



National Academy of Sciences of Ukraine
Institute of Physics



Charge separated state of phenothiazine upon adsorption on crystal of laponite

Yevgeniy Shaydyuk

NANOTECHNOLOGY: from fundamental research to innovations
August 26 - September 2, 2012, Bukovel, Ukraine.

Work team

*Laboratoire de Spectrochimie Infrarouge et Raman, UMR-CNRS 8516,
Bât. C5 Université de Lille 1, 59655 Villeneuve d'Ascq cedex, France.*



**S. Turrell,
A. Moissette,
F. Luchez,
M. Hureau**



*Institute of Biocolloidal Chemistry, NASU, 42 Vernadskii prosp.,
Kyiv 03142, Ukraine*



N. Lebovka

Introduction

Charge separation state (CSS) of dye molecule is temporary loss of electron(s) due to interaction with electromagnetic radiation (*fast electrons, γ -ray, X-ray, far-UV light or visible light*).

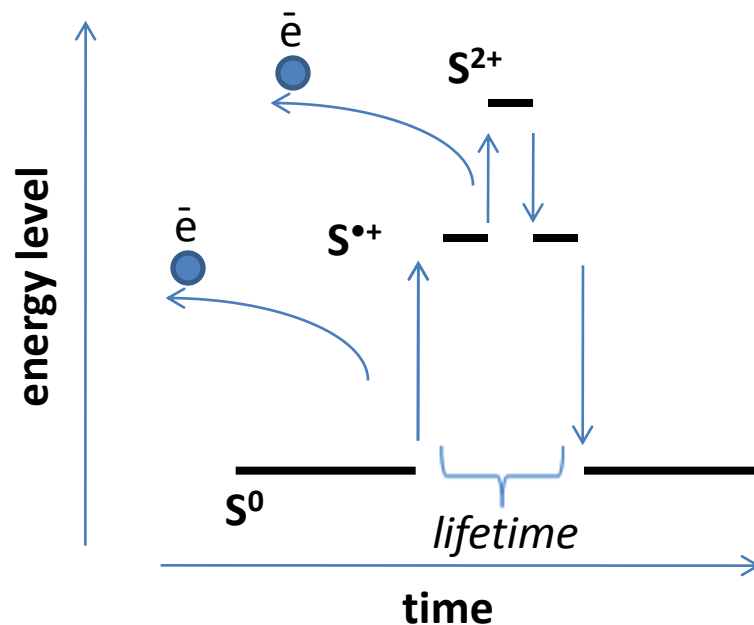
The ***lifetimes of the CSS*** in solid state are about **10^{-15}** seconds and in solution are less than **10^{-6}** seconds. So fast processes produce some technical difficulties in research. Therefore, for study of CSS the molecules are placed in the pores of materials where the lifetime increases up to **10^5 - 10^6** seconds (~from few days up to year).

Such materials can be very interesting for **fundamental studies of CSS**.

The main direction of fundamental study of this composite have a goal to increase the lifetime of the dye's radicals.

Another direction of research is study the effect of radiation on dye's radicals.

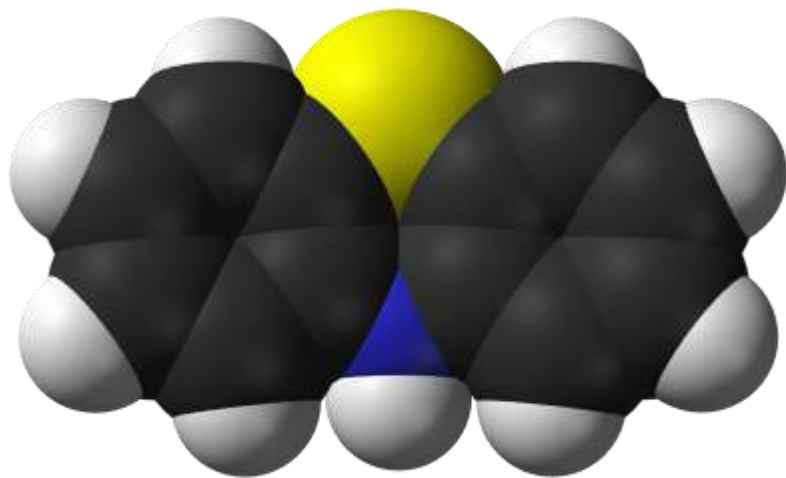
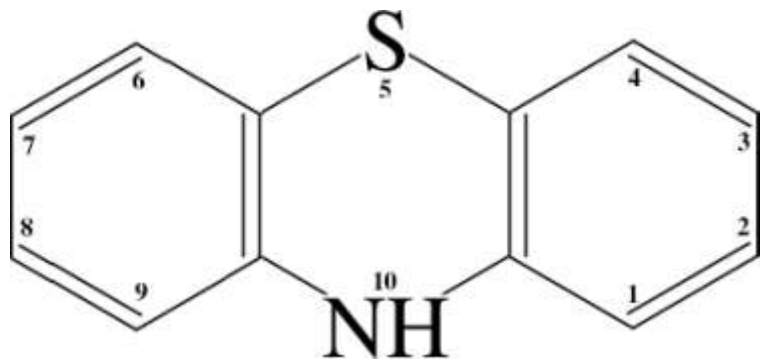
Our main goal of the research is to create composites with as small lifetime as possible.



