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Photoluminescence properties of Zinc White

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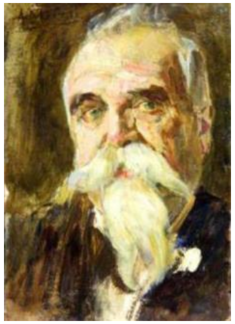
Forecast

Conservative issues in cultural heritage community with **Modern Pigments**:

- Synthetis processes
- Degradation
- Interaction metal-binder



Case of study: **Zinc White Pigment**
Semiconductor pigment
19^{th} - 20^{th} century

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Photo-physical study

Our approach:

- Characterization of recombination mechanisms
- Time resolved analysis: emission dynamics

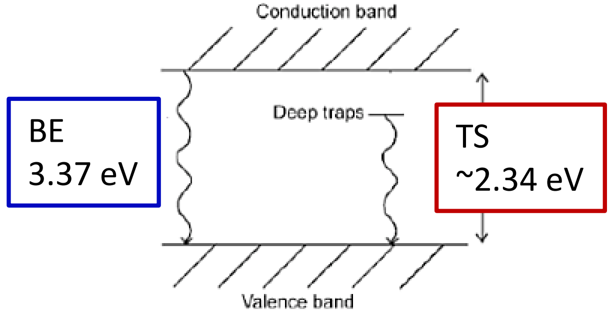
Zinc white made by ZnO

Case of study
Twelve pastel historical samples.
LeFranc Bourgeois (beginning 20th C)

