Visions of tomorrow's chemical technologies:

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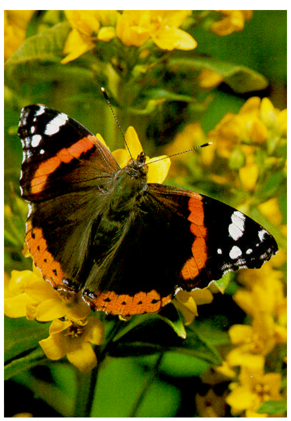
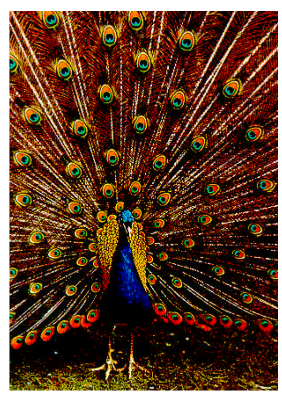
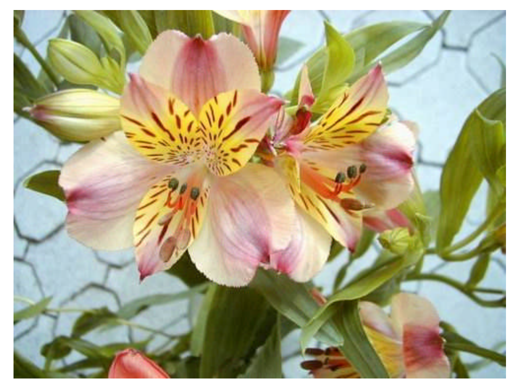
Colour beyond appearance


Colour
is
life

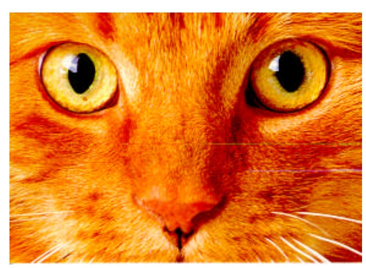
Colour in Nature







Occurrence & potential occurrence of THI (Trichosiderins/Trichochromes) in Nature



Structure of Trichosiderins

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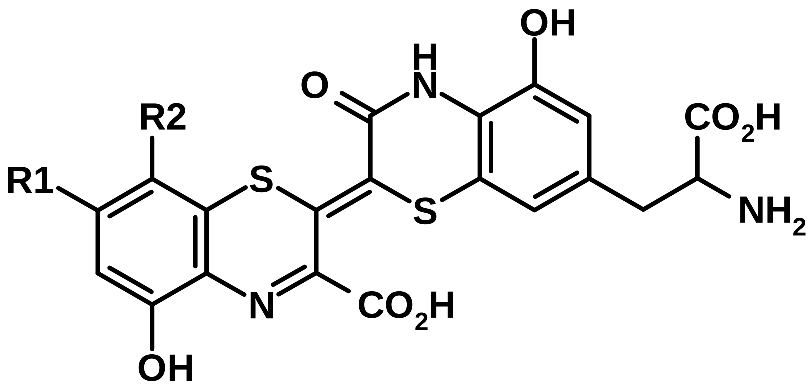
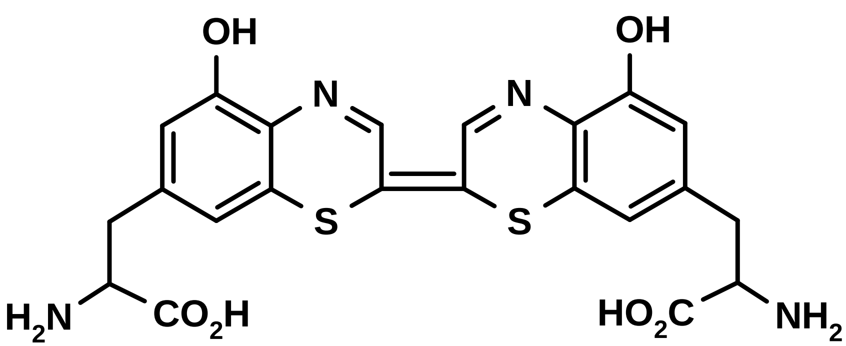
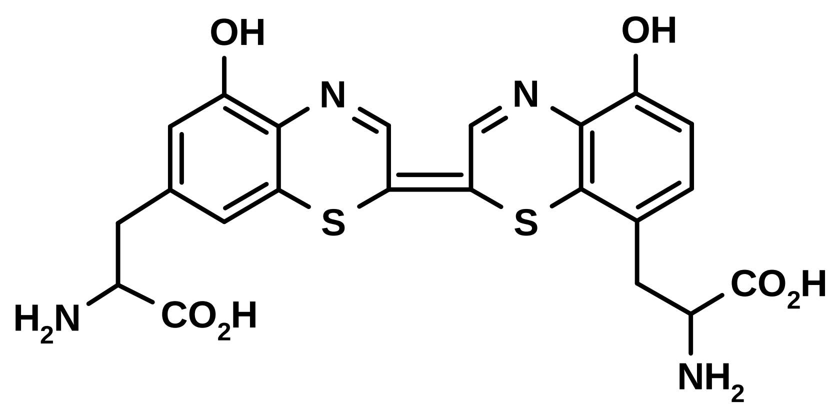


Trichochrome B R1 = H ; R2 = $CH_2CH(NH_2)CO_2H$

Trichochrome C R1 = $CH_2CH(NH_2)CO_2H$; R2 = H





Life-creating and life-sustaining colorants: The secret of life on the planet

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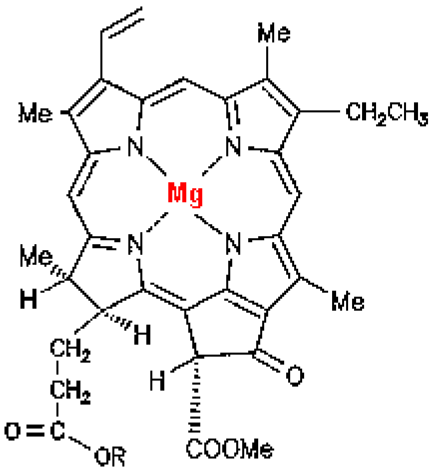
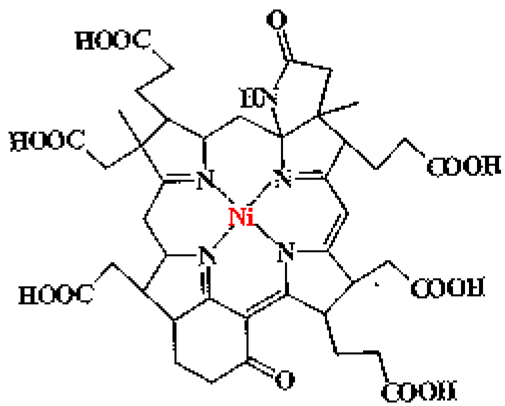
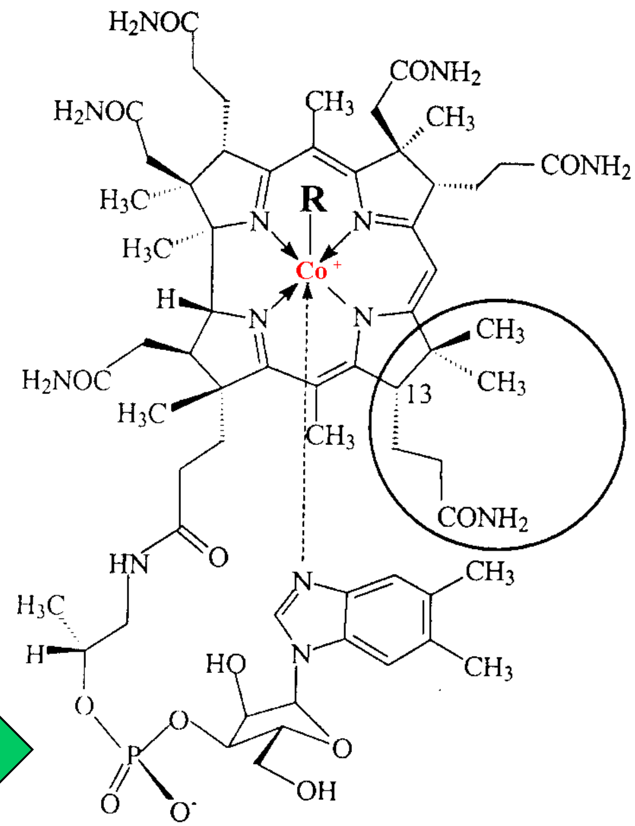
CO2



Chlorophyll a



Coenzyme F 430



O2

Cobalamins
Vitamin B_{12} ; Coenzyme B_{12}

Medicinal colorants

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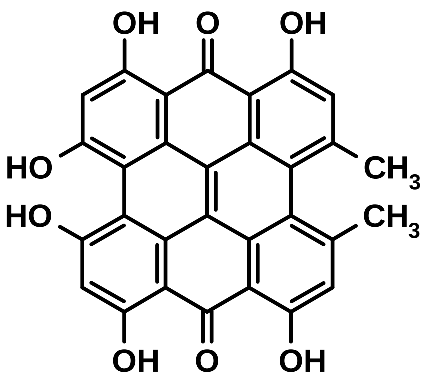
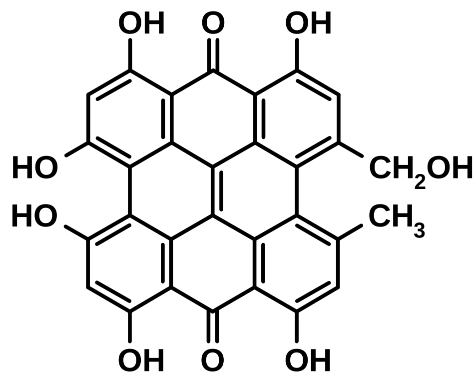
St Johan's wort





Naturally occurring colorants

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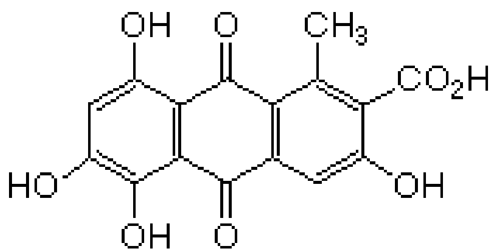
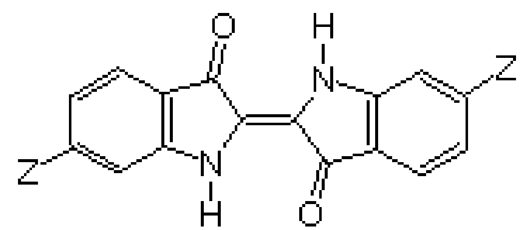
Some Natural Organic Pigments

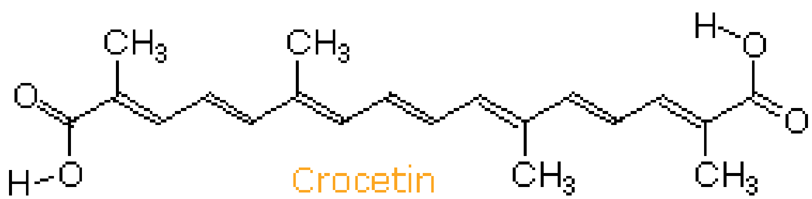


Kermesic Acid
(Carminic Acid)
from the insect *Coccus cacti*

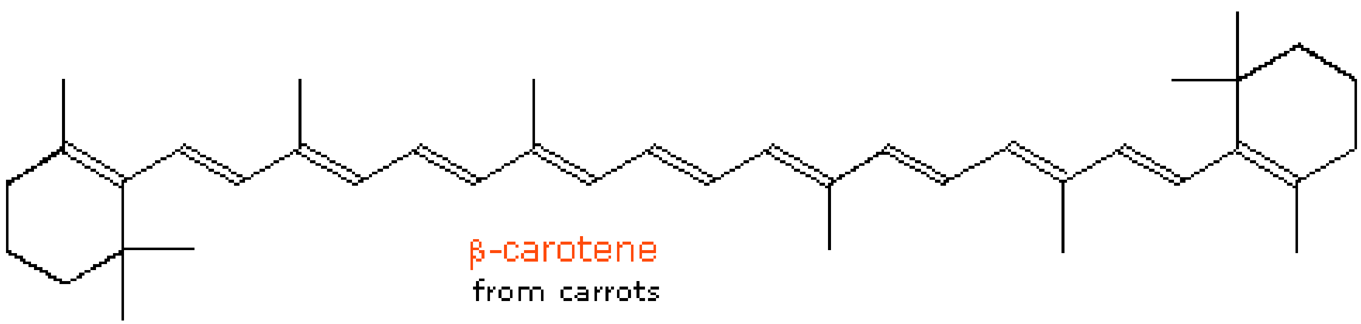


Z=H
Indigo
from *Isatis tinctoria* (woad)

Z=Br
Punicin or Tyrian Purple
from mollusks of the genus *Murex*



Crocetin
from saffron



β-carotene
from carrots

Flavonoids: The passion of KV

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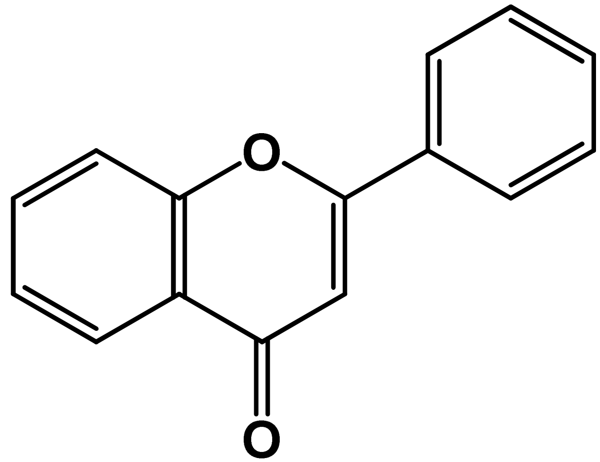

- ➢Plant pigments, creating a rainbow of colours.
- ➢Act as antioxidants and protect plants from damaging free radicals.
- ➢Protect against heart disease and cancer (?).
- ➢Major dietary sources fruit and fruit products, tea, and soy.

