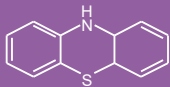


Revisiting the properties of phenothiazine in solution and in silica-hybrid materials

Sylvie Blanc

Chargée de Recherches
IPREM

Tuesday June 30



June 22, 2015

Photosensitizers

- Structure
- Known Properties
- Aim

Spectroscopic characterization

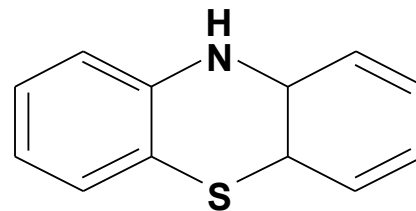
- Electronic spectroscopy (UV- visible absorption and fluorescence)
- Laser Flash Photolysis (transients)
- Singlet oxygen quantum yields (phosphorescence)

Photooxidation Properties

- oxidation of di-n-butylsulfide (DBS) in solution
- Oxidation of dimethylsulfide at the gas-solid interface

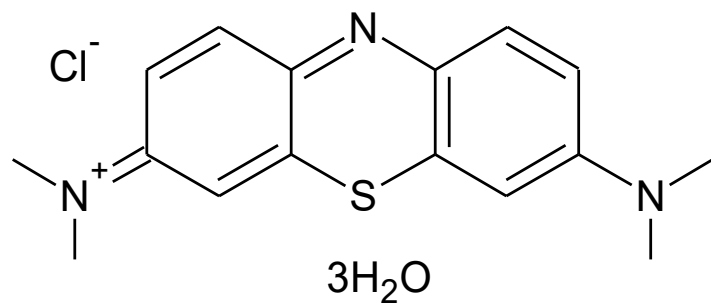


Phenothiazines : structures

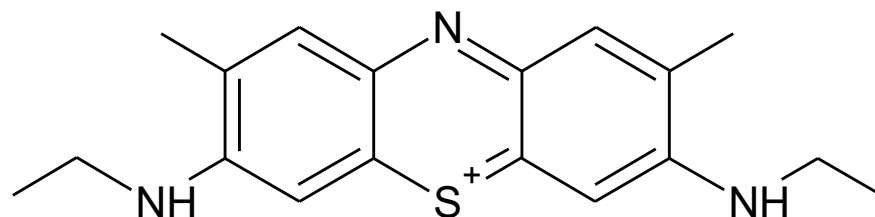


❖ Charged species

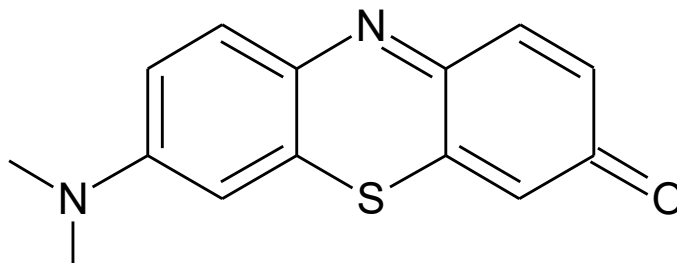
Methylene Blue



New Methylene Blue

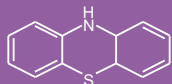


❖ Neutral species



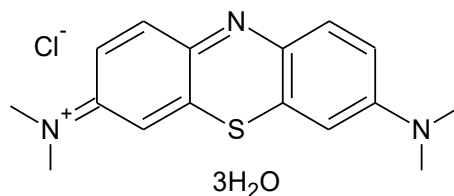
Methylene Violet

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Phenothiazines : known properties

❖ Metylene Blue

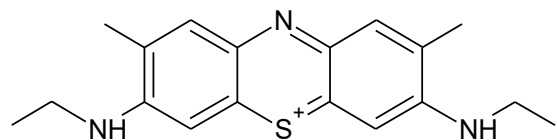


- medicinal and textile stain
- ISO test pollutant for photocatalysis,
- antioxidant and antiseptic
- singlet oxygen sensitizer,
- diagnostic agent
- antidote for cyanide and nitrate,
- drug (malaria, Alzheimer, neurodegenerative diseases)
- photodynamic inactivation (PDI) of viruses and bacteria in blood fractions
- photodynamic therapy (PDT).

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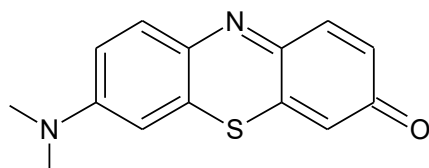
Phenothiazines : known properties

❖ New Methylene Blue



- higher affinity to membranes (*due to its more lipophilic character*)
- easier penetration in cells
increases intracellular PDT activity

❖ Methylene Violet



- higher activity for killing intracellular viruses (a much easier penetration in cells)
- more easily trapped by lipoproteins
- particular affinity towards DNA

suitable potential PS for photodynamic therapy?