S01 S02 S03 S04 S05 S06

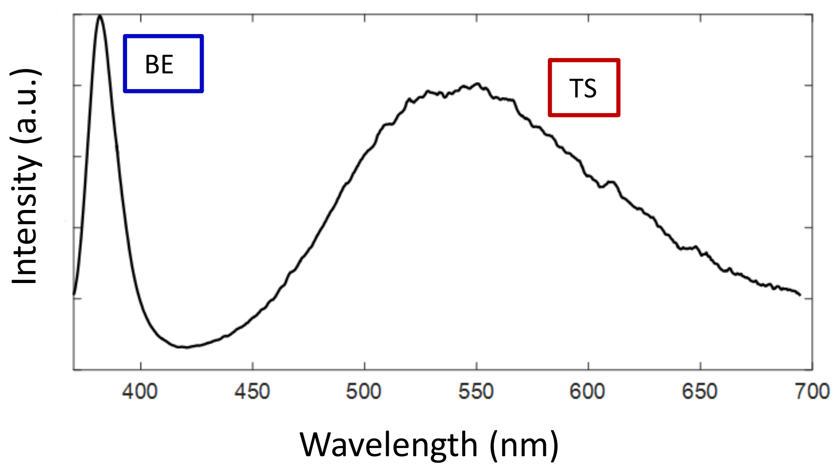
S07 S08 S09 S10 S11 S12

ZnO



IIb-VIa
Semiconductor
- Large band gap
- Direct transition

Photoluminescence spectrum



Different origin of BE/TS emissions
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Different lifetime
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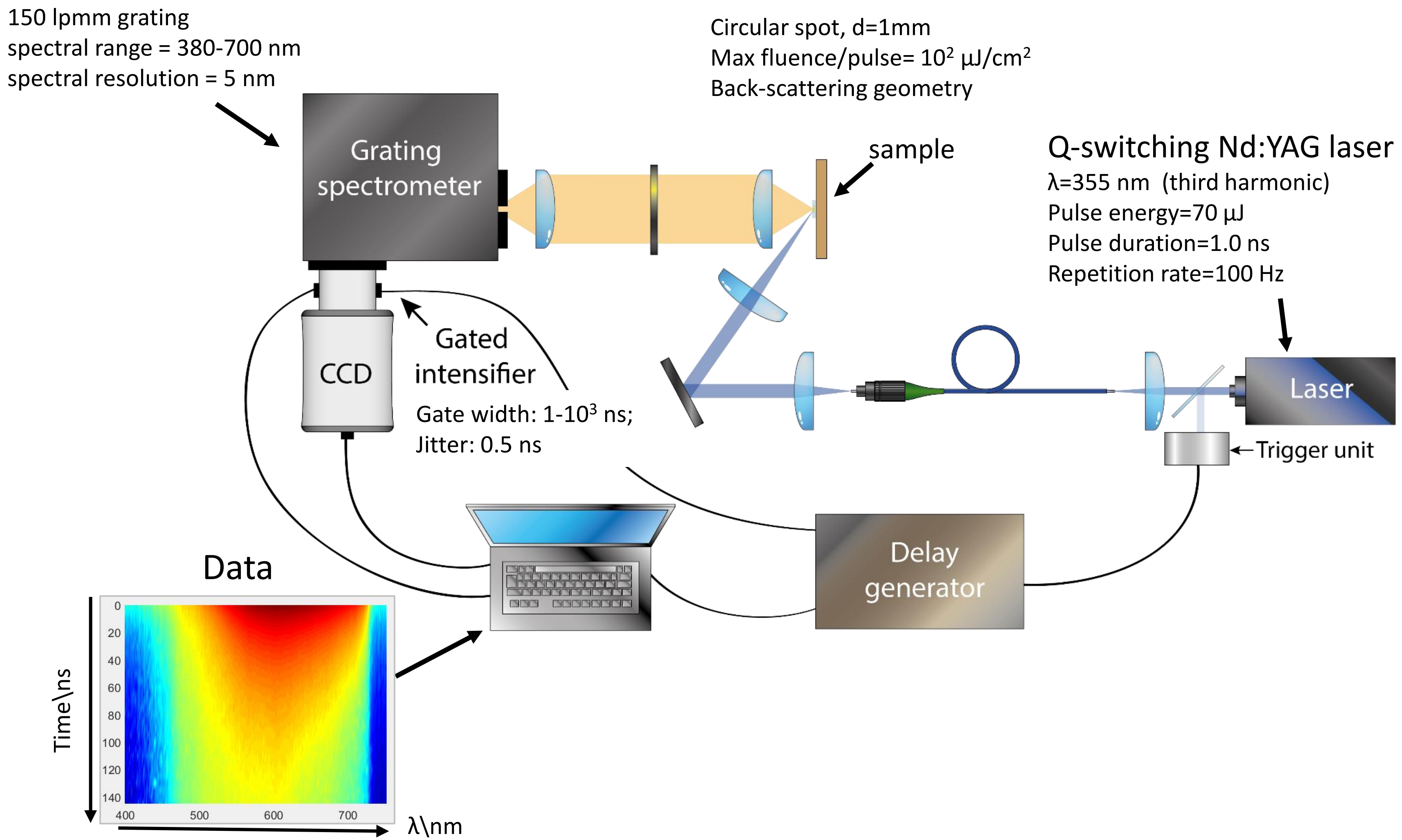
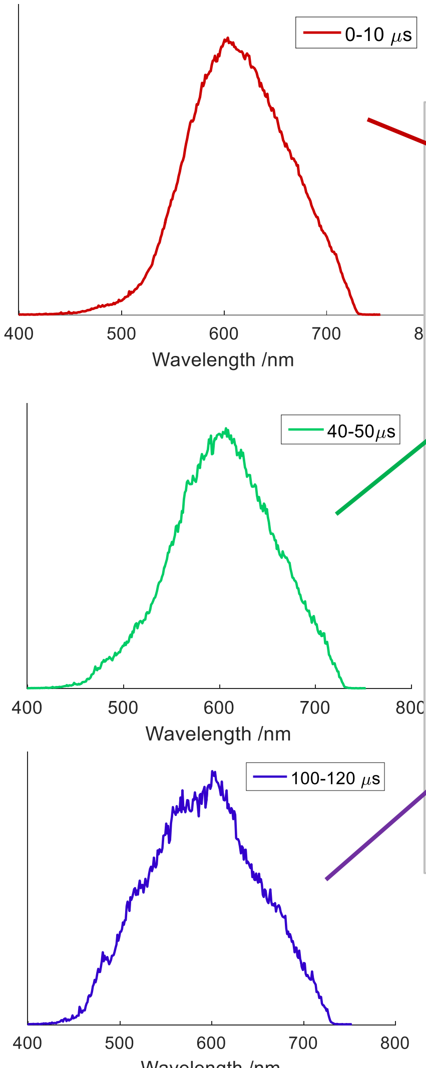
Time Resolved Photoluminescence