Painting Tumours

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"Researchers at Seattle's Fred Hutchinson Cancer Research Centre have created a molecular "paint" that coats cancer cells so surgeons can see the wayward ones that they might otherwise miss."

Time: **Thursday, Jul. 26, 2007**

The Nobel Prize in Chemistry 2008

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How the Jellyfish's Green Light Revolutionised Bioscience

In the 1960s, when the Japanese scientist ***Osamu Shimomura*** *began to study the bioluminescent jellyfish* Aequorea victoria, *he had no idea what a scientific revolution it would lead to. Thirty years later,* ***Martin Chalfie*** *used the jellyfish's green fluorescent protein to help him study life's smallest building block, the cell. Today, scientists are able to study biological processes that were previously invisible with the aid of* ***Roger Y. Tsien's*** *proteins, which glow in all colours of the rainbow.*

Researchers at Harvard University in the USA have coloured the nerve cells in a mouse's brain so that it fluoresces in all the colours of the rainbow. The nerve cells produce different amounts of three GFP-like proteins that fluoresce yellow, cyan and red, mimicking the colours used in a printer. This enables researchers to see how individual nerve cells in the brain are woven together in a network. Photo: Livet et al (2007) Nature 450 56-63.

PHOTODYNAMIC THERAPY (PDT) FOR CANCER

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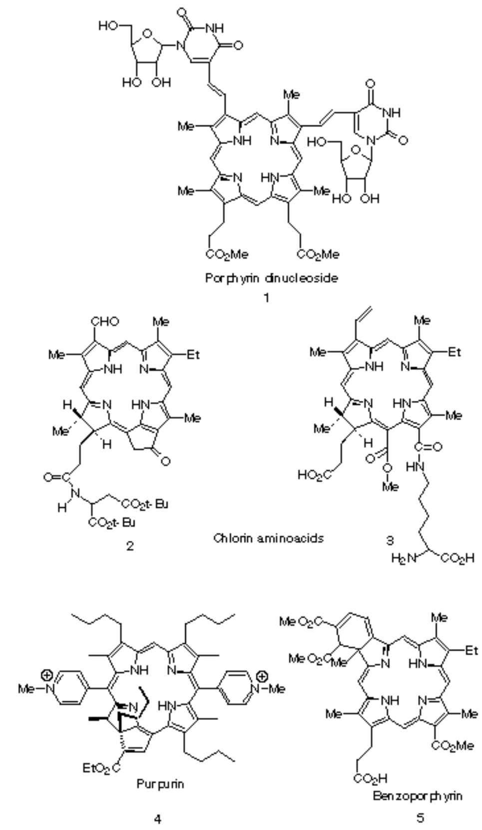
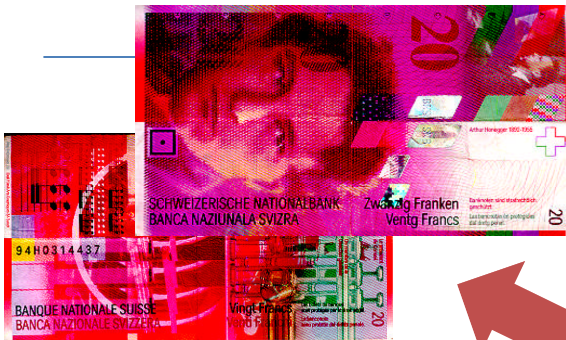
PDT involves the selective uptake and retention of a photo sensitizer in a tumour, followed by irradiation with light of a particular wavelength, thereby initiating tumour necrosis presumably through formation of singlet oxygen. Optimal tissue penetration by light apparently occurs between 650-800 nm





Some Applications of High-Performance Colorants

What is colour?

Colour is light

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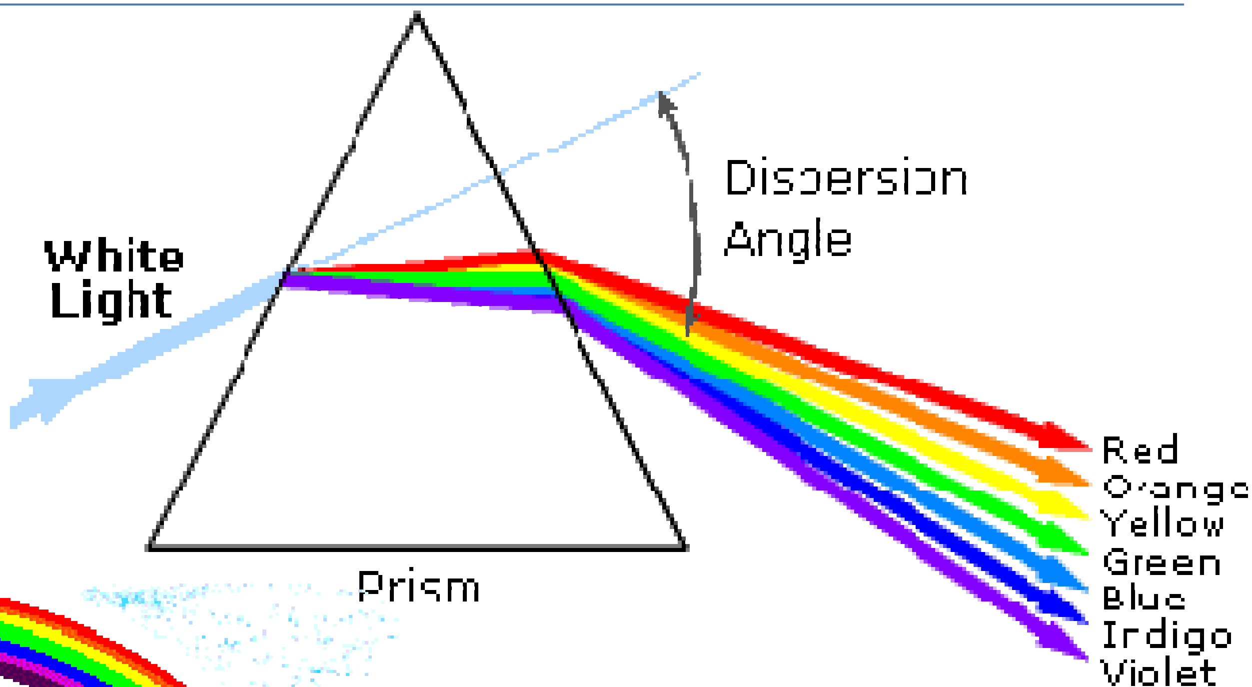

Wavelength and amplitude of absorption of light

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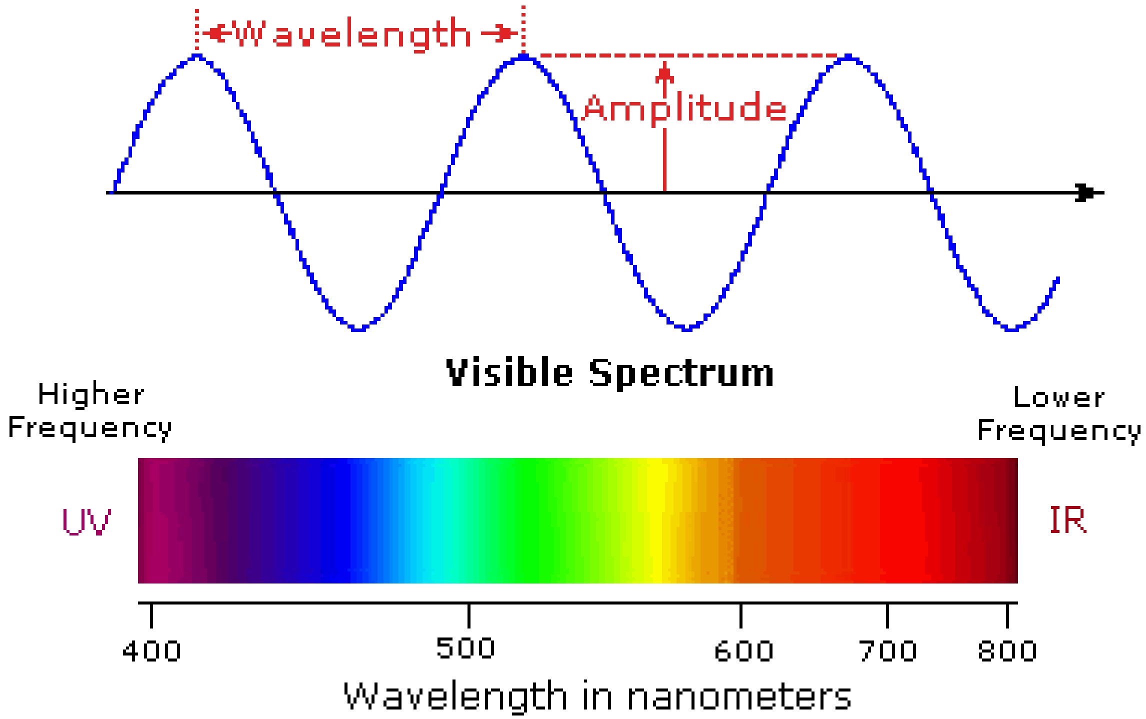
- **Violet: 400 - 420 nm**
- **Indigo: 420 - 440 nm**
- **Blue: 440 - 490 nm**
- **Green: 490 - 570 nm**
- **Yellow: 570 - 585 nm**
- **Orange: 585 - 620 nm**
- **Red: 620 - 780 nm**



complementary colour to the wavelengths absorbed

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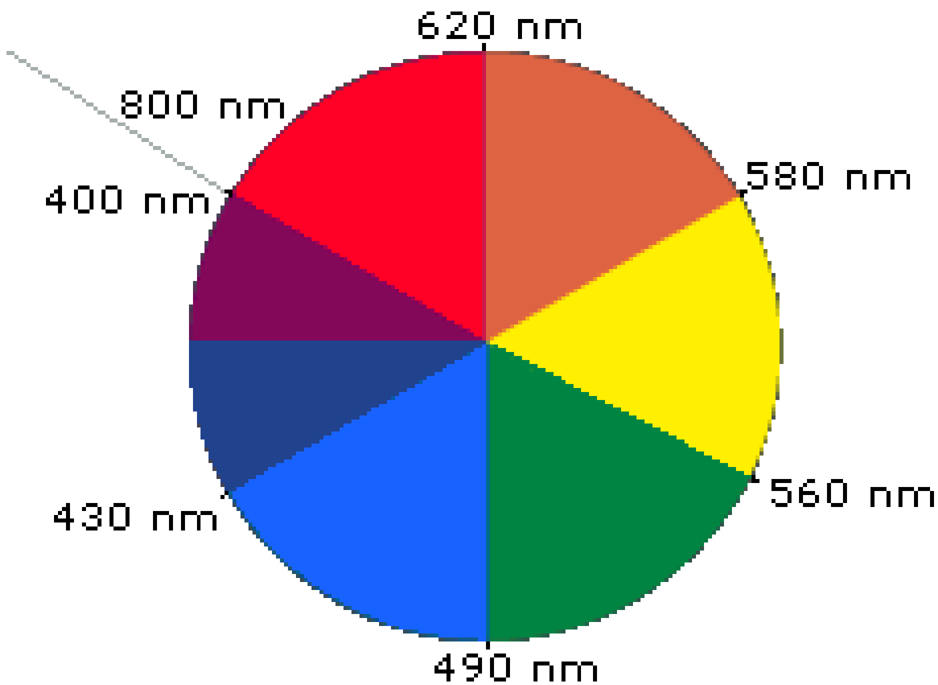

Absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red

Electronic excitation of individual organic molecules upon light (colour) absorption