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Revisiting the properties of phenothiazine in solution and in silica-hybrid materials

Phenothiazines : aim of the studies

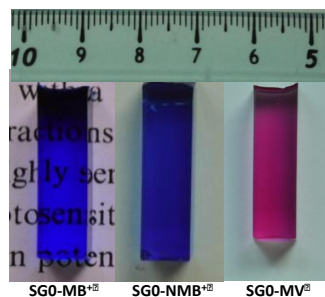
❖ Media

- **Solution**

CH_3CN , MeOH

- **Solid**

Silica sol-gel monoliths



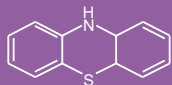
❖ Properties

- **Transient excited states**

- **Singlet oxygen quantum yield**

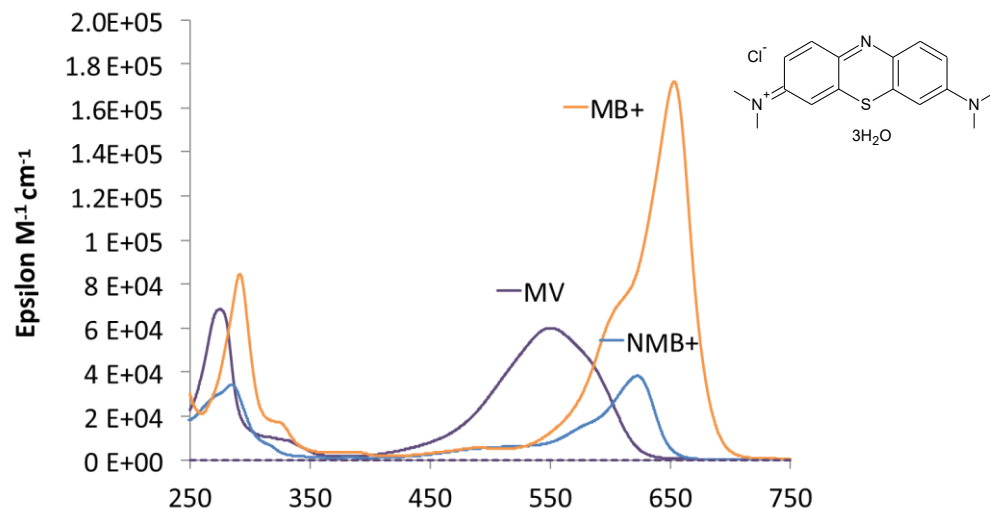
- **Reactivity**

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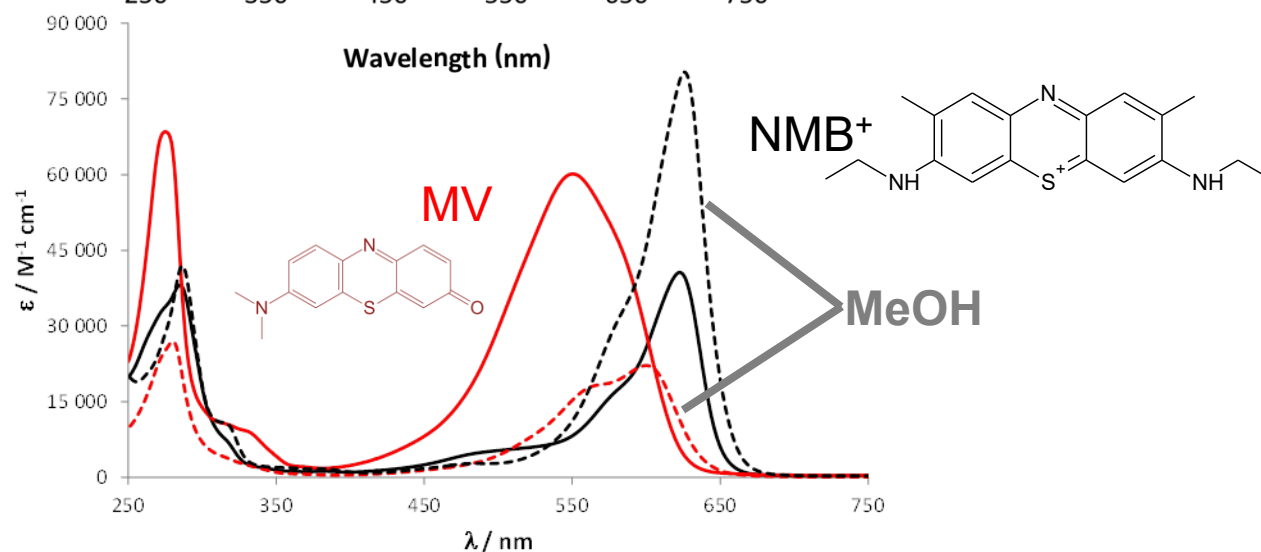