Time Resolved Spectrometer

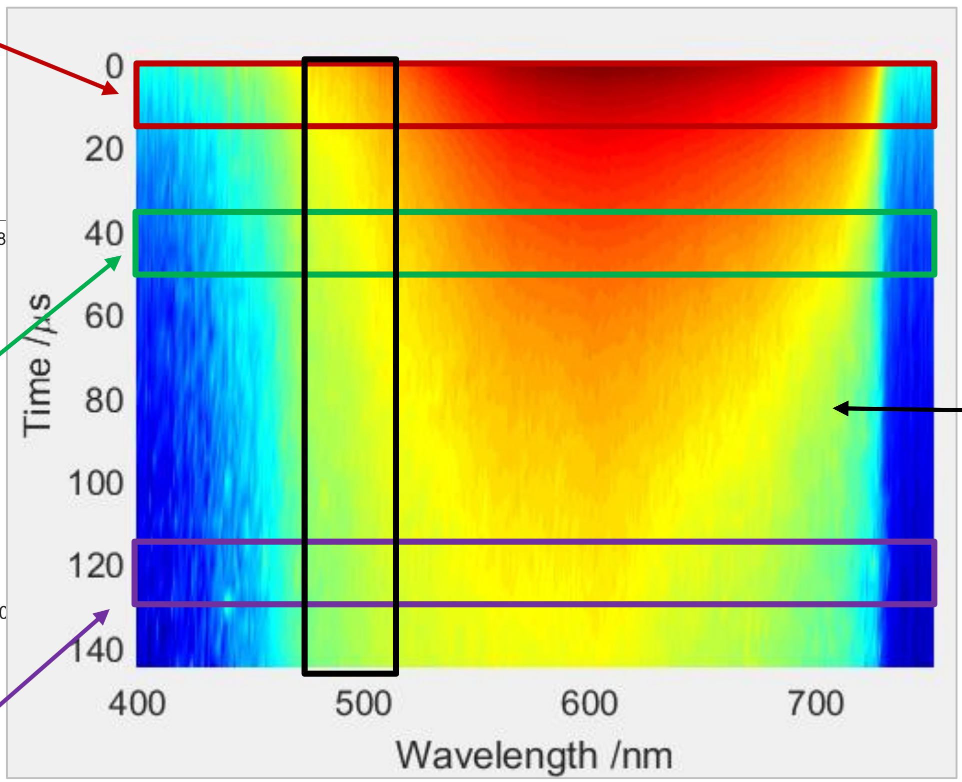


Time Resolved Spectral Map

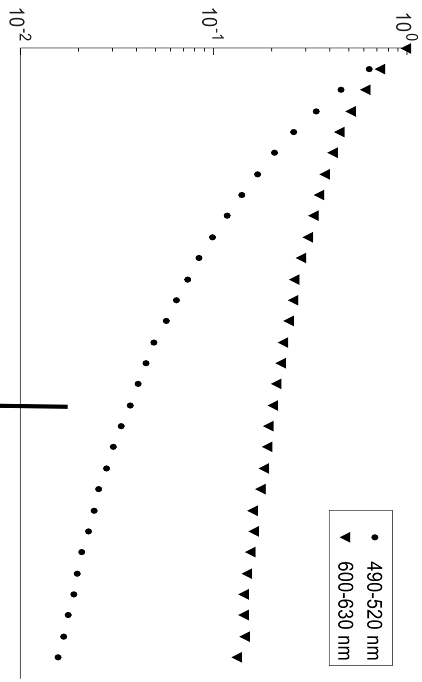
PL spectra



Matrix (n x m) = (times x wavelength)