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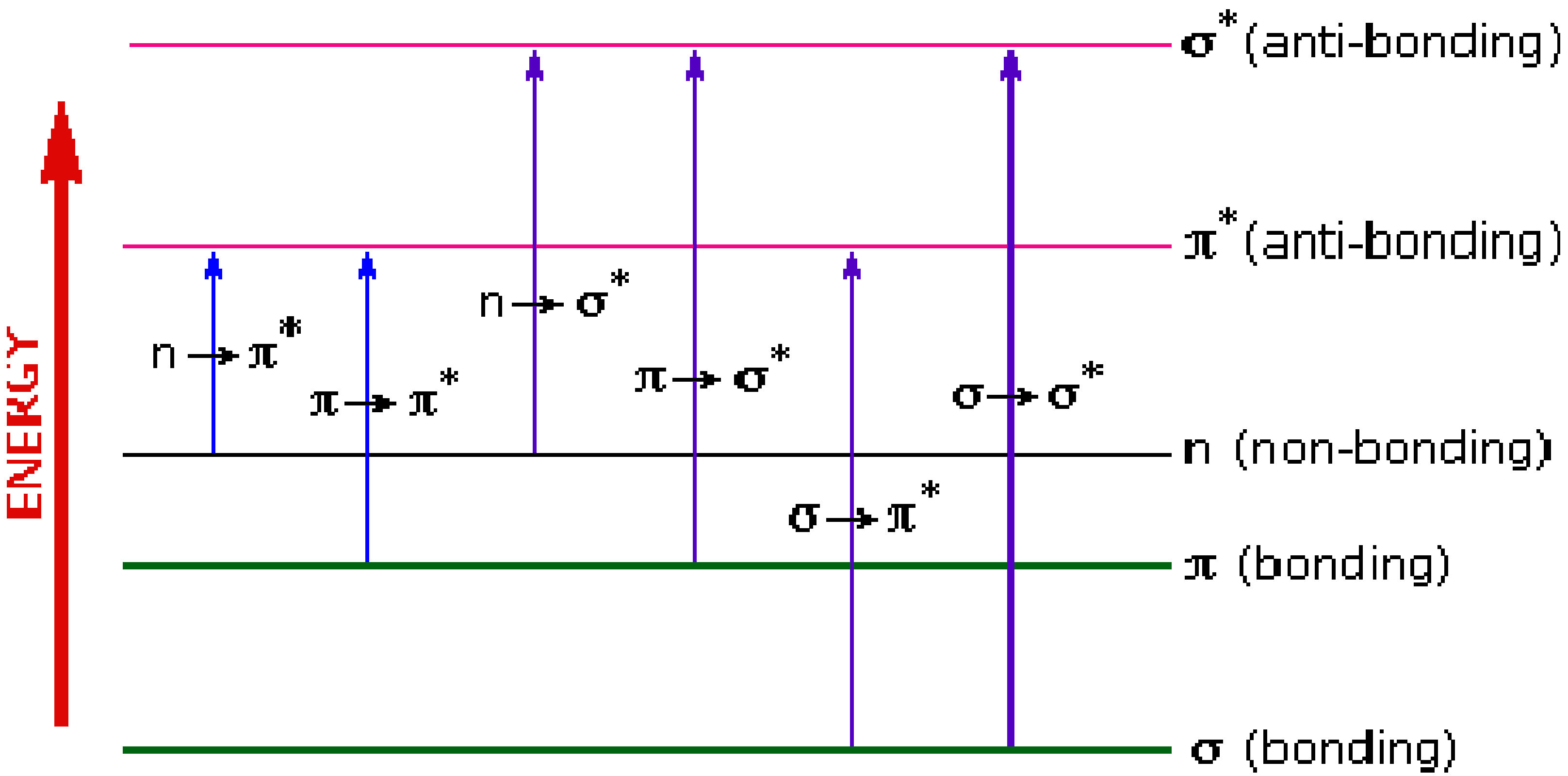

Supramolecular colour phenomenon

Absorption spectra of C.I. Pigment Red 279 (THI Red)

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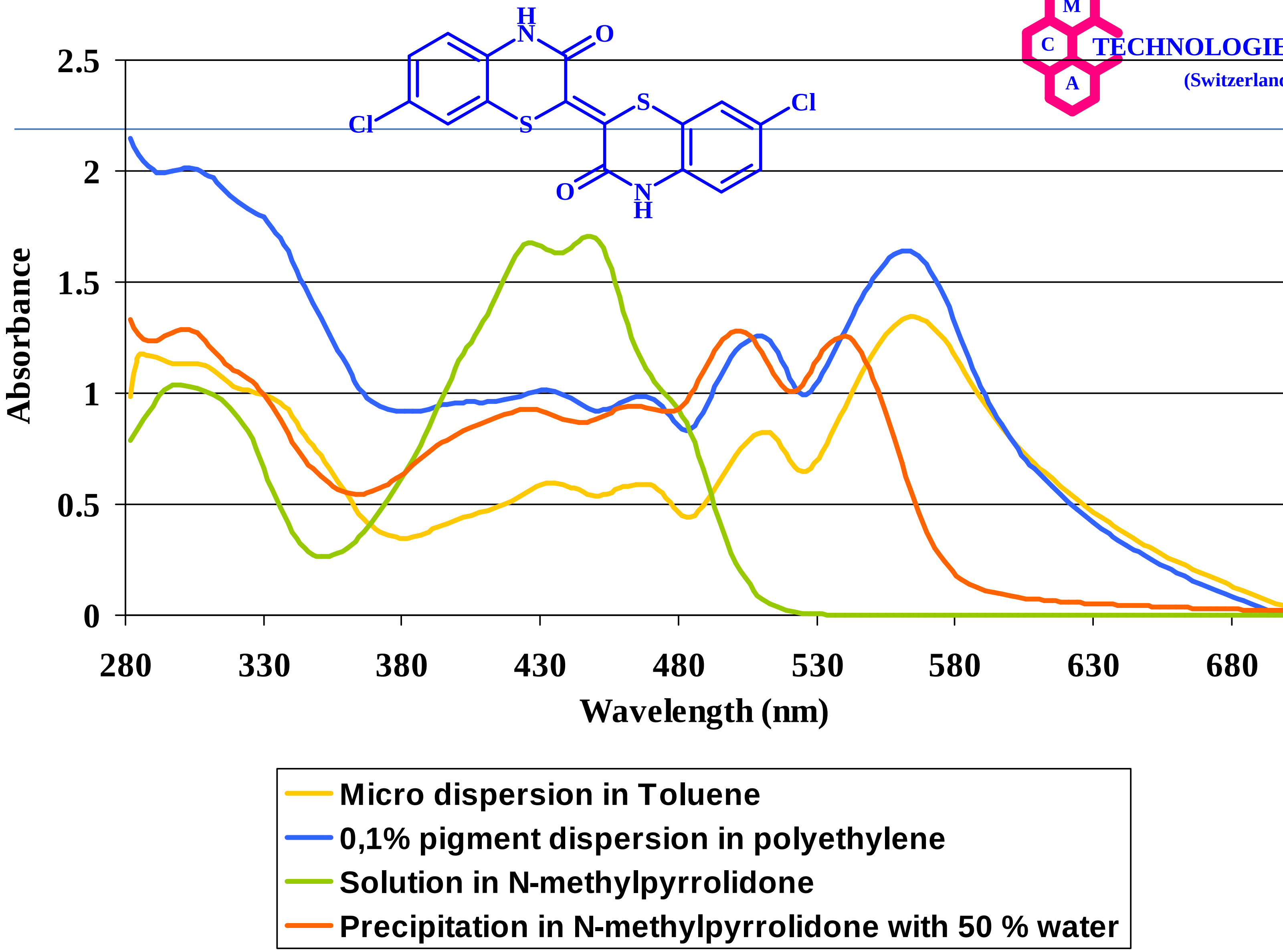
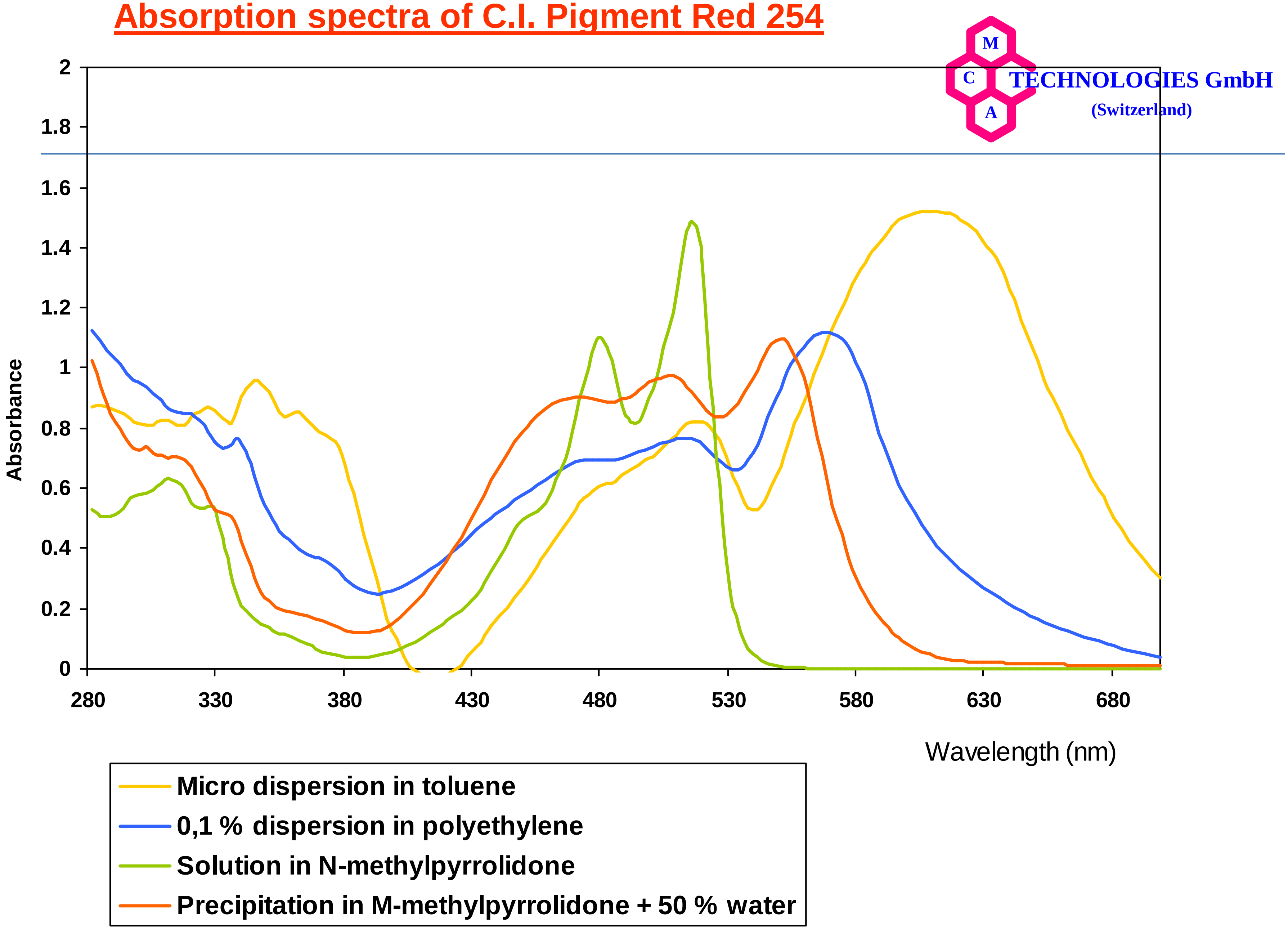


Absorption spectra of C.I. Pigment Red 254



THI Red – Supramolecular crystal Structure

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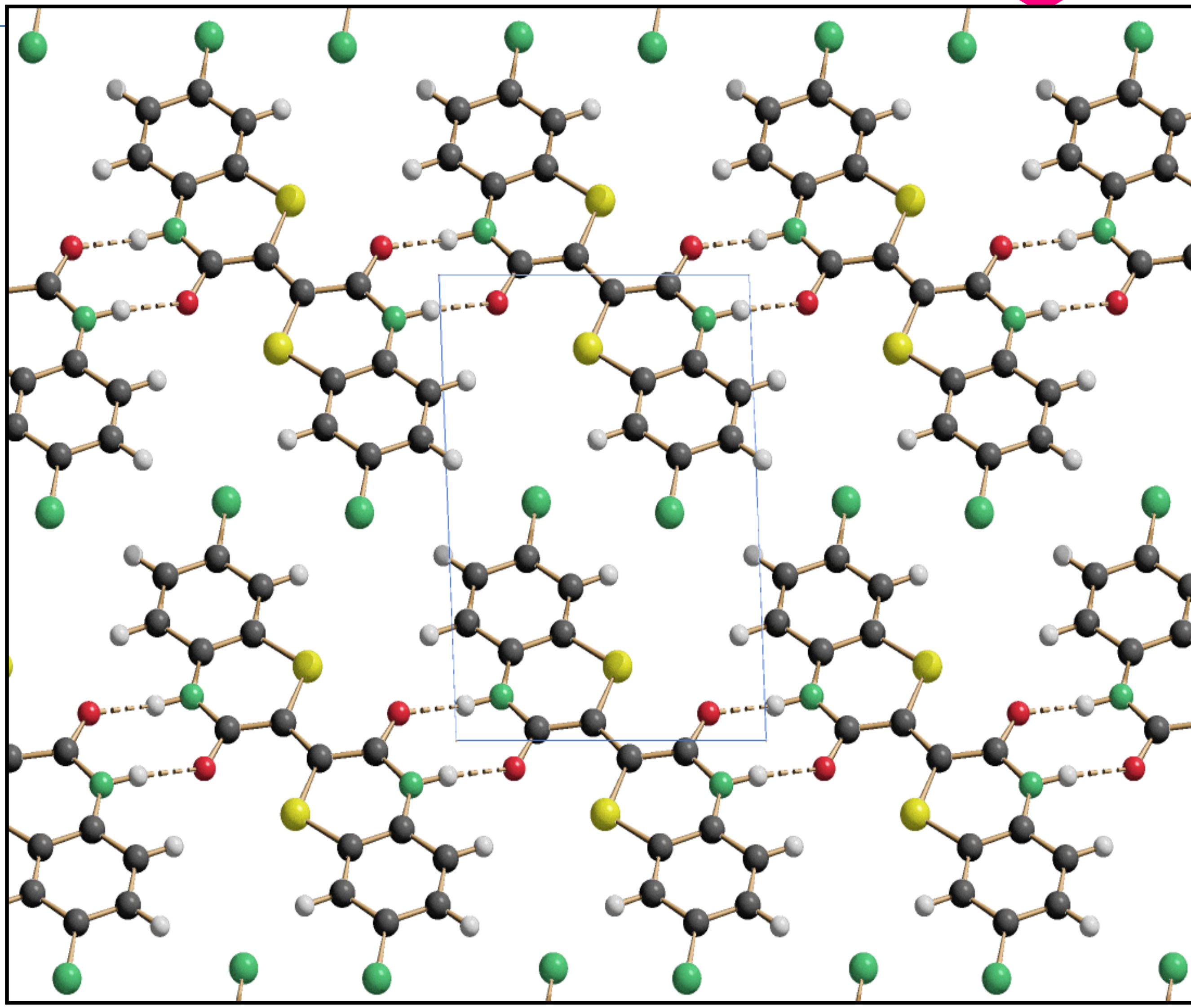

