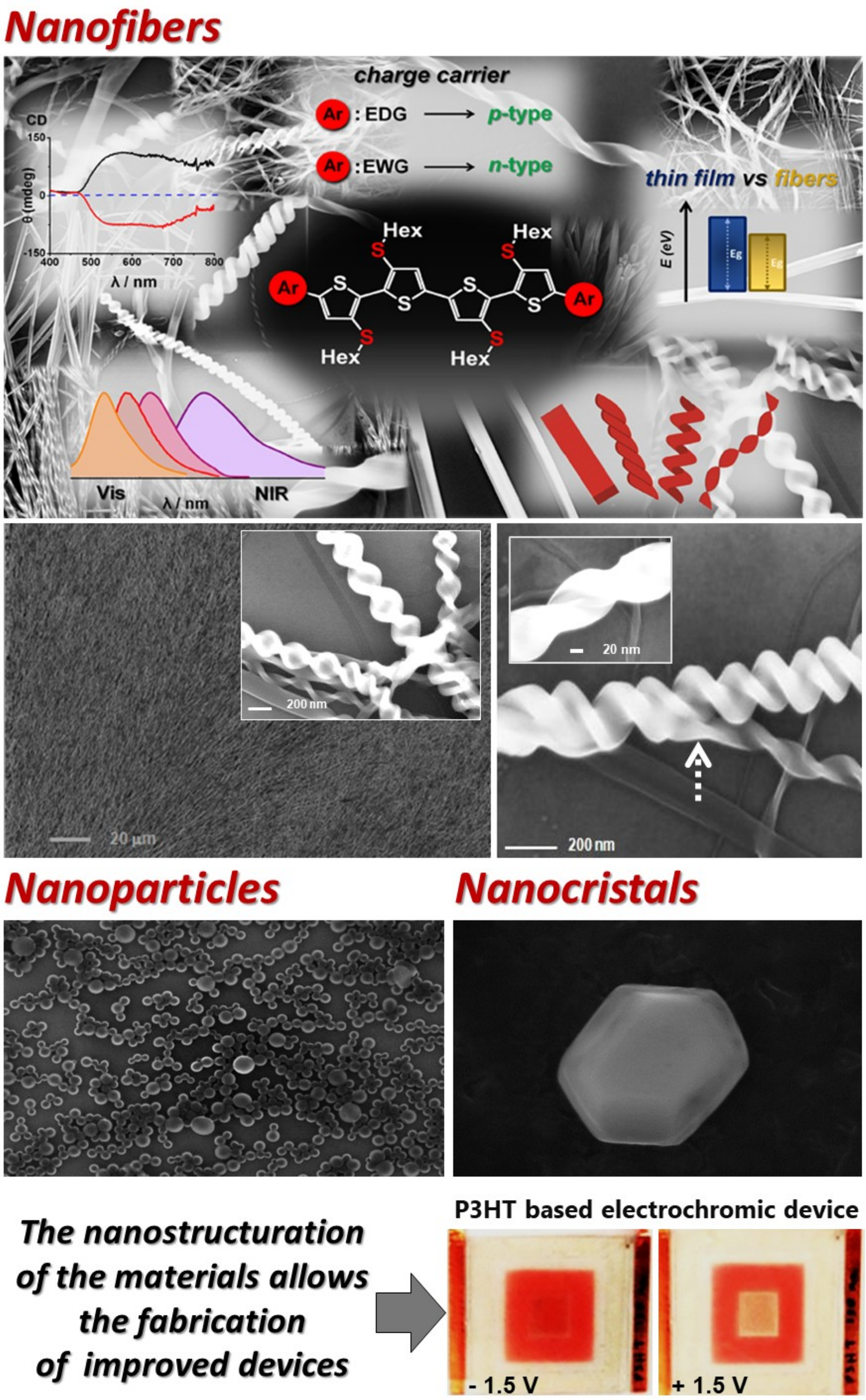
However the route towards organic materials for application at the industrial scale is restricted by difficulties in the control and manipulation of the structural organization at the molecular level and its manifestation at higher scales. Motivated by the potential for significant energy savings, the INFUSION project was composed with the objective of creating a strongly interdisciplinary and inter-sectorial environment in which the principles of self-organization are poured from the Academia into the private sector and vice-versa to create new paradigms to engineer electrochromic devices.