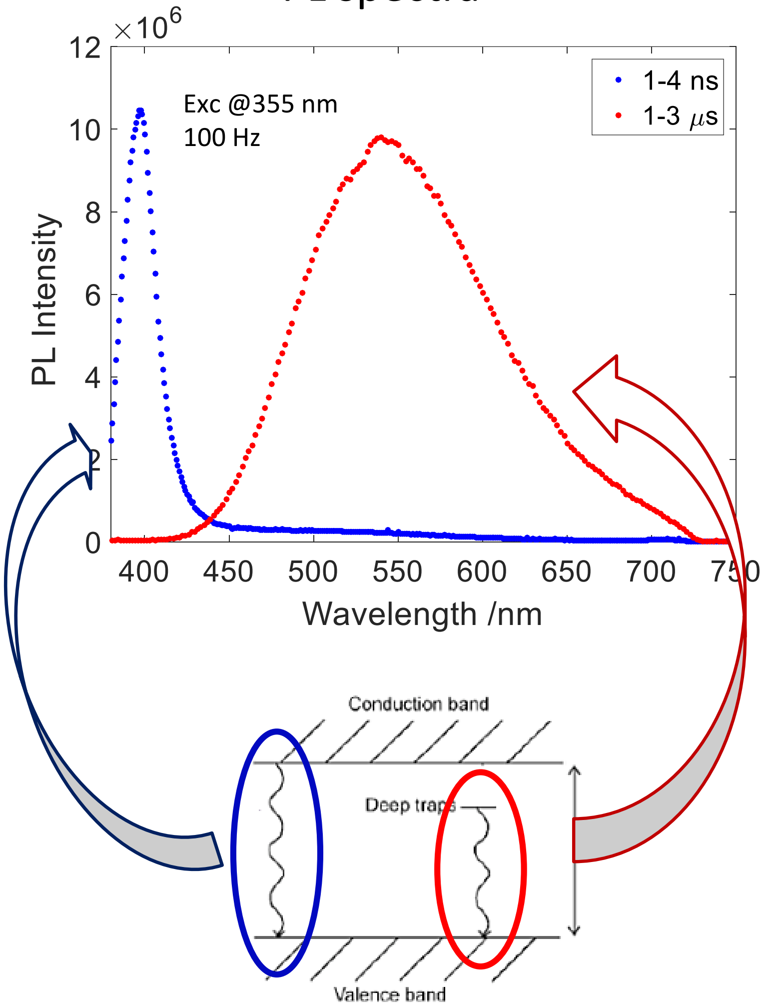


Decay profile

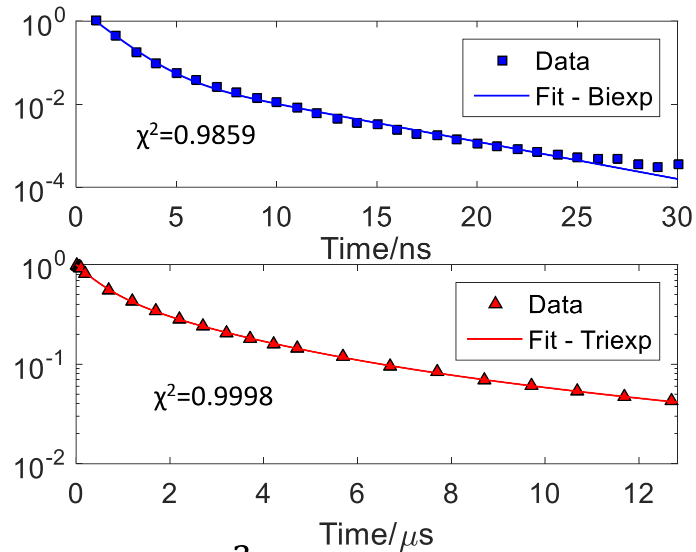


TRPL characterization

PL spectra



Decay profile



Δλ: 390-410 nm
Δt: 0-30 ns

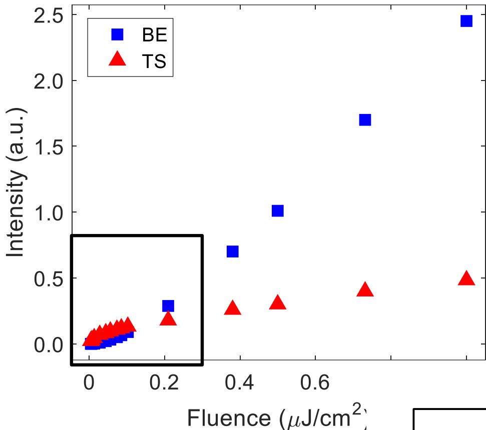
Δλ: 520-550 nm
Δt: 1-15 μs

$$f(t) = \sum_{i=1}^{3} A_i \tau_i \left(1 - e^{-w/\tau_i}\right) e^{-t/\tau_i}$$ w, gate