Supramolecular crystal Structure

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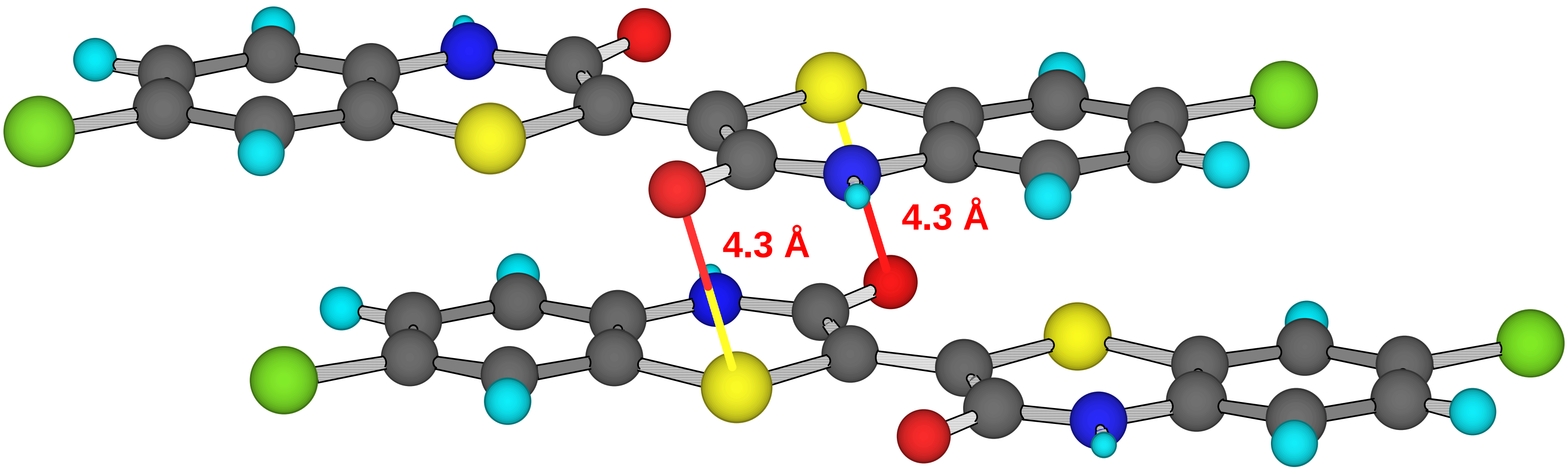

C. I. Pigment Red 279

THI - DPP - Pigments & their Copigmentations

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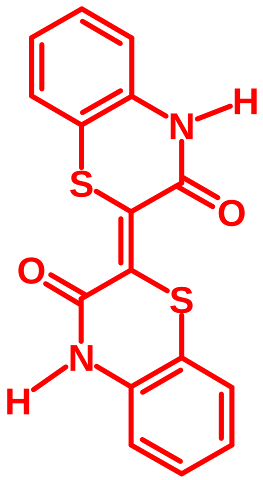
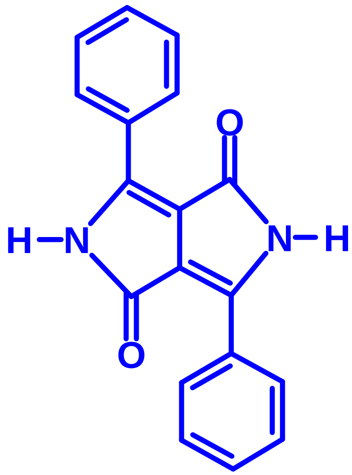
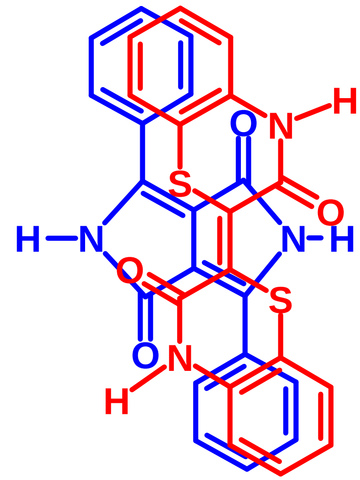


THI Chromophore



DPP Chromophore



Supramolecularly conjugated
THI-DPP chromophores

FTIR Bands (C = O & -C = C-) of THI Red, DPP Red, Their mechanical Mixture & Hybrid

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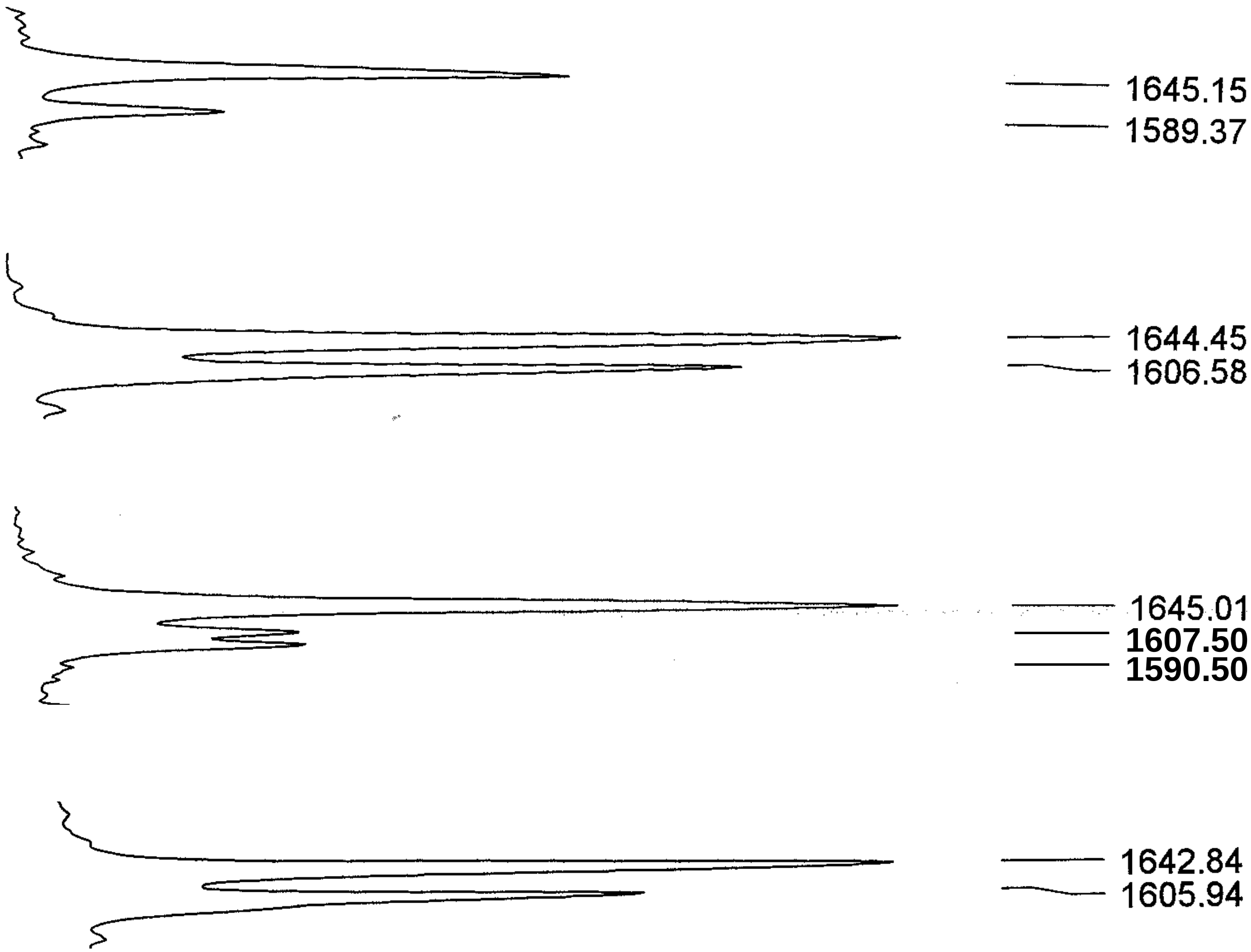

THI RED

DPP RED

THI RED + DPP RED (Mechanical Mixture)

THI RED + DPP RED (Hybrid)

Summary of the applications of light and colour:

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- Conversion of CO_2 into O_2 (Chlorophyll)
- Conversion of O_2 into CO_2 (cobalamin)
- Electronics, storage, and transfer of data
- Visualization and expression of images
- Conversion of light into electricity (Dye-Sensitized Solar Cells)
- Diagnostics and therapy
- Making "invisible" visible
- And so on

Future requirements

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- Real Pigments by definition: Insoluble, Inert, photo stable
- More specifically binding colorants for medicinal applications: for diagnostics and therapy.
- Hair dyeing: Need to be made benign
- Electronics; Durable colorants (LCD , data storage)
- Photostable colorants for exploitation of solar energy
- Colorants for photosynthesis to mimic the capture of CO_2
- Environmentally friendlier processes of fine chemicals
- Unsolved problems in the colouration of textiles (to be dealt with separately)

Pollution

Print Story: World's highest drug levels entering India stream – Yahoo! News 26.01.09 06:54

YAHOO! NEWS PRINT Back to story

World's highest drug levels entering India stream

AP Associated Press

By MARGIE MASON, AP Medical Writer

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- Visibly coloured waste waters of the dyes industry

- Invisible, but highly toxic waste of the drugs industry

- Invisible and simultaneously highly toxic waste needs be dealt with first and foremost.