This figure illustrates a water-soluble photochromic diarylethene derivative that has been demonstrated to present an outstanding light-responsive affinity with cucurbit[8]uril. The latter is a macrocycle molecule having the shape of an open barrel. By confining the open isomer of the guest molecule within the cavity of the receptor, an enhancement by a factor of 8 of the photocyclization quantum yield can be induced.[3]

In particular, INFUSION aims at cross-fertilizing the electrochromic technology by joining specific expertise to realize a bottom-up approach toward the design, preparation and characterization of self-organized organic materials (chromophores, carbon nanostructures, polymers…) at different interfaces (ITO, graphene) and exhibiting superior performances (optical, durability…). The project combines the multidisciplinary expertise of six universities, one research institute, and three companies representing four European and two third countries (Pakistan and Argentina) in the field of organic chemistry, photochemistry, surface science, polymer and materials science, and device engineering.

3 "A visible-near infrared light responsive host-guest pair with nanomolar affinity in water" P. Ferreira, B. Ventura, A. Barbieri, J.P. Da Silva, C.A.T. Laia, A.J. Parola, and N. Basílio – Chem. - Eur. J. 25 (2019) 3477-3482 [doi: 10.1002/chem.201806105].



Scanning electron microscopy (SEM) images of thiophene based nanostructures, i.e., nanofibers, nanoparticles and nanocrystals, obtained from oligomers/polymers containing in their covalent network all the information needed to promote directional, π–π stacking-driven, self-assembly. The integration of conductive pre-organized thiophene-based nanostructures into electrochromic devices provides further opportunities to enhance their performance in terms of switching speed, coloration efficiency as well as colored-to-transmissive optical contrast (© Mediteknology Srl)[4].

4 http://www.mediteknology.it/

ELECTROCHROMISM

Electrochromism refers to the ability some materials have to change their optical properties – transparency, color-- after application of an electric voltage or current. The underlying mechanism can be physical: the transparency of a liquid crystal layer depends on the orientation of the crystals, which can be controlled by application of an electric field. It can be chemical as well: the color of a material can be modified reversibly by exchanging ions or electrons or both (electrochemical mechanism). Some inorganic oxides, organic molecules, conducting polymers, and metallopolymers represent different classes of electrochromic compounds.[5]

Transition metal oxides and hydroxides, such as WO_3, MoO_3, V_2O_5, Nb_2O_5, Ir(OH), NiO_xH_y, are among the first materials where electrochromism has been observed. The prototypical example is tungsten trioxide that, in thin film, is transparent. When a small quantity of positive ions, such as Li^+, coming from an electrolyte, are reversibly incorporated in the film together with electrons coming from an electrode, WO_3 is transformed in a new compound, e.g. Li_xWO_3. In this compound, a fraction *x* of the W atoms are reduced from the oxidation state W^{VI} to the oxidation state W^V. The reduced film acquires an intense blue color due to light absorption that produces a transfer of electrons between adjacent W^V and W^{VI} sites.[6] The switching time between the transparent and colored states, being related to the rate of Li ion transport, can be of the order of a minute.