Phenothiazines : absorption spectra in solution

❖ CH₃CN

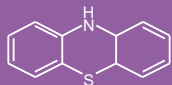


❖ MeOH



MV is very sensitive to the solvent

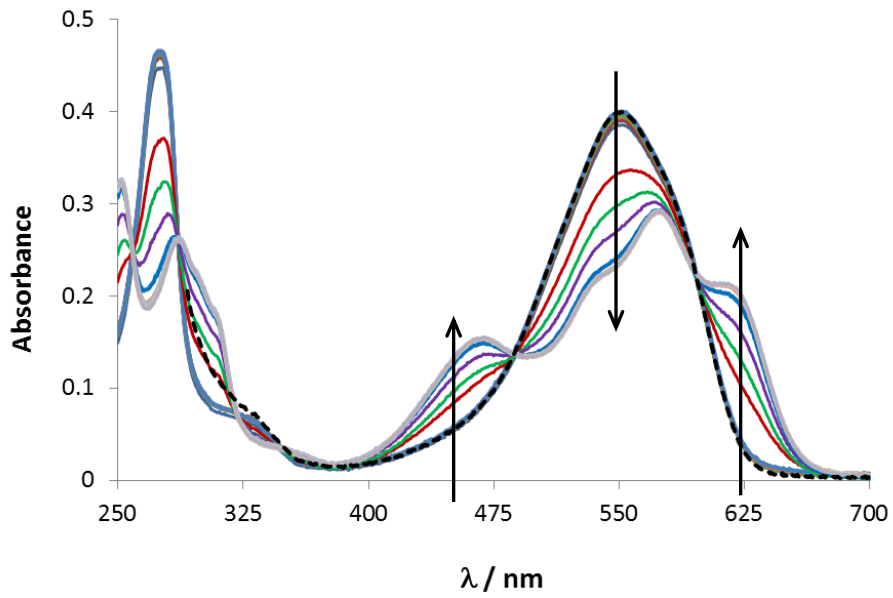
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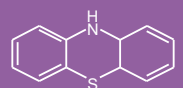
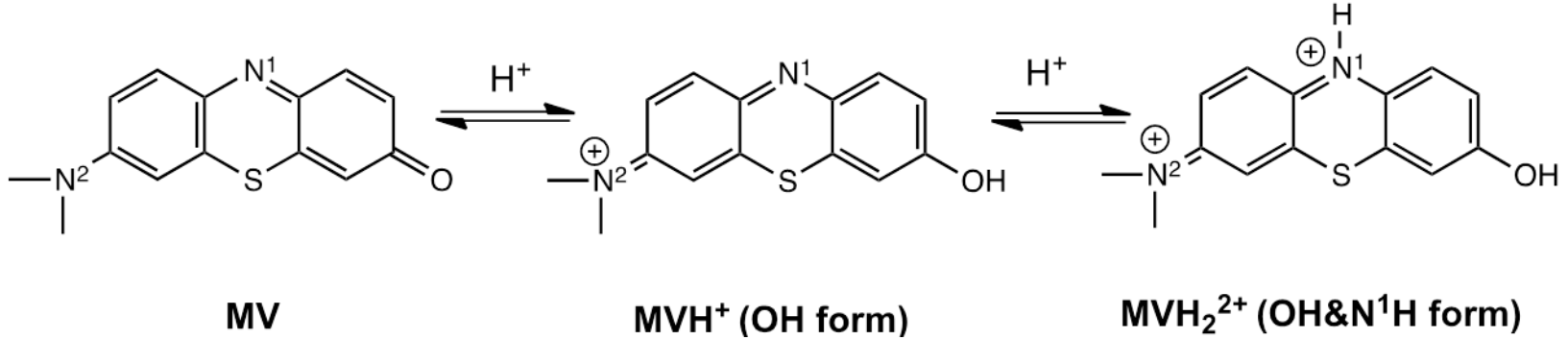
MV : UV absorption spectra in solution

❖ Role of acid

MV in ACN + CH₃SO₃H



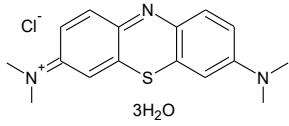
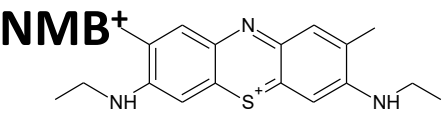
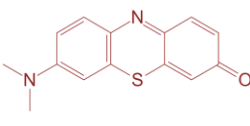
Spectral changes reversible by addition of amine



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Phenothiazines : UV-Visible fluorescence properties

❖ Various solvent

	MB⁺ 		NMB⁺ 		MV 	
	<i>MeOH</i>	<i>ACN</i>	<i>MeOH</i>	<i>ACN</i>	<i>MeOH</i>	<i>ACN</i>
$\lambda_{\text{max,em}} / \text{nm}$	670	670	642	653	642	628
Φ_{F}	0.03	0.05 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.09 ± 0.01
$\tau_{\text{F}} / \text{ns}$	0.60 ± 0.05	1.01 ± 0.10	0.70 ± 0.06	0.86 ± 0.06	0.50 ± 0.05	1.49 ± 0.10

Low quantum yields and short lifetimes in both ACN and MeOH

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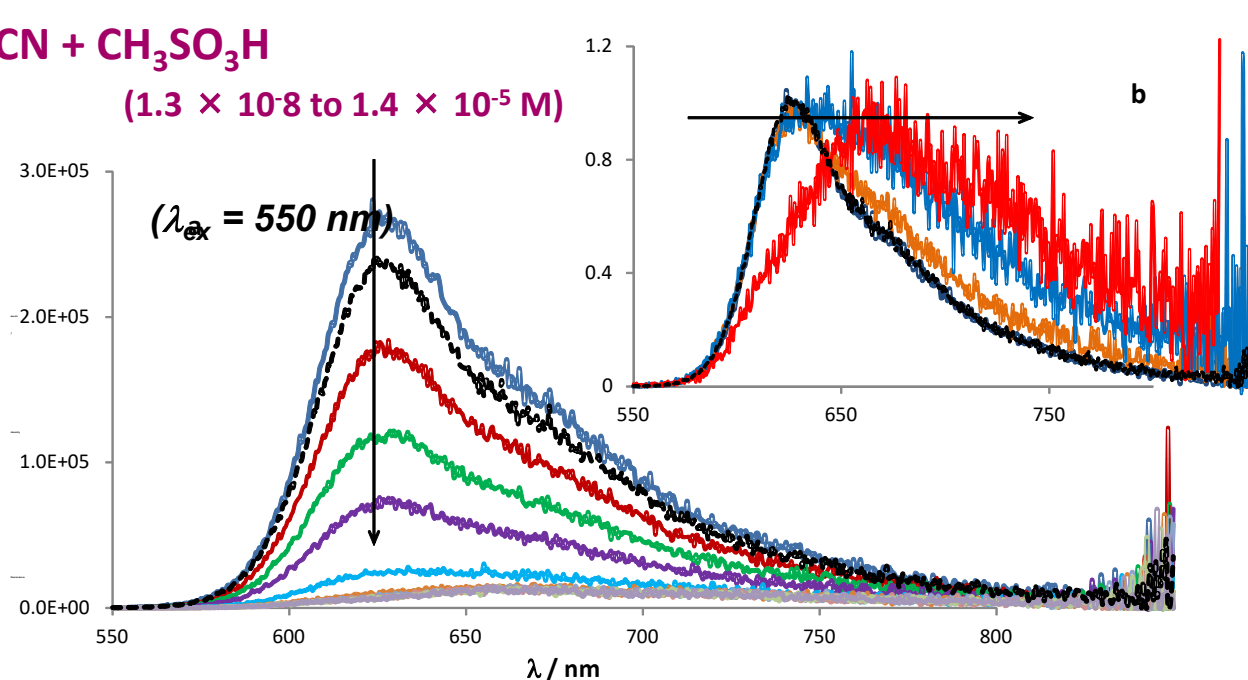
Revisiting the properties of phenothiazine in solution and in silica-hybrid materials