Reactions

Reaction Equation	Event Description
$E_{hv} + S \rightarrow S^*$	Dye excitation
$S^* \rightarrow E_{hv} + S$	Dye relaxation
$S^+ + A^- \rightarrow S + A$	Dye regeneration
$S^* + TiO_2 \rightarrow e_{TiO_2}^* + S^+$	Electron injection
$S^+ + e_{TiO_2}^* \rightarrow TiO_2 + S^*$	Dye recombination
$e_{TiO_2}^* + A \rightarrow A^-$	Electrolyte recombination
$e_{TiO_2}^* + FTO \rightarrow e_I$	Current collection
$e_I + A \rightarrow A^-$	Electrolyte reduction

Phenothiazine (PTZ)



Thermal properties

Melting point	182— 187 °C
Boiling point	371 °C
Temperature of destruction	371 °C

Chemical properties

Solubility in water	0,00051 g/100 ml
Solubility in acetone	20 g/100 ml

Laponite RD*

Single Laponite crystal

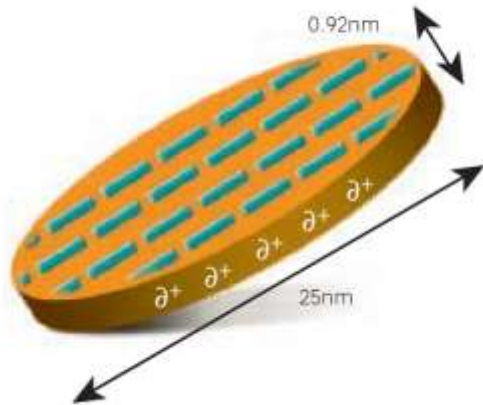
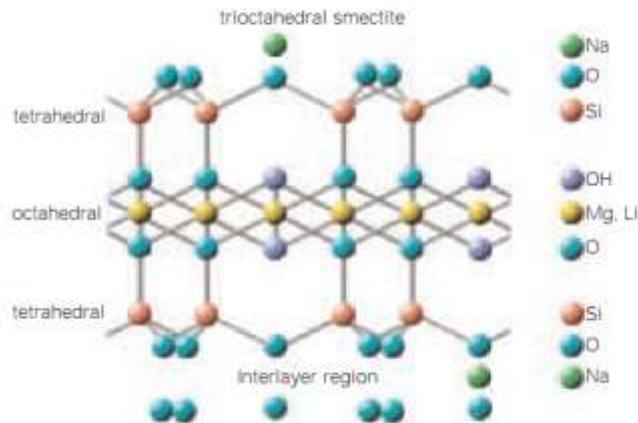


Figure 2. Idealised structural formula



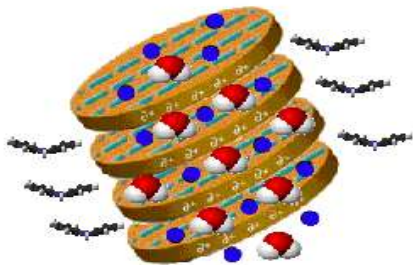
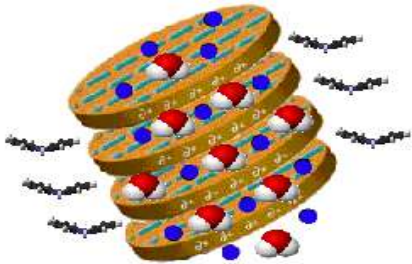
Property	
Appearance	free flowing white powder
Bulk Density	1000 kg/m ³
pH (2% suspension)	9.8
Sieve Analysis	2% Max >250 microns
Surface Area (BET)	370 m ² /g
Chemical Composition (dry basis)	
SiO ₂	59.5%
MgO	27.5%
Li ₂ O	0.8%
Na ₂ O	2.8%
Loss on Ignition	8.2%