CO2 capture as raw material

- Synthesis
- Biosynthesis
- Photosynthesis

RMCO2: Known captures of CO2 in synthetic chemistry/technology

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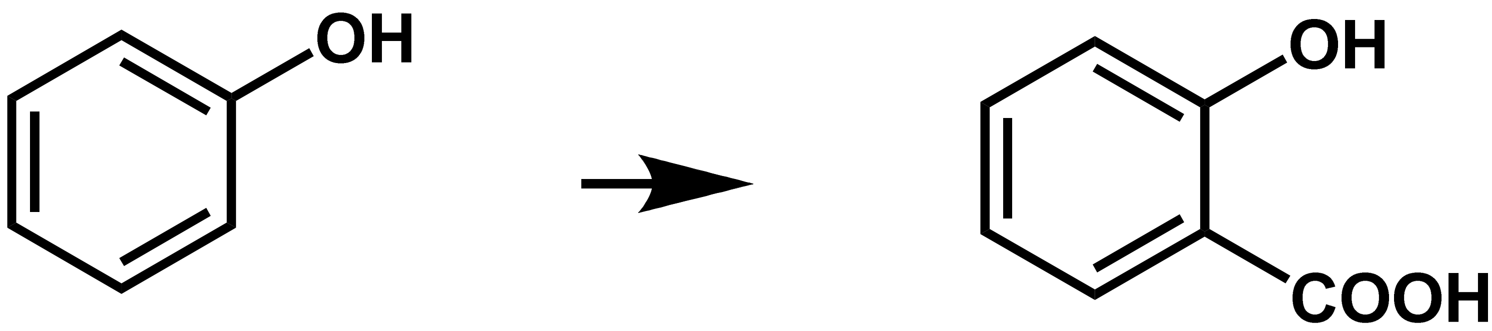

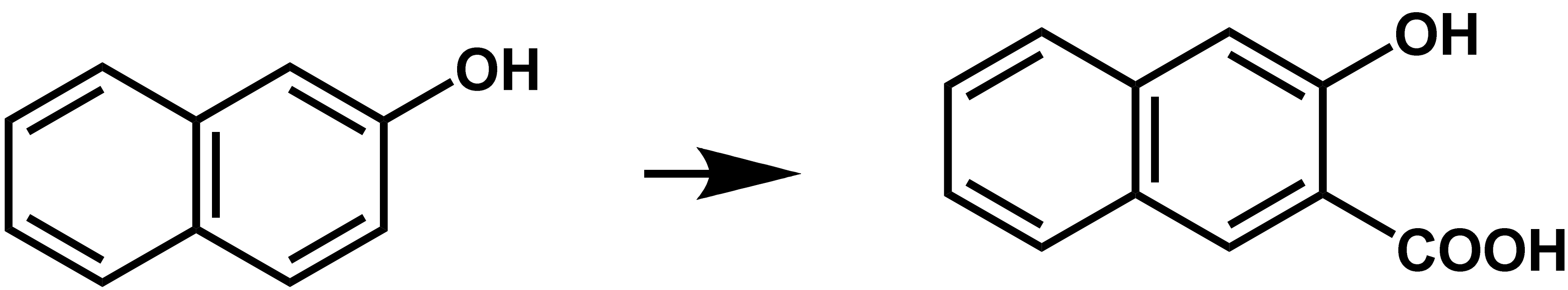

$$Ca(OH)_2 \longrightarrow CaCO_3$$

RMCO2: Known utilisation of CO_2 in synthetic chemistry

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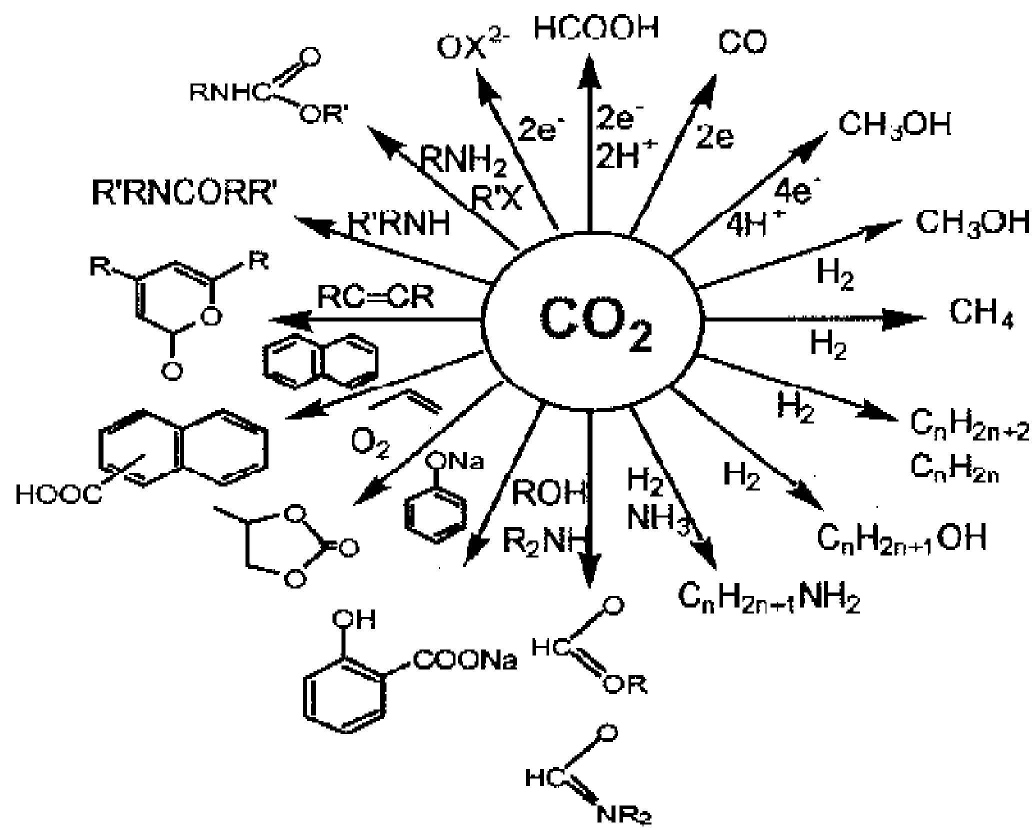
- Intermediate of fine chemicals for the chemical industry
  -C(O)O-: Acids, esters, lactones
  -O-C(O)O-:Carbonates
  -NC(O)OR-: Carbamic esters
  -NCO: isocyanates
  -N-C(O)-N: Ureas
- Use as a solvent
- Energy rich products
  CO, CH_3OH



Aresta, M. 1998. *Advances in Chemical Conversions for Mitigating Carbon Dioxide; Studies in Surface Science and Catalysis 114*, 65-76.

Biobased chemicals: However, all produce CO2 as by-product

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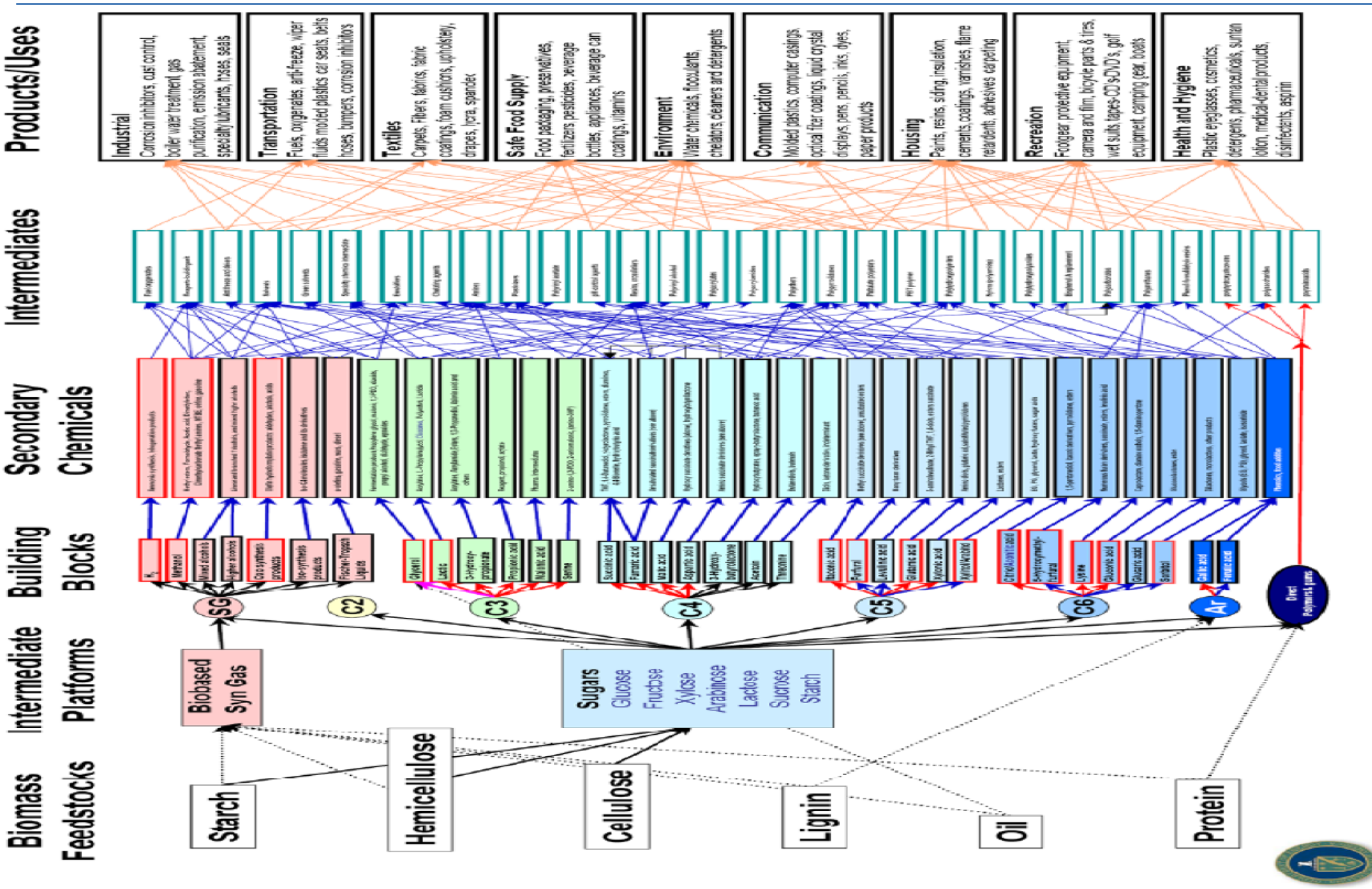

Bio- and chemical synthesis of malonic acid and/or derivatives, capturing CO2 as raw material

Why malonic acid ?

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- **Widely and broadly used building block** for high-value chemicals: Vitamins B1 andB6, barbiturates(CNS), pyrimidins (anti-viral) , agrochemicals, electronic chemicals for LCD displays, high-value pigments, textile and paper dyes

- World Demand of down-stream products: **Approx 5 Billion USD**

- **Rich (84.6%) in CO_2**

- **Naturally Occurring**, (The calcium salt of malonic acid occurs in high concentrations in beetroot), hence a good benign candidate for bio-tech synthesis

Malonic acid: State-of-the-art synthesis

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Step 1: $CH3COOH \longrightarrow HOOCCH_2Cl$

Problems: Hazardous, Polluting, By-products

Step 2: $HOOCCH_2Cl \longrightarrow HOOCCH_2CN$

Problems: Hazardous, Polluting,

Step 3: $HOOCCH_2CN \longrightarrow HOOCCH_2COOH$

Problems: Hazardous, Polluting, By-products

Overall:

High carbon and energy demand; Environmentally unfriendly; Hazardous reactions and reactants

MCA: RMCO2 :Project 2

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Development of solar cells for mimicking photosynthesis

Fire retardance of plastics and coatings

Why Plastics ?

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- **Plastics materials of choice over metals, wood, paper, glass & ceramics etc. due to their:**
  - **Light weight for the sake of energy and fuel saving (particularly in the transportation industry)**
  - **Ease and low cost of processing & re-processing**
  - **Service properties**
  - **Ability to be easily disposed of by incineration, without trace, after their service life**

➢**Plastics are used for cables, required for safe and efficient physical transportation of electrical current and data in various forms, without influencing or getting influenced by the surroundings.**

➢**But for the non-conducting and insulation characteristics of polymers and resins, their easy processibility, and their light-weight, the E&E industry would have been almost non-existent today**

Why fire resistance of plastics?

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- Plastics and coating materials classified as solid (fossil) fuels, hence the need and even requirement by law of their fire resistance for safer service life

- With every occurrence of major fire accident related to plastic components, and particularly the wire & cable insulations and jackets, regulations regarding their fire resistance expected to get more stringent

- Besides the concerns of the heat of glow and flame hazard, the generation of excessive smoke and its toxic nature in a fire scenario have gained more and more attention, provoking very stringent governmental regulations

Limiting Oxygen Index (LOI) Versus actual fire scenario

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LOI Test

Actual Fire Scenario

Fire & flame retardance beyond LOI and UL 94

- Maximum smoke density concentration
- Maximum and total concentration of the lethal carbon monoxide (formed under all circumstances)
- Nature and concentration of other gases and volatile components formed
- Maximum heat and rate of combustion
- Nature & characteristics of the flame itself: Such as its colour spectrum, the microgravity, the turbulence and speed of propagation

All these parameters better quantifiable than LOI and UL 94 classifications. And are "Reality" oriented particularly for fire fighting

Some Major State-of-the-art Fire/Flame Retardant Types

- Inorganics and nanocomposites
- Halogenated (brominated & chlorinated)
- Phosphorus and organo phosphorous including polyphosphonate homopolymers and copolymers of FRX Polymers
- Nitrogen-containing, Including N-alkoxy hindered amine
- Others: Such as sulfonate salts (PC)

Main Draw-backs of State-of-the-art Fire/Flame Retardants

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- <u>Unusually high</u> loadings: Mineral fire retardants, need to be added in amounts even far exceeding the weight of the polymer itself
- <u>Brominated FRs</u> : High smoke density and non-compatibility with HALS light stabilizers, inherent potential of causing collateral damage by generating corrosive and toxic gases and other volatile components in the event of fire. Use of BFRs is being restricted, worldwide
- <u>Liquid & low melting FRs:</u> Can act as plasticizers, thereby greatly influencing the mechanical properties of the plastics
- <u>Melamine Derivatives</u>: Not recommended for polyolefins (due to chalking)

PPM Triazine HF: for FR by intumescence

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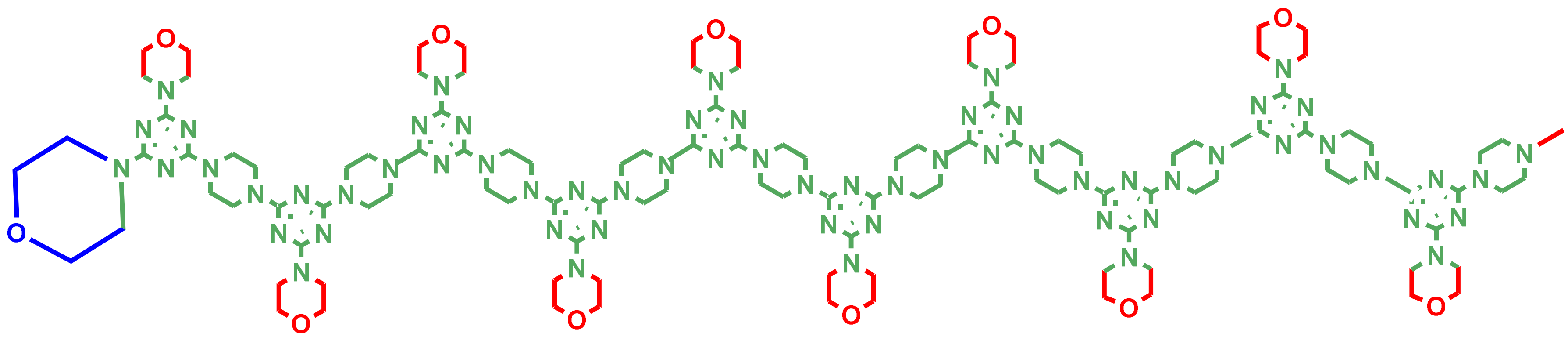

<u>Mechanism:</u> **Air-bag principle/oxygen scavenging, and intumescence**

What is Intumescence ?