MV : UV-Visible fluorescence properties

❖ Presence of acid

MV in ACN + CH₃SO₃H

(1.3×10^{-8} to 1.4×10^{-5} M)



Addition of acid :

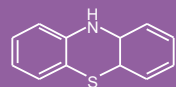
decrease of the fluorescence

red shift of the emission spectrum

reversible by addition of amine

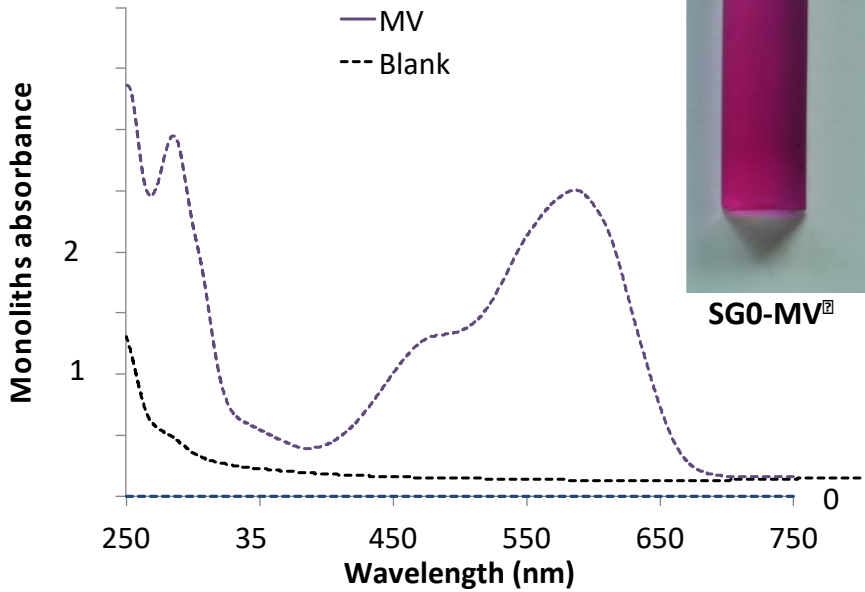
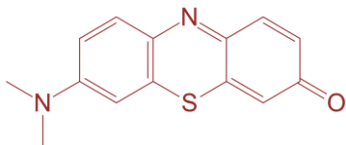
$\tau_F = 0.35 \pm 0.05$ ns; $\Phi_F = 0.01$

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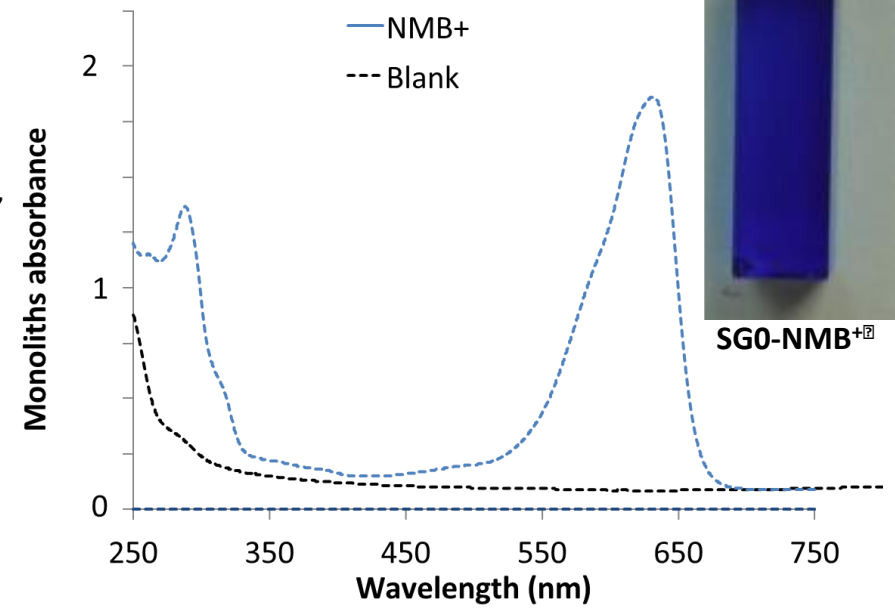
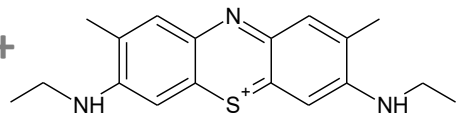


UV-Visible absorption of transparent silica monolith

❖ MV

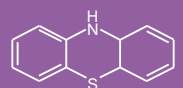


❖ NMB⁺



NMB⁺ : absorption spectrum very similar to that in MeOH

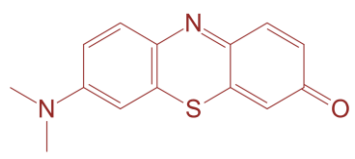
MV : broad bands suggesting the presence of both acid and neutral forms