*http://www.scprod.com/product_bulletins/PB%20Laponite%20RD.pdf

Methods of preparation

Method 1

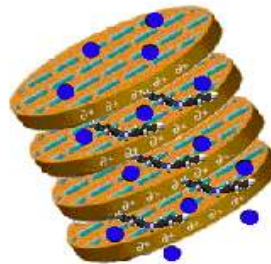
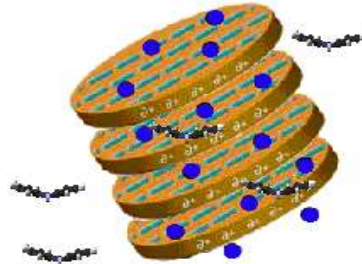
1. + PTZ



Method 2

1. Heat (200°C)

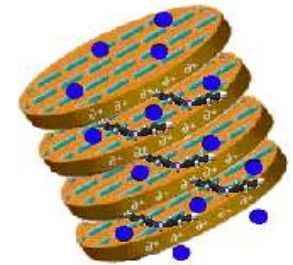
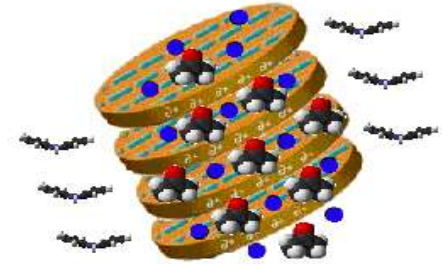
2. + PTZ



Method 3

1. + acetone

2. + PTZ



- PTZ



- H_2O



- acetone



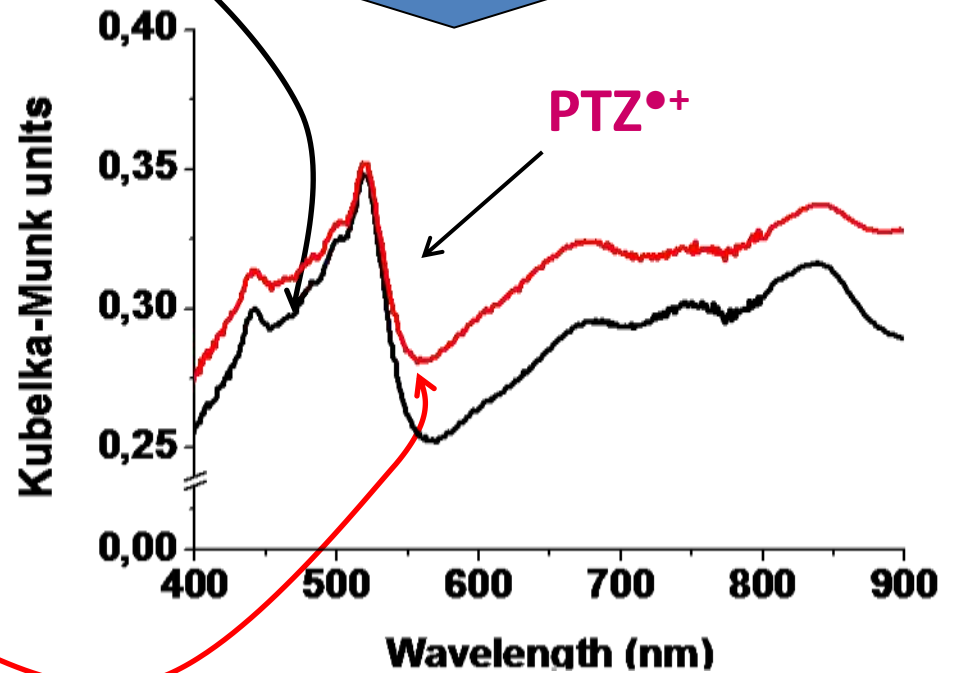
- Na^+

Diffuse reflection visible absorption spectroscopy (method 1)