$$\tau_{eff} = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i}$$

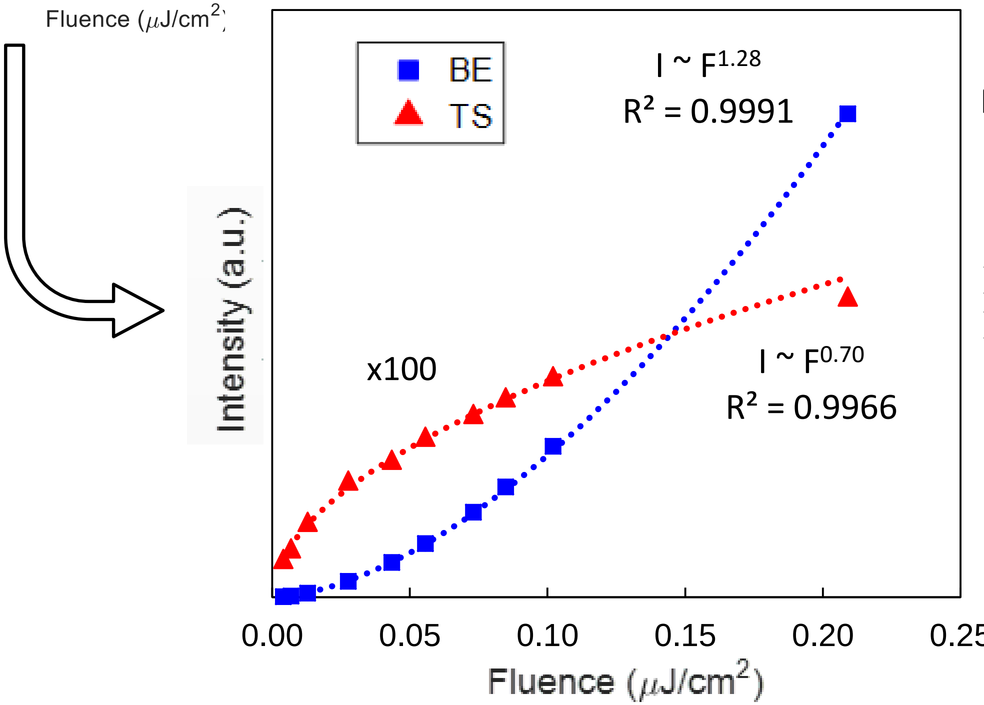
	Historical samples	Reference ZnO
BE	τ_{eff} = 1.3 ns (σ = 0.2 ns)	τ_{eff} = 0.55 ns
TS	τ_{eff} = 3.3 μs (σ = 0.6 μs)	τ_{eff} = 5.27 μs

TRPL characterization



Zinc white behaves as semiconductor material.
In particular:

- TS emission is favoured at low fluence;
- Increasing fluence, saturation of TS levels.

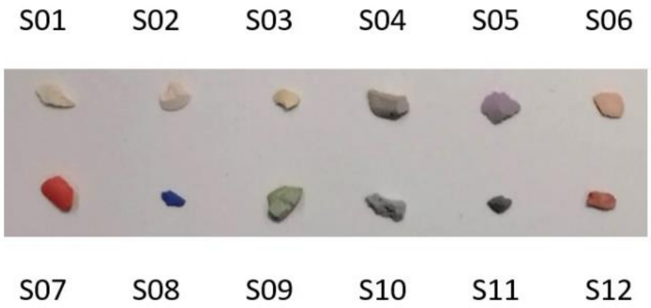


PL intensity (I) vs Fluence (F) law:

$$\mathbf{I \sim F^k}$$

- If $k > 1$: exciton-like transition → BE
- If $k < 1$: free-to-bound and donor-acceptor transition → TS