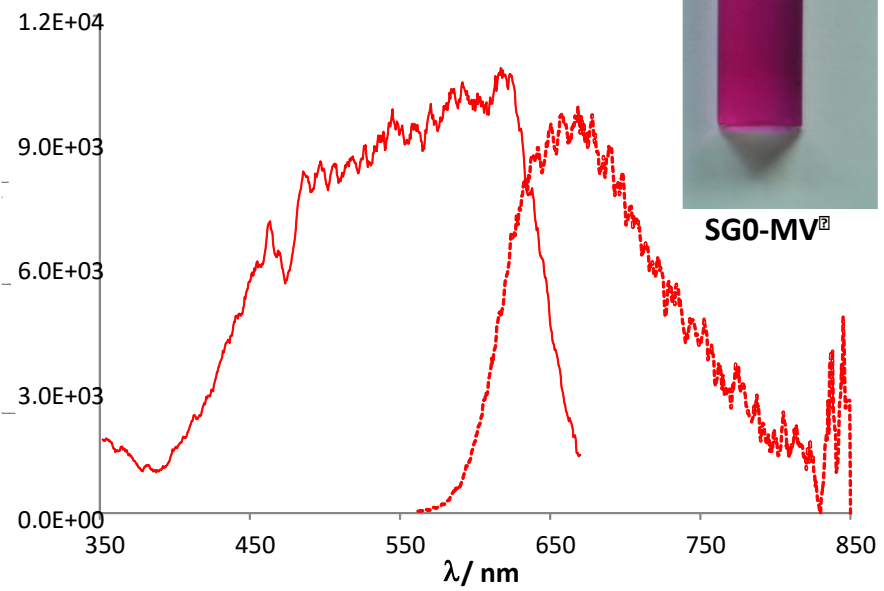
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Fluorescence of transparent silica monoliths

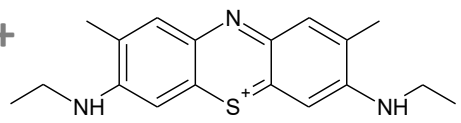
❖ MV



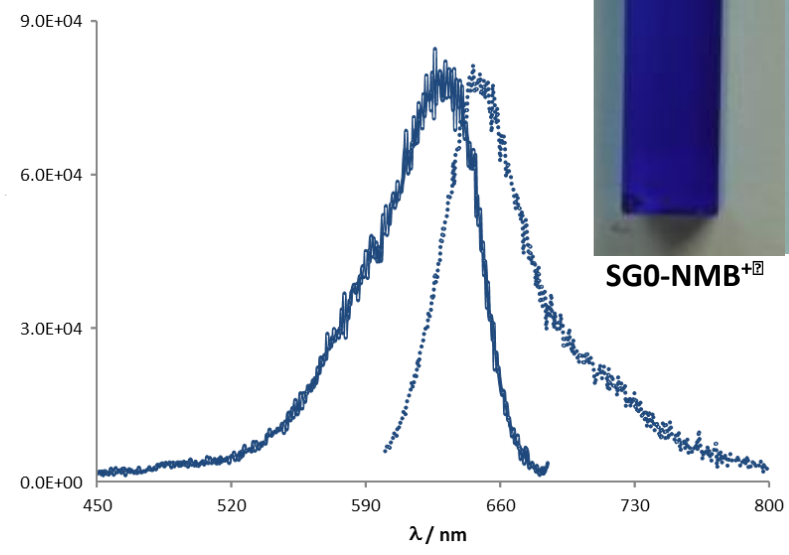
SG0-MV²



❖ NMB⁺

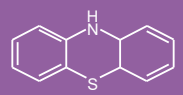


SG0-NMB⁺



$\tau_F / \text{ns } 0.70 \pm 0.07$
very short lifetimes

Fluorescence spectra very similar to those in MeOH



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Singlet oxygen detection

❖ quantum yields and lifetimes

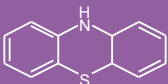
	$\Phi_{\Delta}^{\text{PS}}$		
	ACN	CD ₃ OD	Monolith
τ_{Δ} (μs)	62	227 (10 in MeOH)	19
MB ⁺	0.58	0.52	-
NMB ⁺	0.66	0.82	0.6
MV	0.60	0.73	1.0

Phosphorescence at 1270 nm

Continuous measurements relative to PN  **in the same solvent or in SiO₂, assuming $\Phi_{\Delta}(\text{PN}) = 1$**
IMRCP, Toulouse