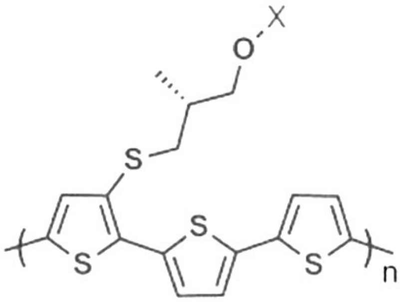
Organic molecules have many advantages as electrochrome: lower cost and ease of processing, high optical contrast between the colorless and the color states, fast response to an electric stimulus, good optical memory. The latter property means that the color stays for a long time after the application of the stimulus, which implies low power consumption. When the same molecule has several accessible redox states, it may present different colors. A redox reaction (either reduction or oxidation) changes the molecular energy levels and, hence, the absorption spectrum of the optically active part of the molecule, called chromophore. In this respect, viologens --organic molecules composed of conjugated bi- or multi-pyridyl groups ($–C_5H_4N$)-- constitute an important class of redox chromophores.[7] Derivatives of polythiophene, a conjugated polymer made of thiophene (C_4H_2S), and polyaniline, a chain of benzene rings linked by amine (C–NH–C) or imine (C=N–C) bonds, may present remarkable optoelectronic properties useful for electrochromic devices,[8] among other applications.

5 "New electrochromic materials" N.M. Rowley and R.J. Mortimer, Science Progress 85 (2002) 243–262 [DOI: 10.3184/003685002783238816].

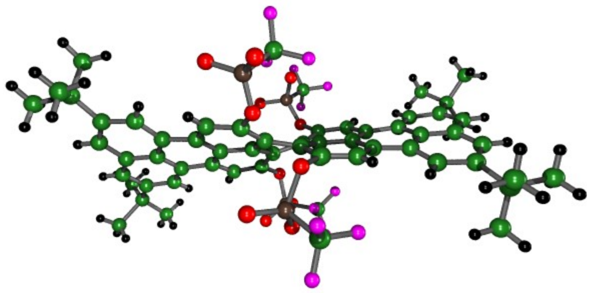
6 "Structure and properties of WO_3 thin films for electrochromic device application" M.C. Rao, J. of Non-Oxide Glasses 5 (2013) 1-8.

7 "Viologen-based electrochromic materials and devices" K. Madasamy, D. Velayutham, V. Suryanarayanan, M. Kathiresan, and K.-C. Ho J. Mater. Chem C 7 (2019) 4622-4637 [DOI: 10.1039/C9TC00416E].

8 "New organic electrochromic materials and theirs applications" J. Żmija and M.J. Małachowski, Journal of Achievements in Materials and Manufacturing Engineering 48 (2011) 14-23.



Nanoparticles of an enantiopure polythiophene derivative with alkyl side chains containing a chiral carbon not only have interesting optical properties but do also demonstrate specific antibacterial activity.[9]

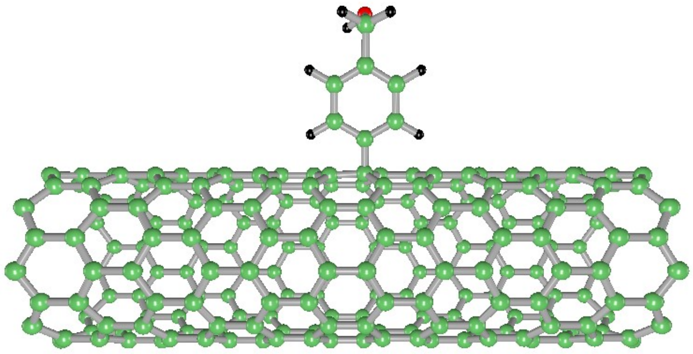


Quaterrylene ($C_{40}H_{20}$) is a promising candidate for organic electrochromic applications because of its broad absorption in the visible and UV range. The structure illustrated above is a derivative featuring peripheral tert-butyl (–$C(CH_3)_3$) substituents and sterically hindering, core-anchored triflate groups (–O–SO_2CF_3). This unique core-twisted rylene strongly absorbs in the visible region and presents a phosphorescence far in the near infra-red spectral region at 1716 nm.[10] *In the above ball-and-stick model, the brown balls represent sulfur atoms, the red balls represent oxygen, and the purple balls represent fluorine atoms. Carbon is represented in green and hydrogen is in black.*

Organic electrochromic molecules can be attached in huge quantity on nanopartices thanks to the large surface area the latter present. With such hybrid nanostructures, excellent efficiency and chromatic contrast can be achieved, together with the possibility to tune the color, which is truly important for display applications.