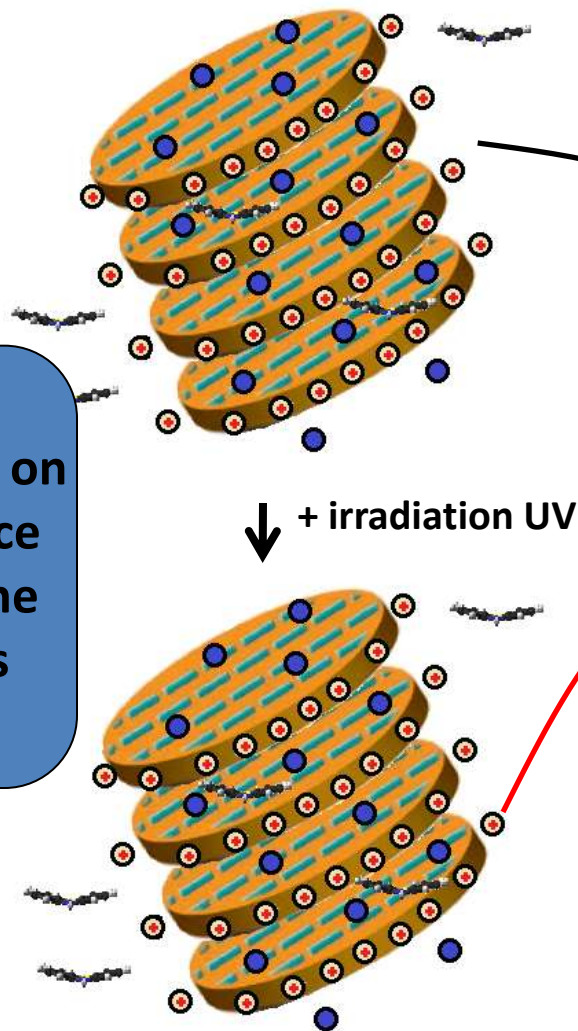
No big difference, all the electrons are already trapped (no confinement)

Electrons move here

+ irradiation UV

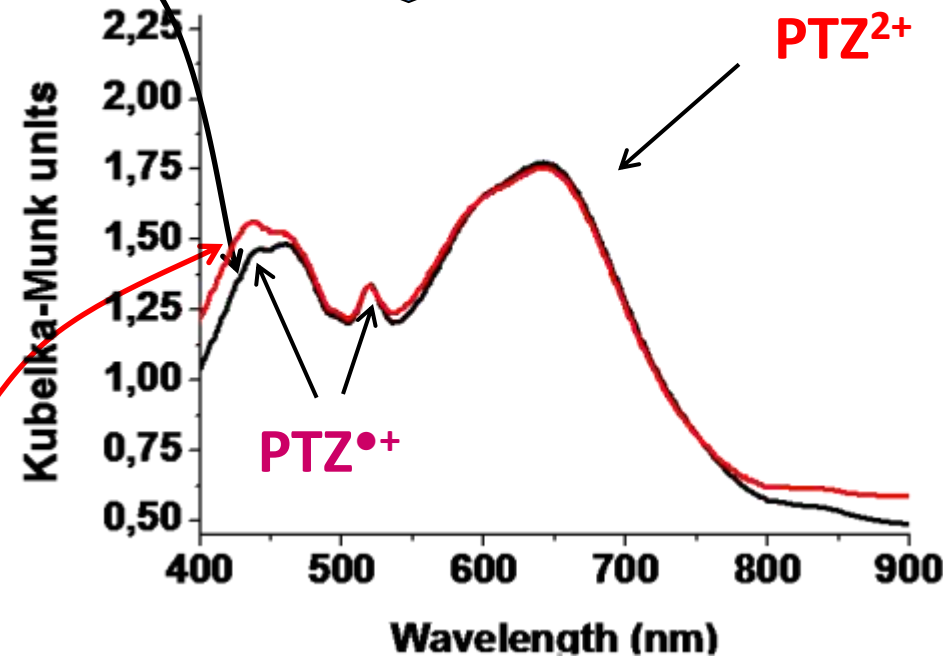


Diffuse reflection visible absorption spectroscopy (method 2)