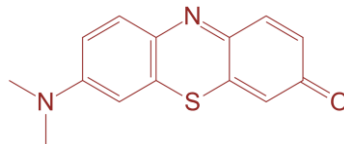
MV: Good ¹O₂ sensitizer in SiO₂

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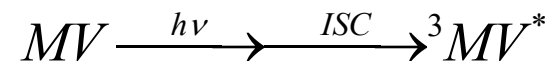
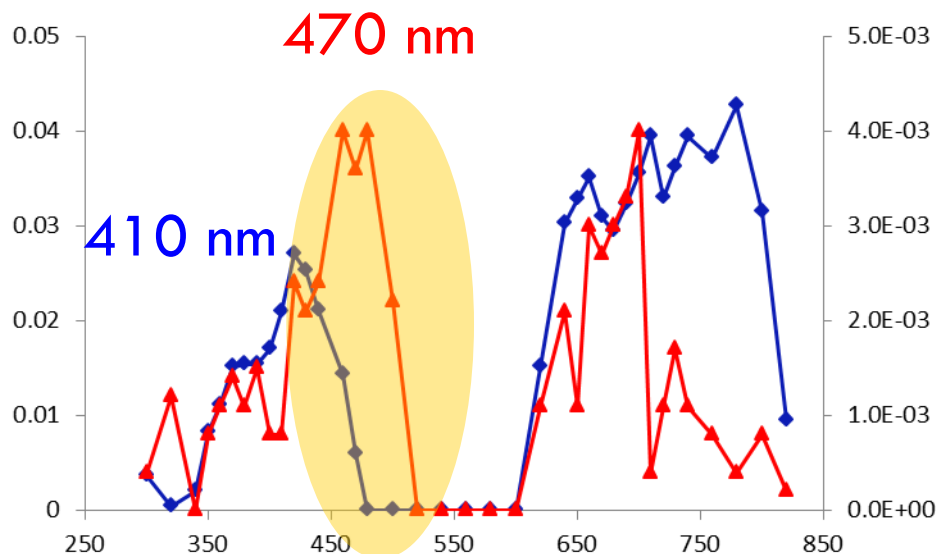


Revisiting the properties of phenothiazine in solution and in silica-hybrid materials

MV transients spectra

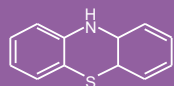


❖ ACN



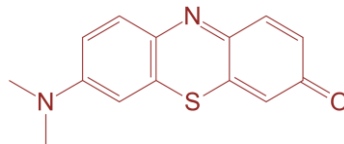
Formation of ${}^3MV^*$ and $MV^{\bullet+}$

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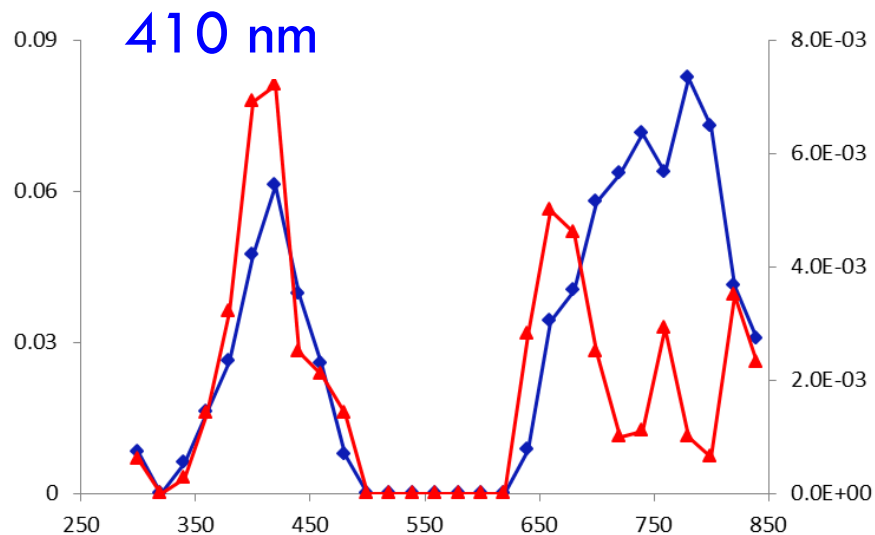


Revisiting the properties of phenothiazine in solution and in silica-hybrid materials

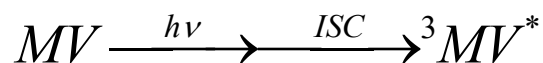
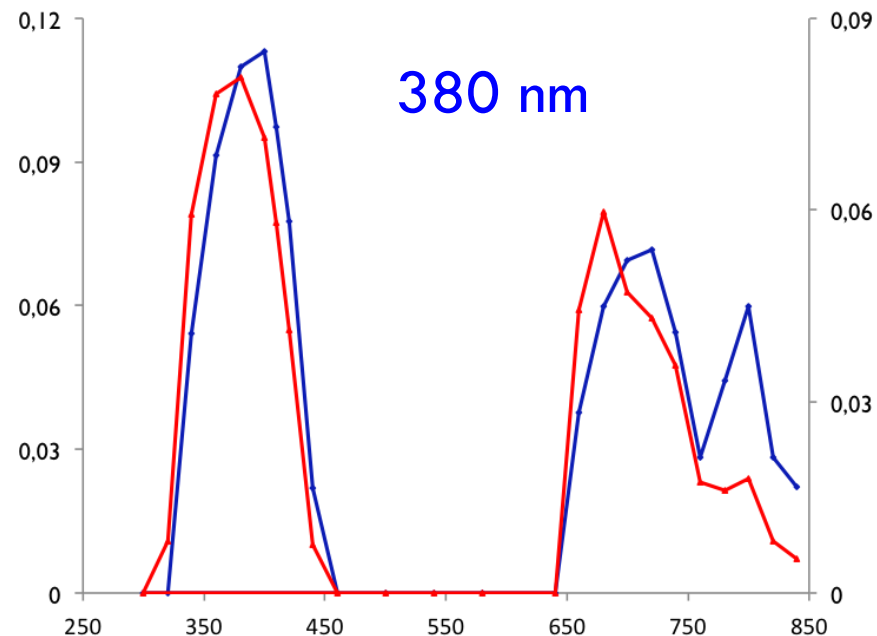
MV transients spectra