9 "Enantiopure polythiophene nanoparticles. Chirality dependence of cellular uptake, intracellular distribution and antimicrobial activity" I.E. Palamà, F. Di Maria, M. Zangoli, S. D'Amone, G. Manfredi, J. Barsotti, G. Lanzani, L. Ortolani, E. Salatelli, G. Gigli, and G. Barbarella, RSC Adv. 9 (2019) 23036-23044. [doi: 10.1039/C9RA04782D].

10 "A twisted bay-substituted quaterrylene phosphorescing in the NIR spectral region" T. Miletić, A. Fermi,I. Papadakis, I. Orfanos, N. Karampitsos, A. Avramopoulos,N. Demitri, F. De Leo, S.J.A. Pope, M.G. Papadopoulos, S. Couris, and D. Bonifazi, Helv. Chim. Acta 100 (2017) e1700192 [doi: 10.1002/hlca.201700192].



A single-wall carbon nanotube after functionalization with 4-aminobenzyl alcohol has benzil alcohol groups covalently attached to its sidewall. These groups gives electrons to the nanotube, affecting thereby its electronic and optical properties. Detailed experiments combined with DFT calculations demonstrate that the nanotube photoresponse, such the I-V characteristics under illumination, can be tailored by functionalization.[11]

LIGHT SCREENING APPLICATIONS

Electrochromic materials are already widely used by glass industry. Important applications are dimming windows and anti-dazzle rear-view car mirrors.

How to control the transparency of a window by application of an external voltage dates back to the 1950's. Industrial dimming windows are generally composed of two sheets of glass supporting each a conductive transparent layer that serves as an electrical contact to a few volt DC external power supply. On one contact layer, a film of electrochromic material –typically WO_3-- a fraction of µm thick is deposited. The other conducting layer is coated by a Li-doped material acting as counter electrode. The two films are separated by a lithium ion conductor. The window darkens or brightens electrochemically depending on the polarity of the voltage applied between the two contact layers. Switching between the clear and tinted states of the electrochromic film can be triggered by a light sensing system that measures the level of sun radiations. While in these two states, the window does not consume any electrical power.

Auto dimming anti-dazzle rear-view car mirrors appeared in the 1980's. The mirror has two electrodes, one is transparent while the other, at the back side of the mirror, is a reflecting metal. There is a liquid electrolyte or a gel in between, containing two electrochromes, one of which is oxidised at the anode and the other is reduced at the cathode as an electric current flows through the gel. The gel darkens from its initial transparent state in proportion to the intensity of the current. The current is controlled by a photoelectric cell that detects car headlight from the rearview to prevents the conductor's eyes to be dazzled at dark time. The initial transparency of the electrochrome solution is restored when the current is suppressed.

The same kind of gel placed between two transparent electrodes can work as a dimming curtain. The fraction of light passing through the gel depends on the intensity of the applied current. The windows