A natural phenomenon of the fire resistance for example of silk against cotton

PPM Triazine HF : Synthesis of

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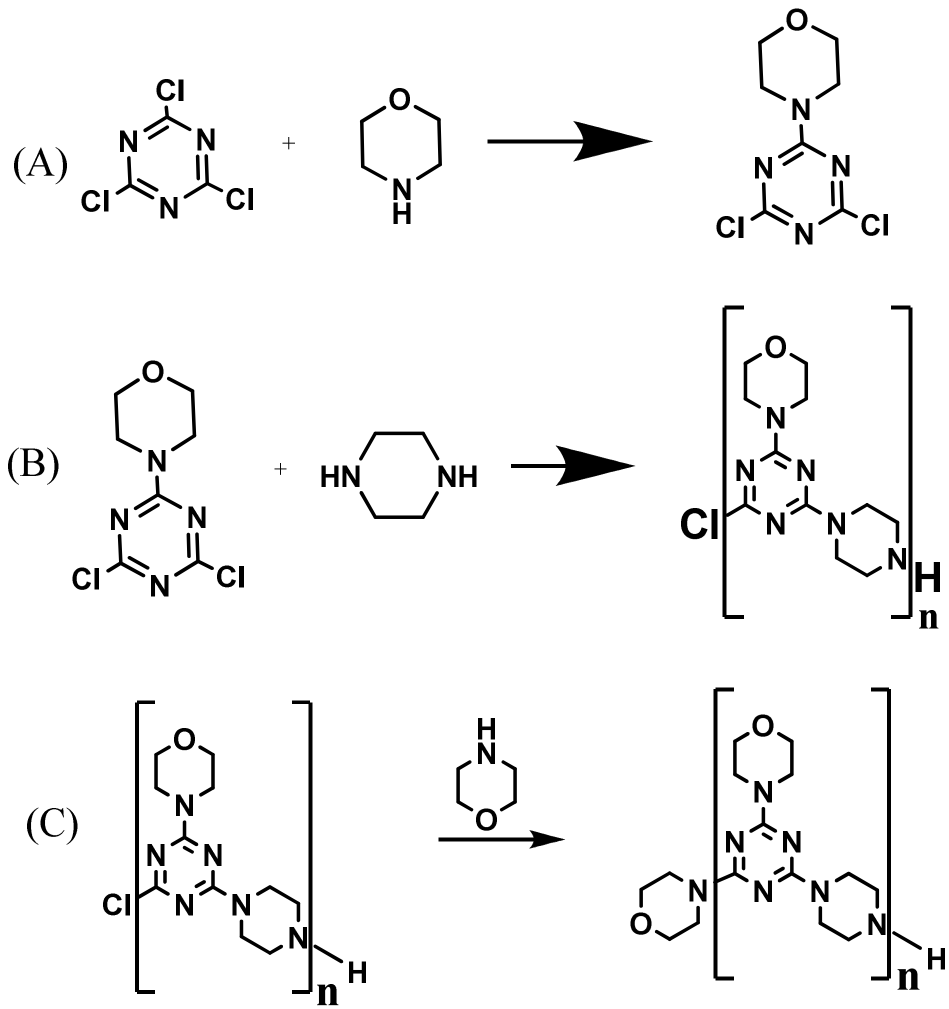

PPMT

PPMT HF

MCAT's Proprietary Volatile-Organic-Solvent-Free Technology

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Suspension polymerisation in the presence of catalysts

Examples: PVC made by suspension polymerisation
PP made using Ziegler-Natta process

Patent applications :
"Polytriazinyl compounds as flame retardants and light stabilizers"
European Patent application 2130854.
US patent application US 2009/0281215 A1
Also in China, India, Japan & Taiwan

MCA® PPM Triazine HF, Scanning Electron Microscope Pictures (x10,000)

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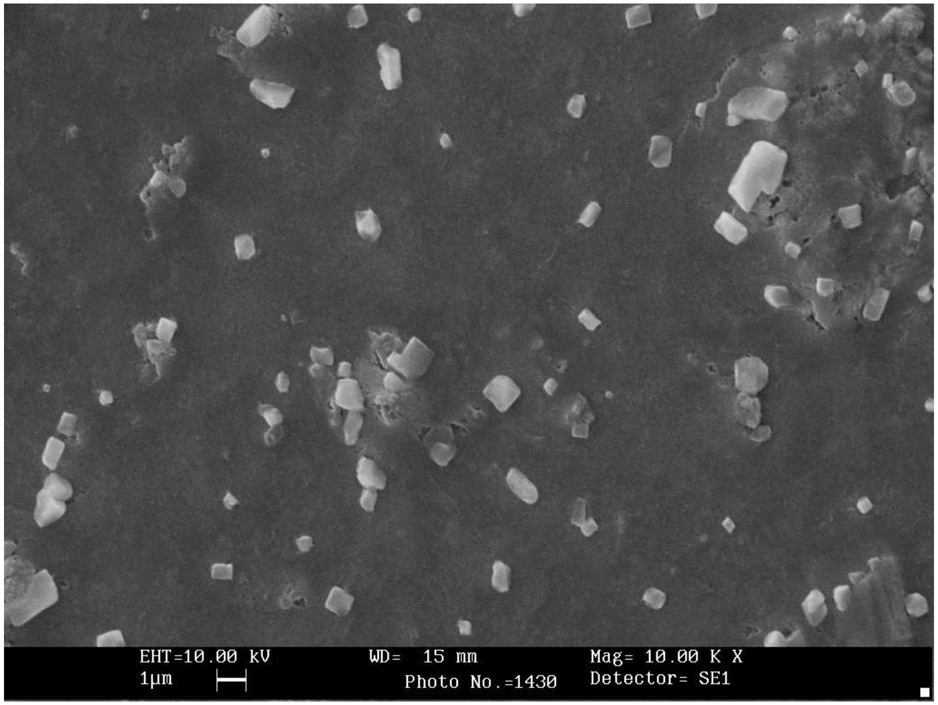

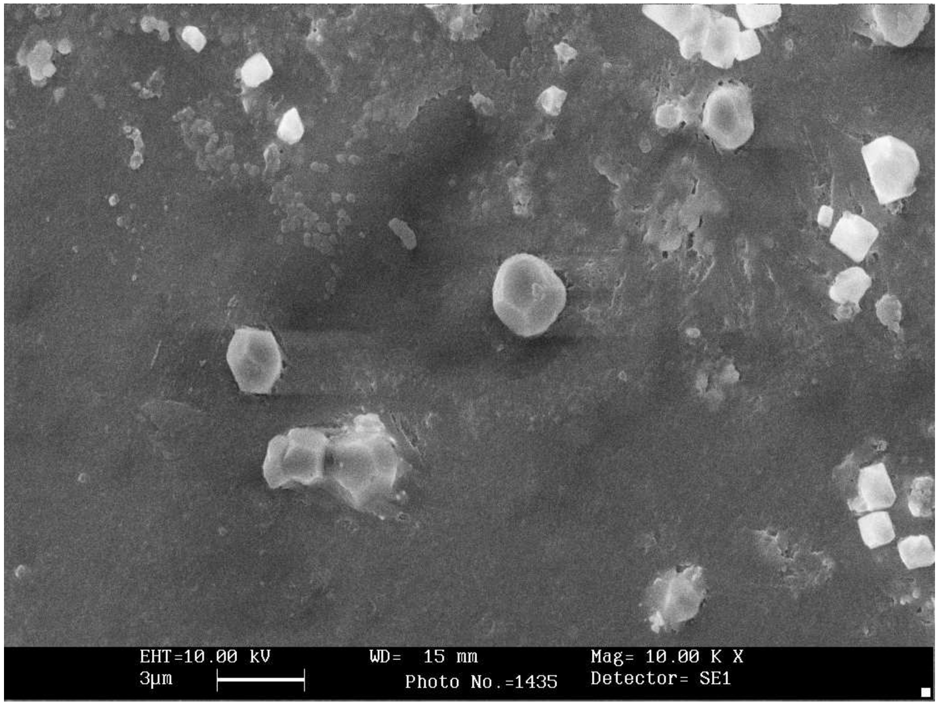

Individual particle size:
< 1 µm

Individual particle shape:
Diamond like

Specific Optical Smoke Density (Ds) of Fire-Retarded Polypropylenes: V-0 Formulations 1.6 mm: Intumescent System versus Brominated

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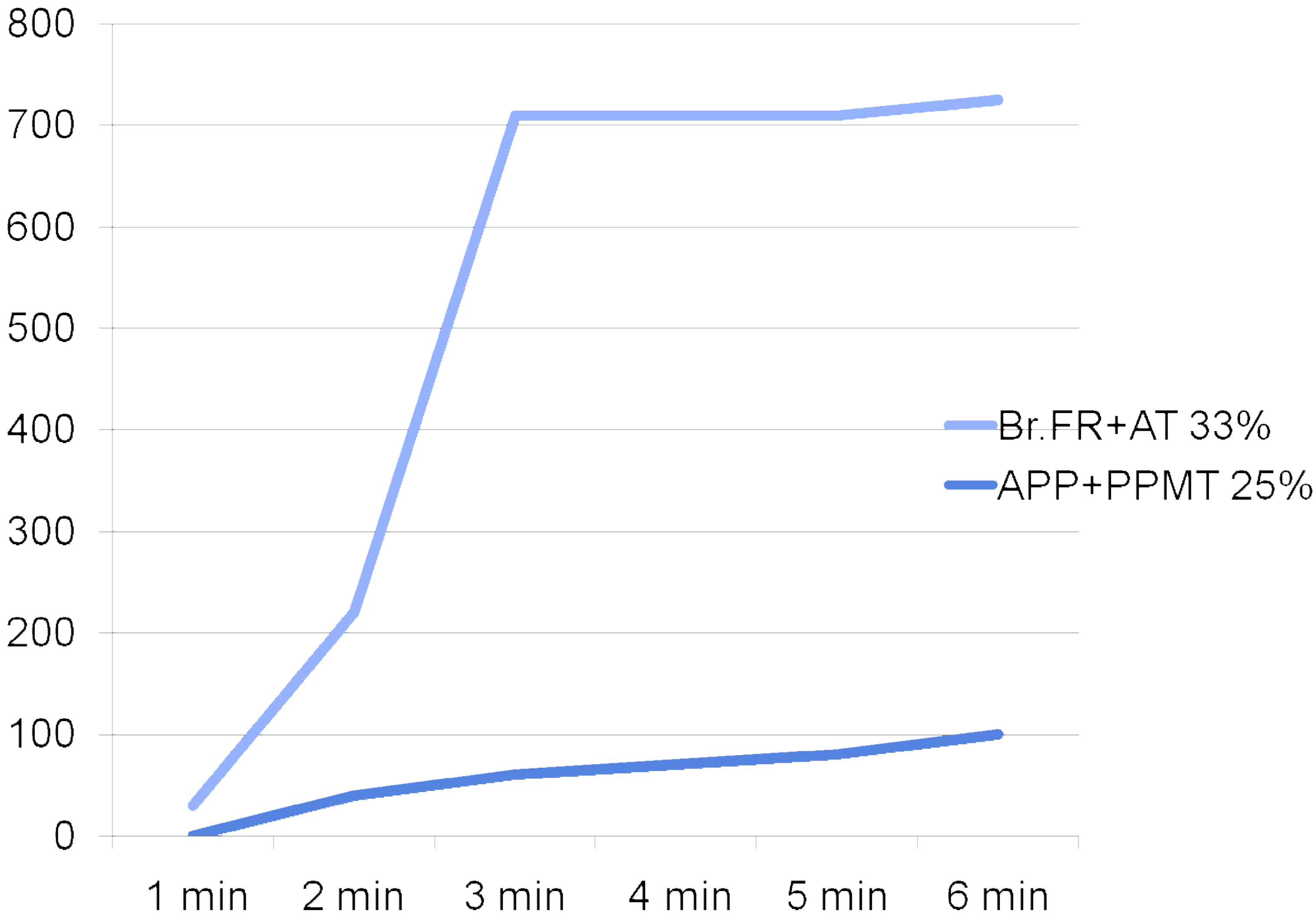