❖ MeOH



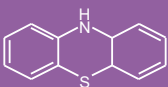
❖ Silica monolith



Only formation of ${}^3MV^*$

Species in SiO_2 similar to MeOH but blue-shifted

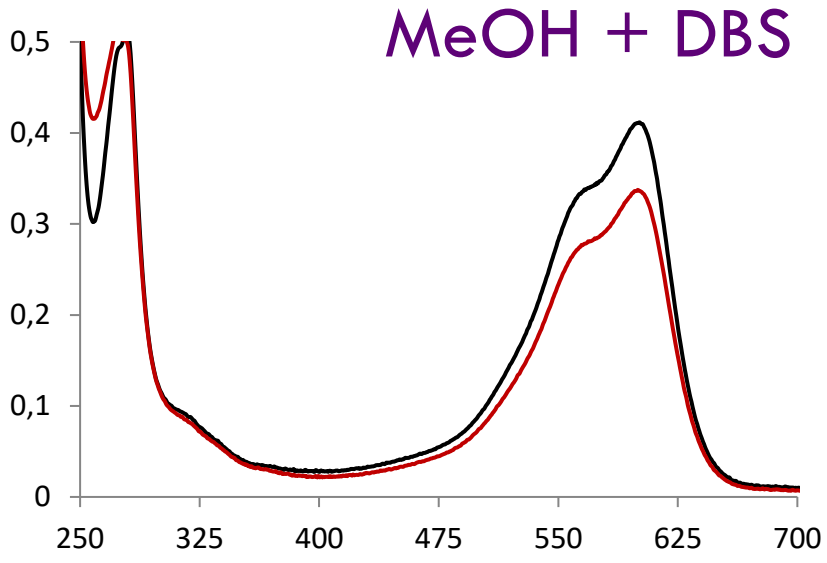
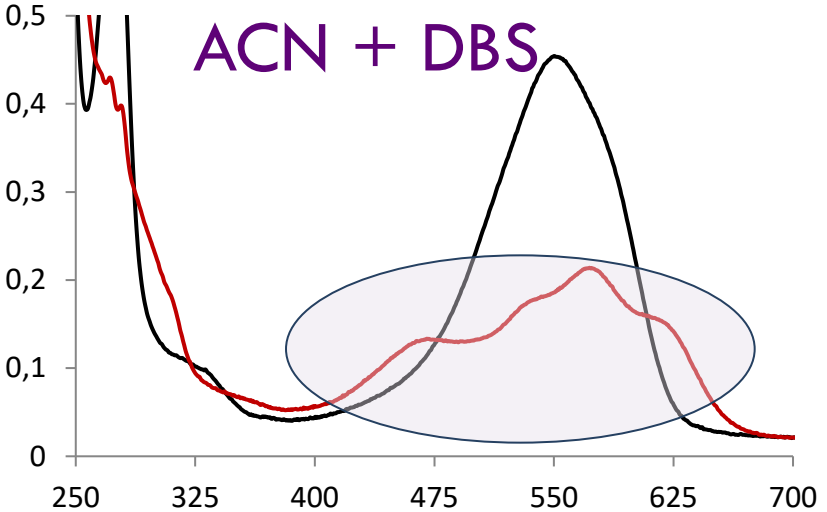
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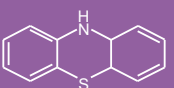
Reactivity of MV in solution

❖ Main reaction products of di-n-butylsulfide (DBS) oxidation

- From NMR: sulfoxide and sulfone
- from UV visible MV spectra after irradiation :



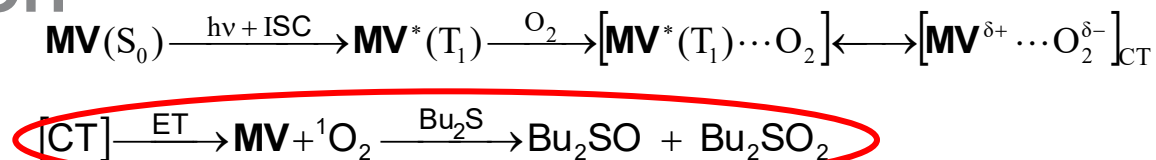
Presence of sulfonic/sulfuric acid after irradiation of DBS only in ACN



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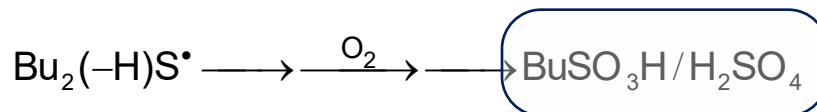
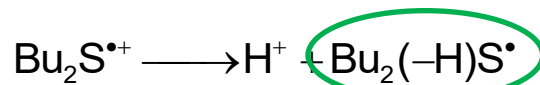
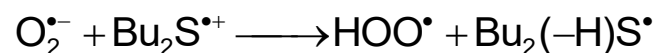
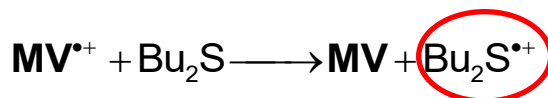
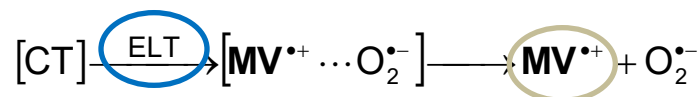
Mechanism of di-n-butylsulfide (DBS) oxidation by MV

❖ ACN and MeOH

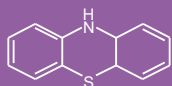


Mainly energy transfer and 1O_2 production (Type II reaction)