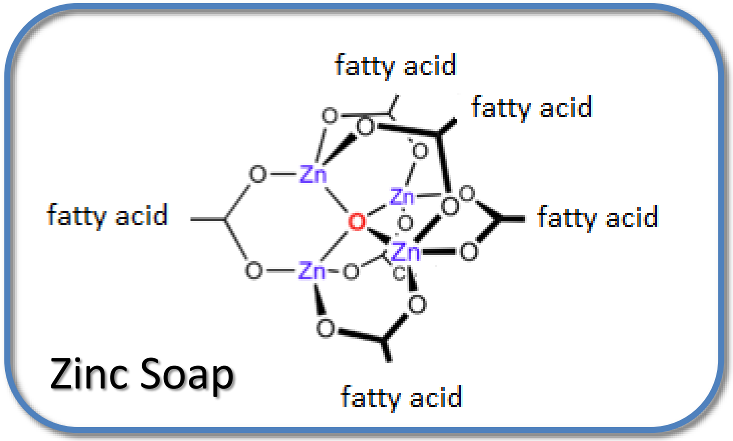
Possibly the change of the BE/TS emission lifetime is caused by the interaction Zn ⟷ Organic binders



Our samples are made by a complex matrix of:

- **ZnO**
- Additives (Colored pigments)
- Binders (Wax, **Linseed Oil**)
- Degradation products

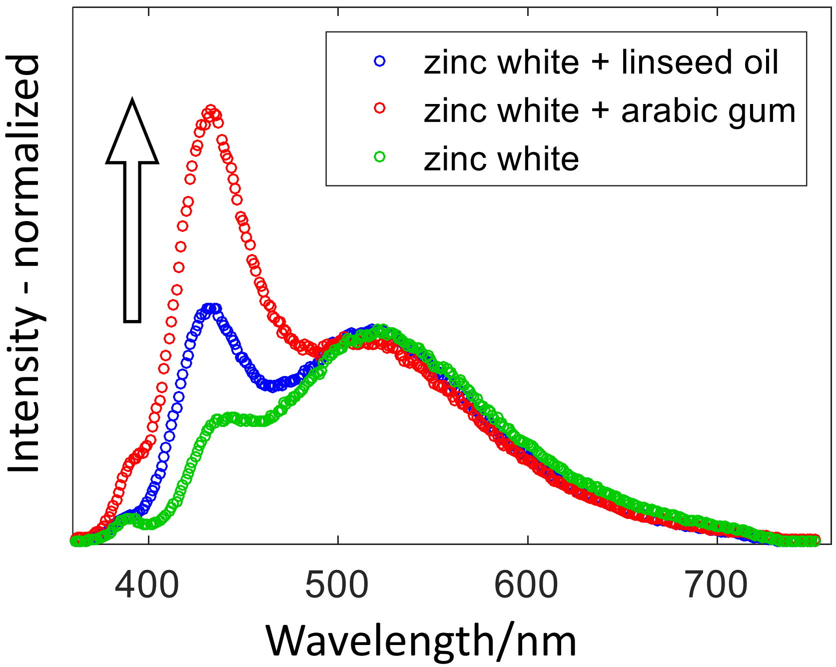
Fatty acids of oleic binder react with metal ion of semiconductor pigment.



Open problem: how does the complex environment in pigments affect the PL properties of Zinc oxide?

Open problem

Zinc white powder mixed with binder



Top results:

- Enhancement of blue emission (at 430 nm)
- Changing in lifetime of green emission (at 530 nm)
- Increasing in lifetime for BE emission

→ Interaction pigment-binder needed further studies

Conclusions

- Zinc white pigment shows a long living photoluminescence emission that can be ascribed to defects of crystalline structure in ZnO semiconductor

- More work is needed to understand the reason for the variation in the lifetime of emissions in Zinc white when mixed with binders

- Time resolved photoluminescence could become a valuable non-invasive tool to study the degradation of modern pigments