PPM Triazine & ATH Martinal OL-104 LEO in EVA compound (19% VA) for a W&C application*

(* Special courtesy of Albemarle-Martinswerk GmbH)

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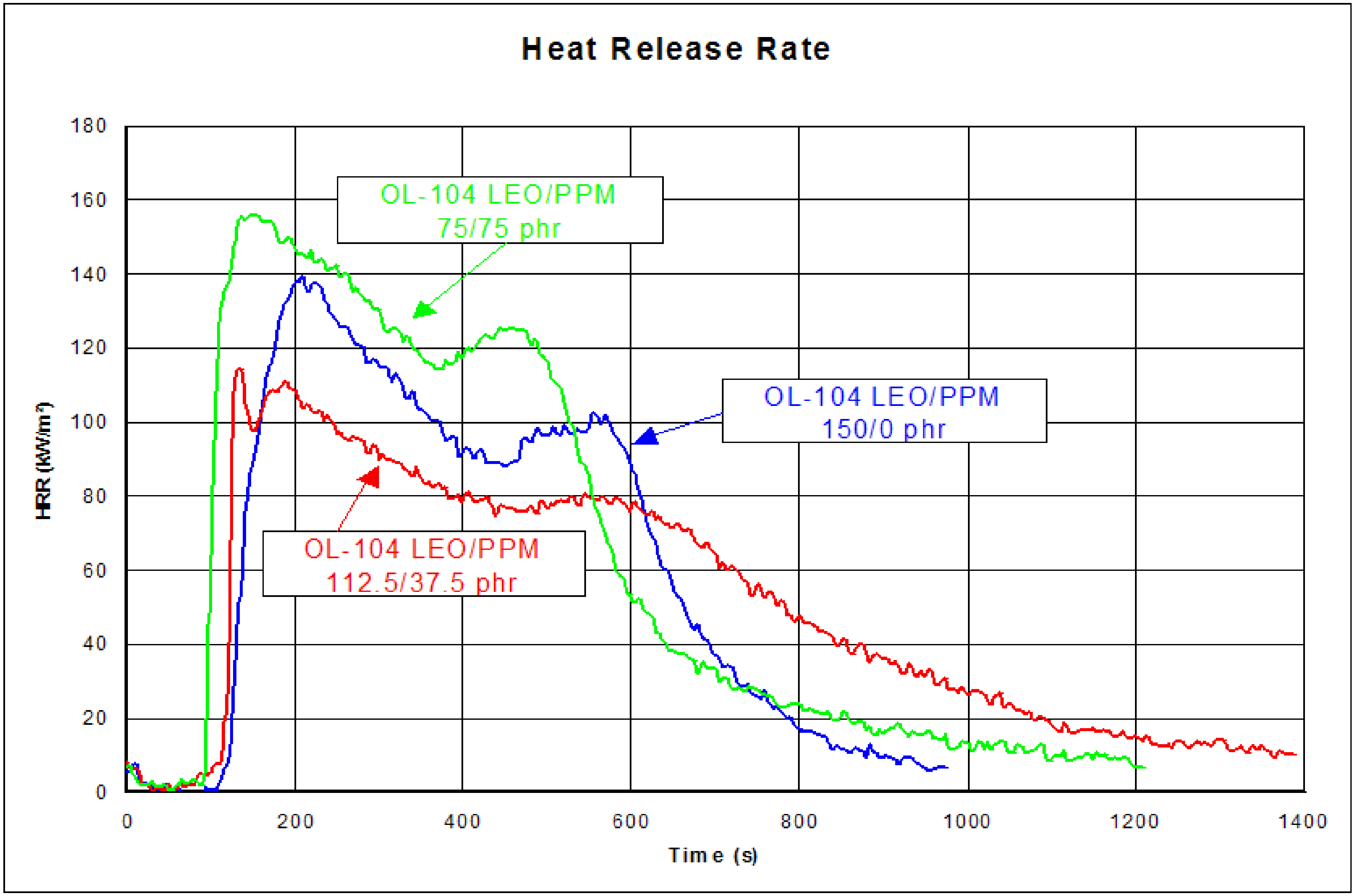

Pointers of Future Developments in Flame Retardants :

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- High efficacy & effectiveness
- Easy to compound and process
- Better service performance
- Environmental friendly

Promising Pathways

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- A proper understanding of mechanism of fire, flammability and combustion
- Better reality oriented specifications and testing procedures
- Intumescence processes
- Simpler, less expensive and more effective "air-bag" principle

"Seed" concept in textiles.

Colouration of textiles (leather and paper)

- Wet colouring processes continue to be tedious, high-energy and water consuming.
- Manufacture of many dyes and their precursors highly polluting.
- Not very many textile dyes fully meet the very basic requirement of perfect wash-fastness in modern washing machines and against the aggressive detergents.
- Also, choice of dyes for many applications, such as for outdoor and automotive uses is limited.

One of the pathways

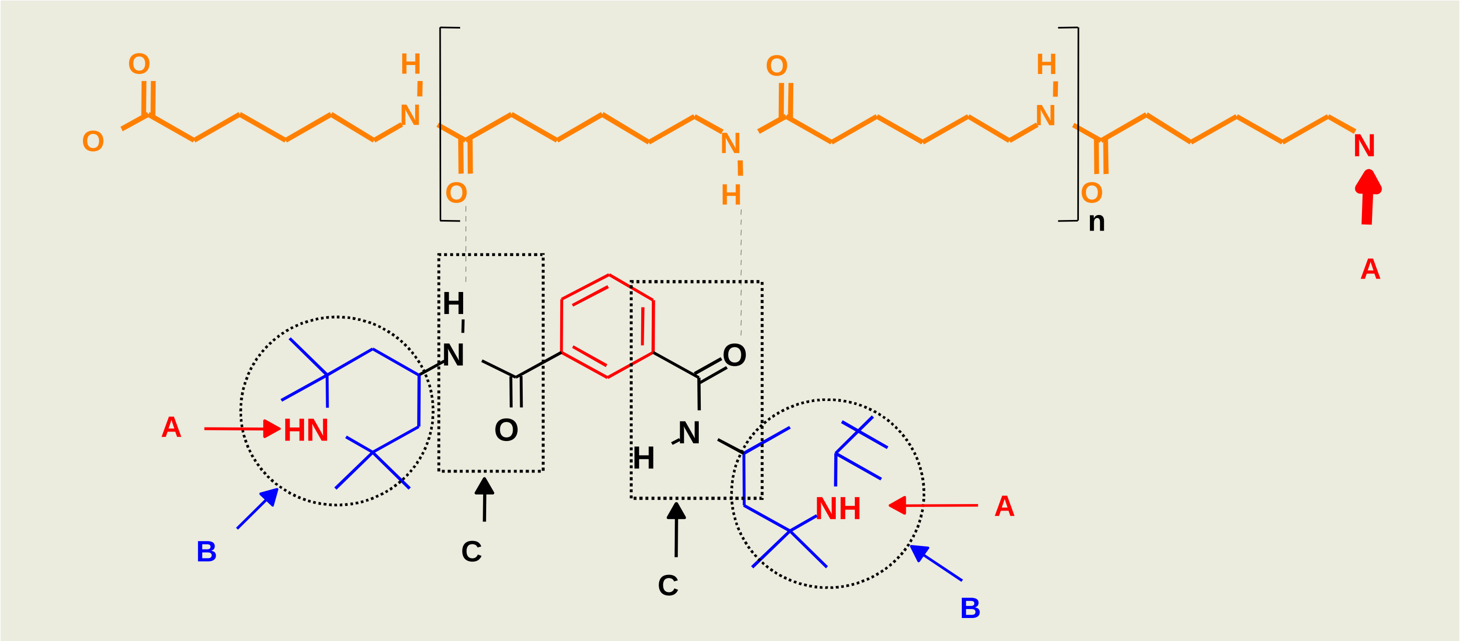
"Dry" processing over wet processing

Spin/solution/dope dyeing during the manufacture of (synthetic) fibres

« SEED » Concept for multipurposes

TECHNOLOGIES GmbH
(Switzerland)

Bonding to POLYAMIDE-6 by Molecular Recognition



- a) Dye binding sites
- b) Dye and substrate stabilizing groups (radical scavengers)
- c) Amide thermally and photochemically stabilizing groups, and substrate binding sites

Nylostab S-EED: Versatile multifunctional additive

MCA TECHNOLOGIES GmbH (Switzerland)

S ⇒ For the Strength and Stability of the Substrate & Colourants applied thereto

⇒ For the higher Speed in polymer processing and fibre production

E ⇒ For Economy & Ease of Dyeing & Printing

E ⇒ For Ecology & Environmental Concerns in Dyeing

D ⇒ For Deep Dyeability

⇒ For Permanency of Efficacy due to Molecular Recognition and/or Crossamidation

Influence of NYLOSTAB S-EED on Dyeability of PA6.6 Fibres

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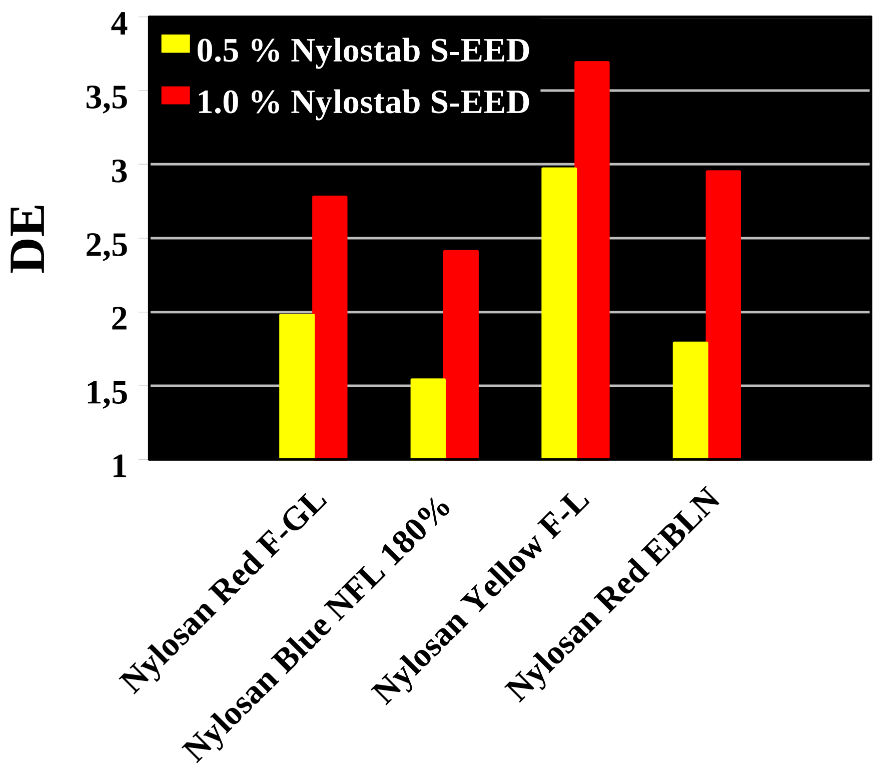
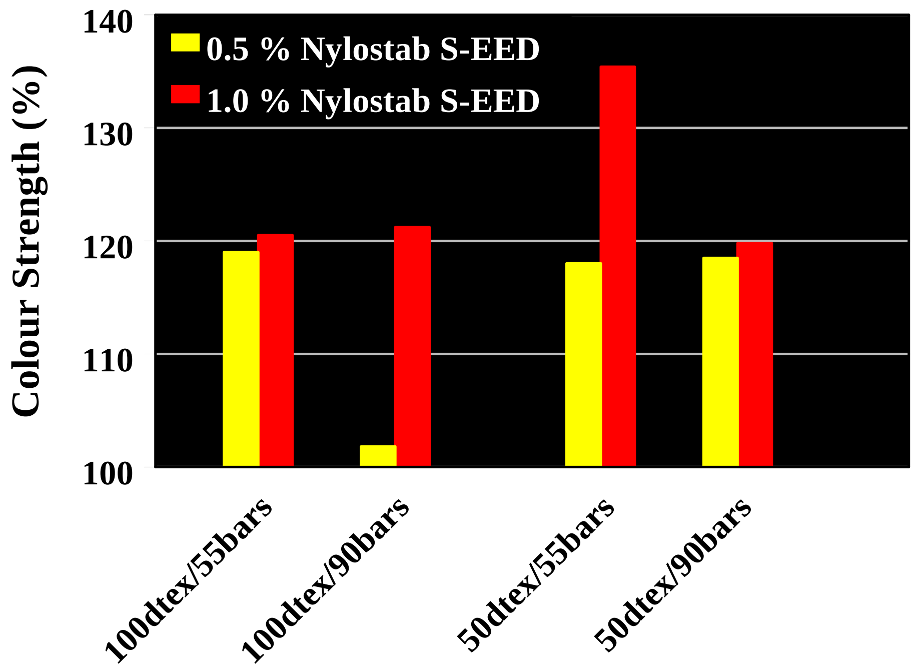
(Switzerland)