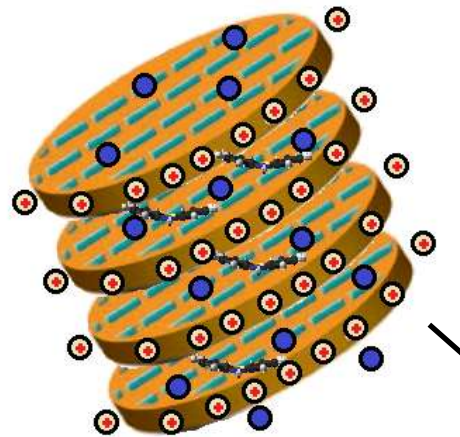


Molecules are adsorbed both on the outer surface and between the Laponite sheets

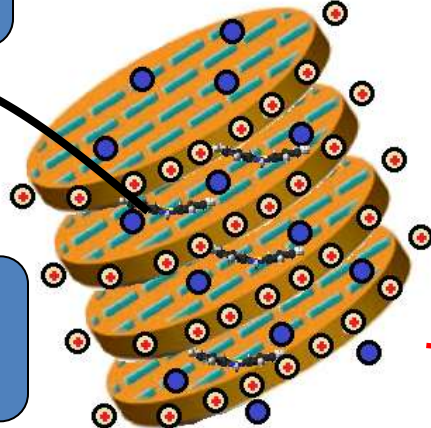
No big difference, all the electrons are already trapped



Diffuse reflection visible absorption spectroscopy (method 3)



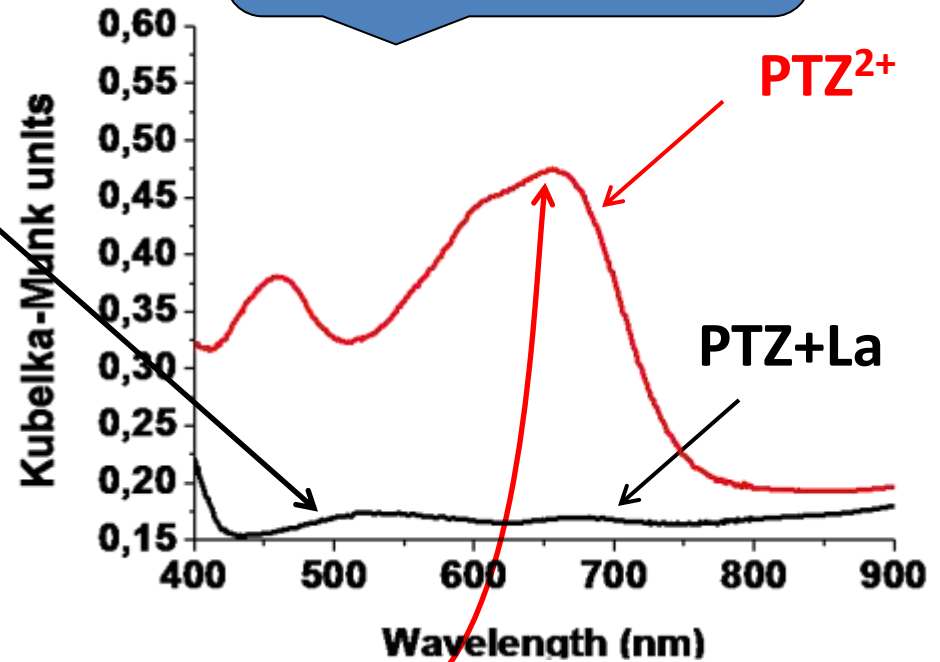
↓ + irradiation UV



Electrons
move here

Now it's a trap
for electrons

Evidences extraction of
two electrons



Conclusions

- 1. Prepared and studied composites based on Laponite platelets and dye PTZ exhibit the long lived CSS with small lifetime of 2 electrons state, which is absent in the pure PTZ under the same conditions.**
- 2. The methods of preparation affect spontaneous ionization of the dye molecules and allow obtaining of composites with different ionization properties.**
- 3. Extraction of 2 electrons from one PTZ molecule is observed for composites prepared using method 3.**
- 3. Relaxation of dye molecules to their original state occurs in the absence of light. This effect can be promising for future application in solar panels.**