❖ ACN

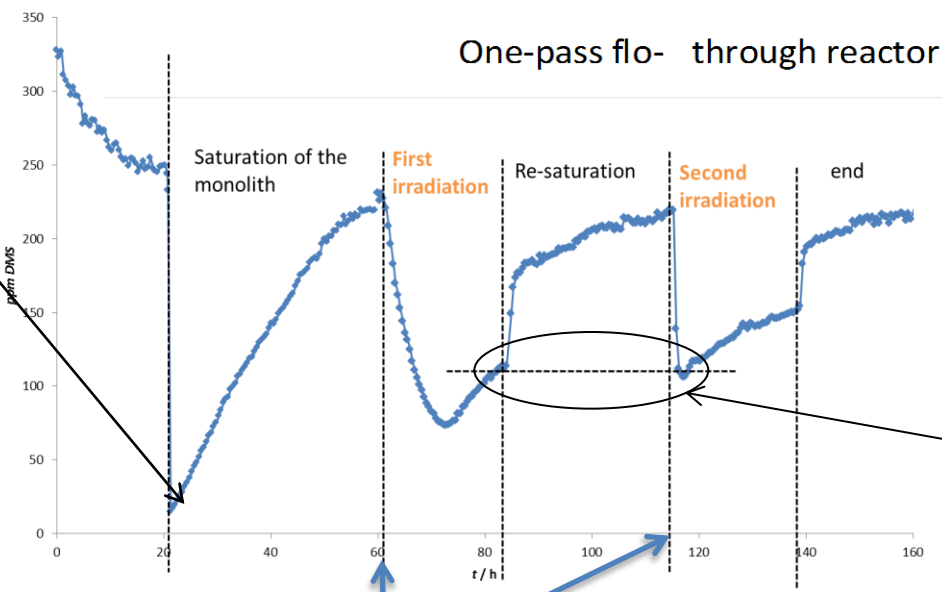
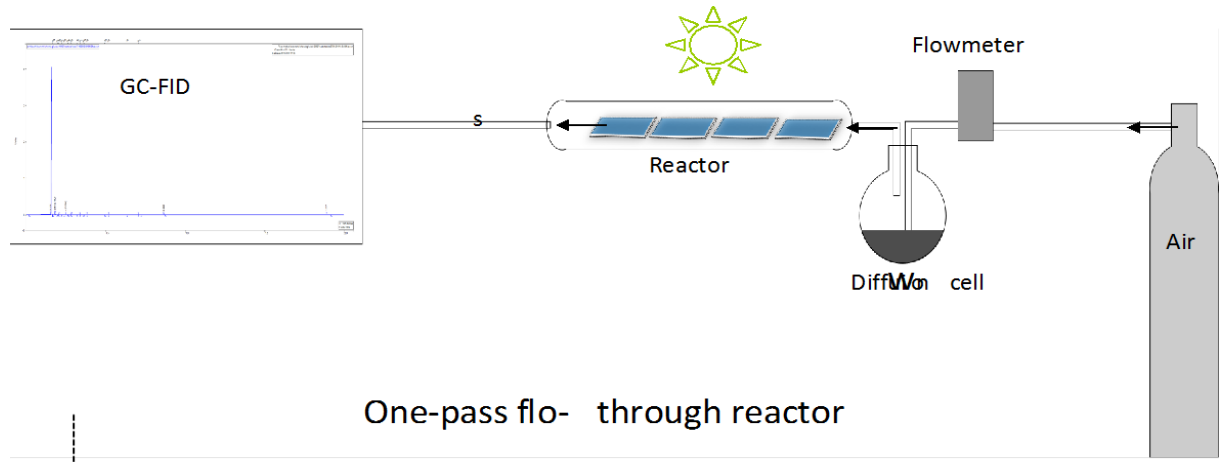


Side electron transfer/radical reaction (Type I reaction)



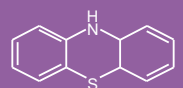
Oxidation of dimethylsulfide at the gas-solid interface

❖ Results



High adsorbing of silica in the dark

Adsorption of reaction products limits activity



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Solvent free oxidation of dimethylsulfide with monoliths

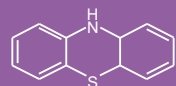
❖ Results

PS	PS amount (mol g ⁻¹)	<i>P</i> (mW cm ⁻²)	Conversion (%)		Bleaching (%)
			cycle 1	cycle 2	
MB ⁺	4.7 × 10 ⁻⁷	16.5	1.6	1.0	65
NMB ⁺	8.5 × 10 ⁻⁸	15.1	3.7	2.2	90
MV	5.0 × 10 ⁻⁷	16.2	2.5	0.6	90

Only sulfoxide and sulfone detected

E. Arzoumanian, F. Ronzani, A. Trivella, E. Oliveros, M. Sarakha, C. Richard, S. Blanc, T. Pigot, S. Lacombe, ACS Appl. Mater. Interfac., 6, 275-288 (2014).

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Revisiting the properties of phenothiazine in solution and in silica-hybrid materials

Conclusions

❖ Phenothiazine properties

- NMB⁺ and MV: good singlet oxygen photosensitizers
- NMB⁺
 - no sensitivity of the photophysical properties of to the medium
 - only energy transfer mechanism (type II)
- MV
 - highly sensitive to the solvent and to acidity (easy protonation to MVH⁺)
 - mainly energy transfer
 - with possible side-electron transfer reaction in aprotic solvents (type I)

❖ Singlet oxygen formation

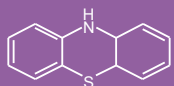
- preferably use protic solvents to favor ¹O₂ production (type II),
- Efficient in silica monoliths embedding phenothiazines

❖ Monoliths

- practical and efficient photoactive materials
- Solvent-free oxidation of sulfides at the gas-solid interface

June 22, 2015

Revisiting the properties of phenothiazine in solution and in silica-hybrid materials



Aknowledgment

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