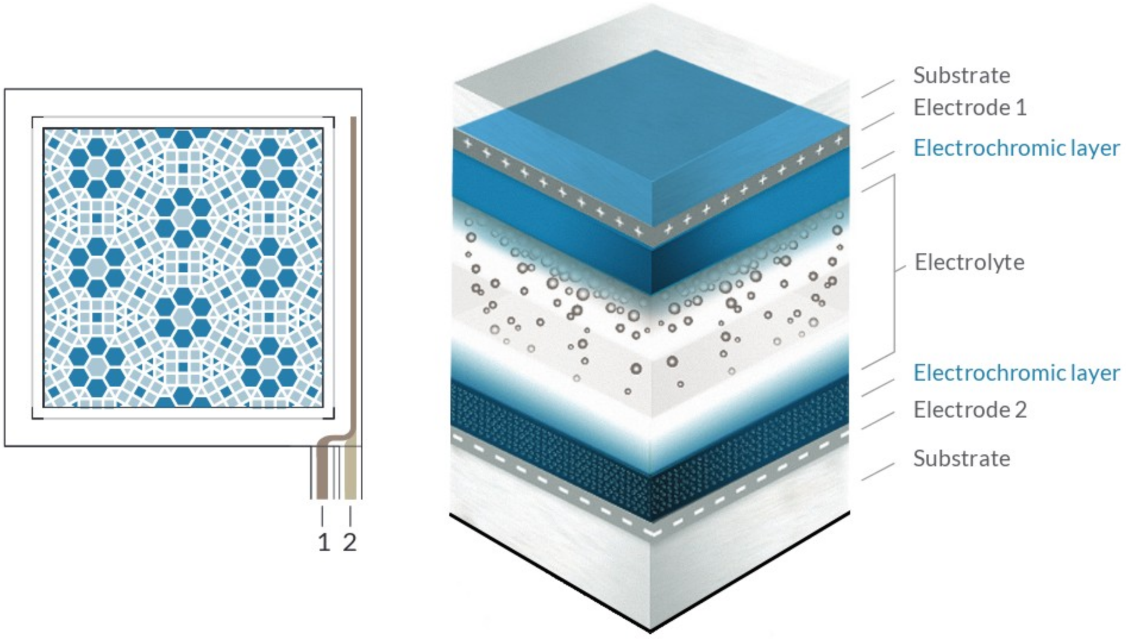
11 "A tool box to ascertain the nature of doping and photoresponse in single-walled carbon nanotubes" A. Santidrián, J.M. González-Domínguez, V. Diez-Cabanes, J. Hernández-Ferrer, W.K. Maser, A.M. Benito, A. Anśon-Casaos, J. Cornil, T. Da Ros, M. Kalbáč, Phys. Chem. Chem. Phys. 21 (2019) 4063-4071 [doi: 10.1039/c8cp06961a].

of the long-haul B787 aircraft incorporate such a dimming curtain. The passenger sitting next to a window can customize how much light goes through it simply by turning a knob. The cabin crew have a master control on the darkness of the windows, which they may use to create an artificial night during the flight.

DISPLAY APPLICATIONS

At the moment, computer or television displays are based on techniques not involving electrochromic effect. One of the reasons is that the response of electrochromics is still too slow to allow for the minimum 50 or 60 Hz refresh rate of the monitor. By contrast, more static panel boards, such as those displaying traffic, railway, or flight information, not mentioning advertisement panels, would be perfectly suitable for electrochromic displays. Beside their intrinsic low energy consumption, improved electrochromic displays can be used in any open environment without any particular electrical wire connections as they can work with simple solar batteries. Yet, reaching long enough cycle lives and generating a large color pallet for rendering colorful advertisements are challenges that INFUSION aims to address. This objective is pursued by the development of new composites obtained by self- assembly of functionalized carbon-based materials (nanotubes, graphene flakes, nanodiamonds, etc.) with tailored polythiophenes and dyes.

Besides displays, myriad of smaller size applications can be though of regarding electrochromic printed electronics and (re-)writeable labels. Label writing requires a transition of the electrochrome into an state that can be maintained without external voltage and current supply.



Electrochromic flexible panel kit commercialized by the company Ynvisible,[12] partner of INFUSION. The device illustrated on the left-hand side can display two pre-recorded images (image 1 needs to apply +1.5 V on electrode 1 with electrode 2 grounded; image 2 is obtained by applying +1.5V on electrode 2 with electrode 1 grounded). The structure of the device is shown on the right-hand side.

12 https://www.ynvisible.com/company