PA6.6 fibres 50dtex/55bars

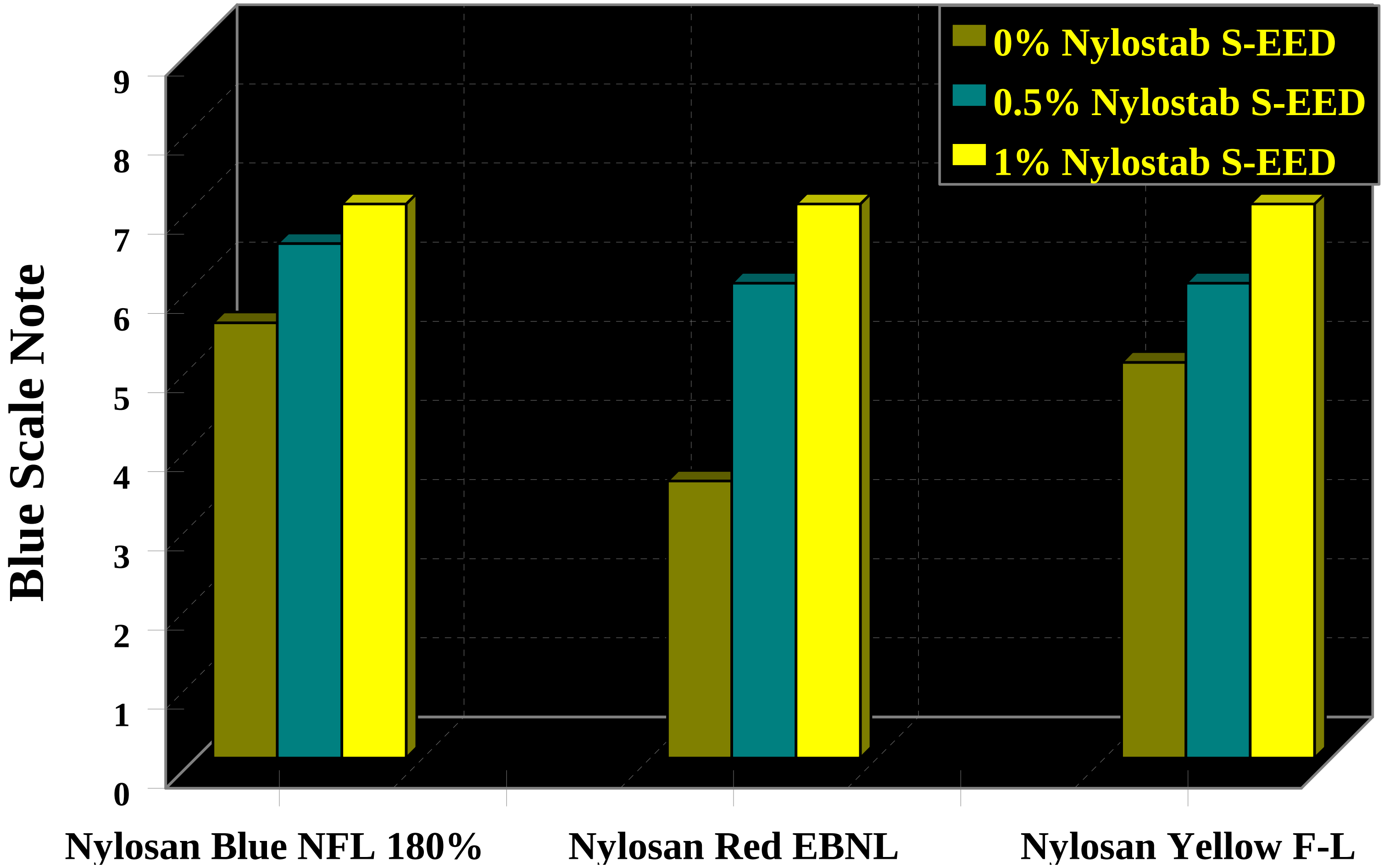


Nylosan Blue NFL 180% (2%)



Influence of NYLOSTAB S-EED on Dye-Light Fastness of PA6.6 Dyed Fibres (100 dtex/55bars)

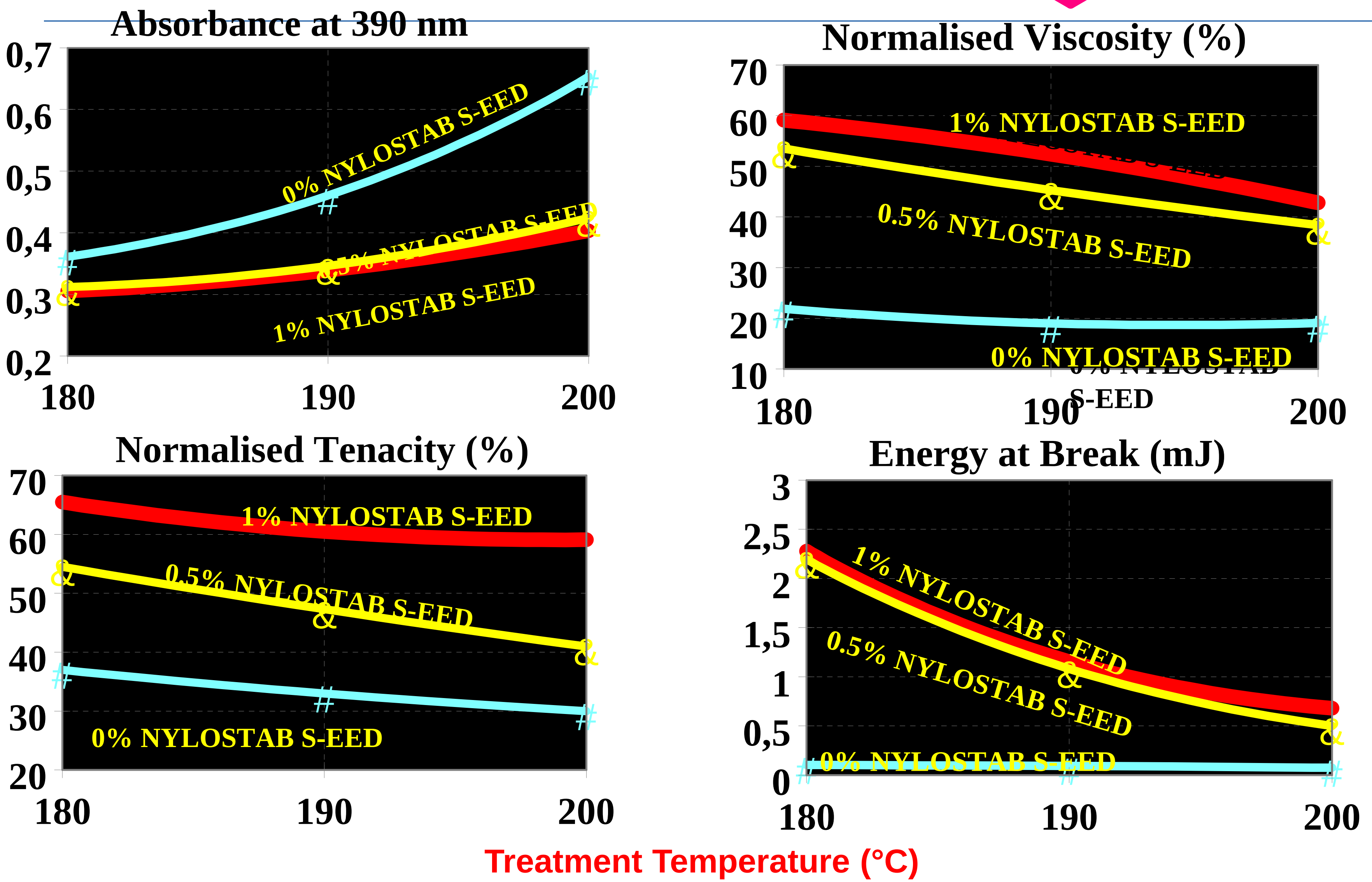
TECHNOLOGIES GmbH
(Switzerland)



(*) Dye concentration : 2%
Period of Exposure to Xenon lamp 200 hours

Influence of NYLOSTAB S-EED on Thermal Stability of PA6.6 (100dtex/55bars) Fibres.

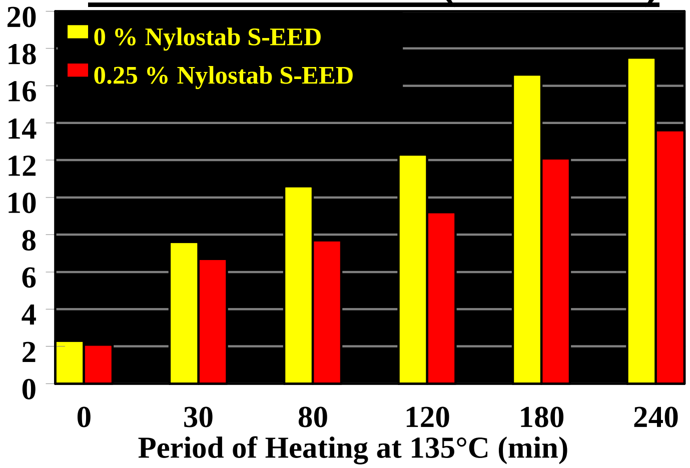
M C A TECHNOLOGIES GmbH
(Switzerland)



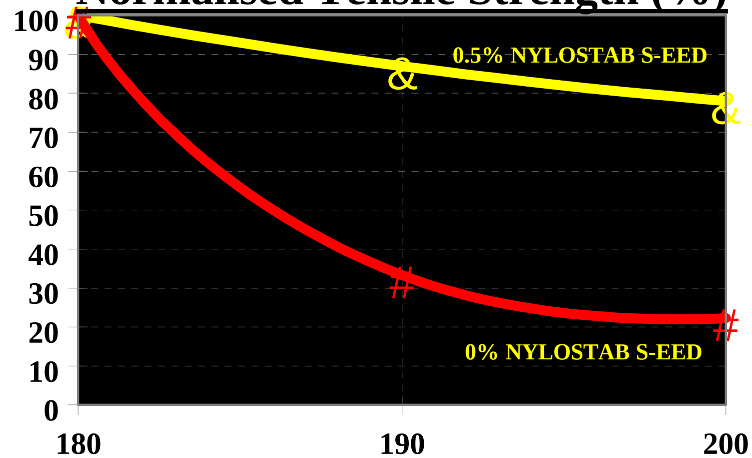
Influence of NYLOSTAB S-EED on Thermal Stability of PA6 (1200dtex) Carpet Fibres.

MCA TECHNOLOGIES GmbH (Switzerland)

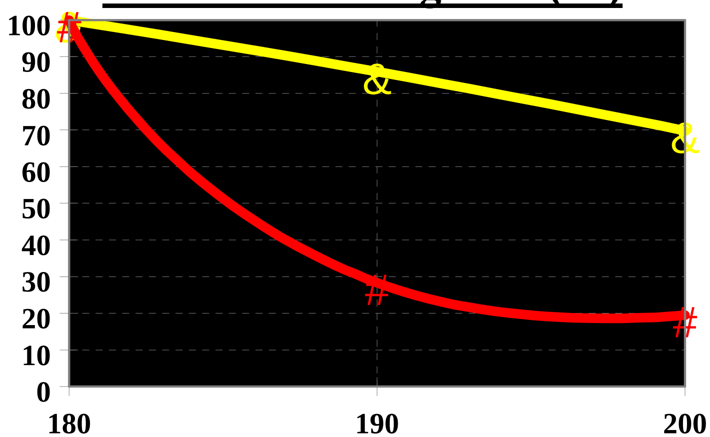
Yellowness Index (DIN 6167)



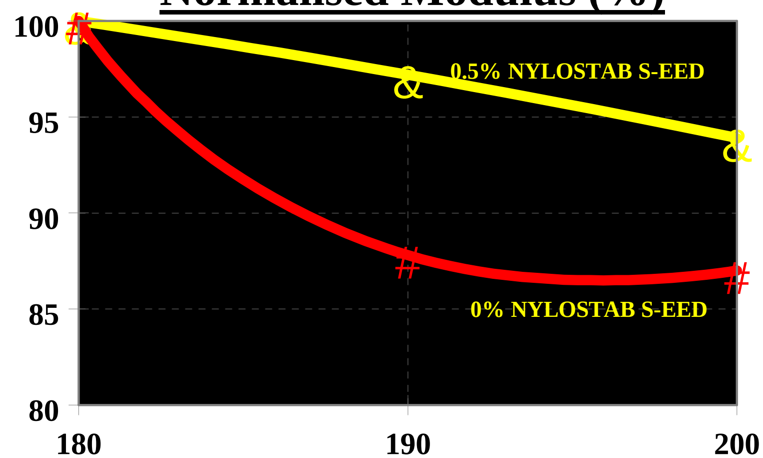
Normalised Tensile Strength (%)



Normalised Elongation (%)



Normalised Modulus (%)



Treatment Temperature (°C)

Dedicated to future geneations for the visions of tomorrow

END