

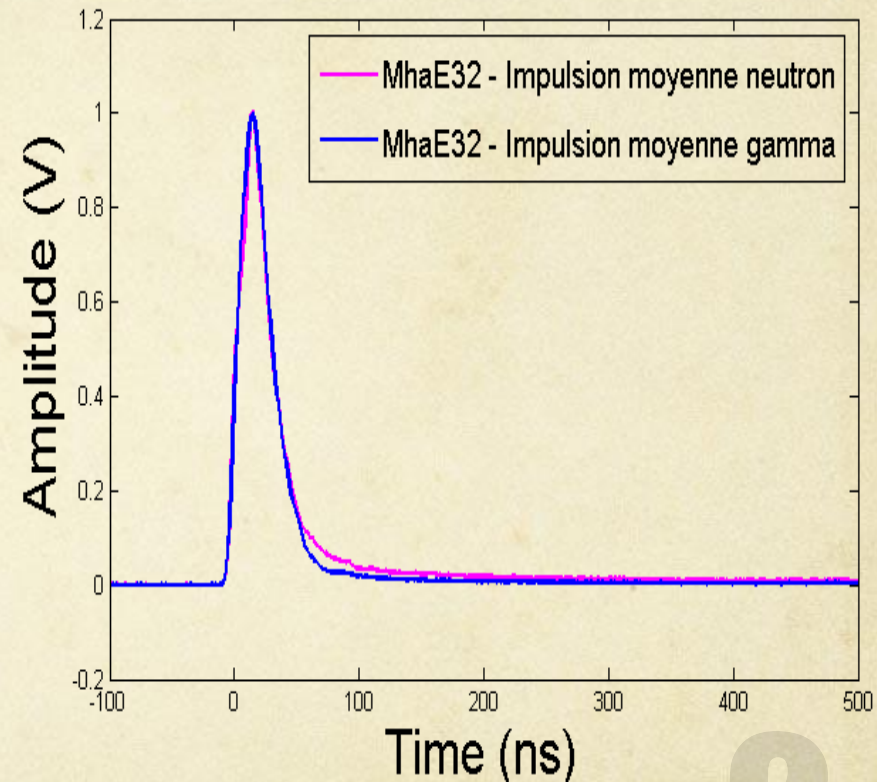
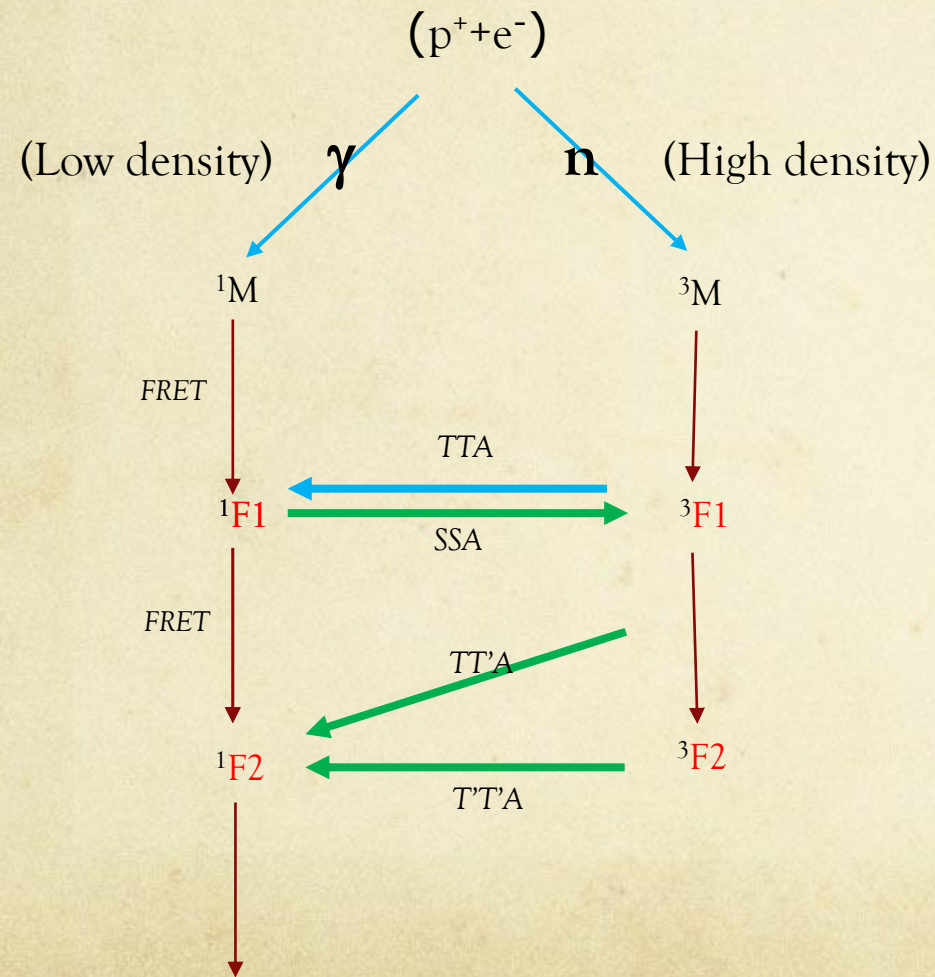
On the temperature
dependence of the
quenching in TADF solids

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Aurelie Stallivieri,^b Matthieu Hamel,^c Sylvain Gaillard
^b and Robert B. Pansu

Synopsis :

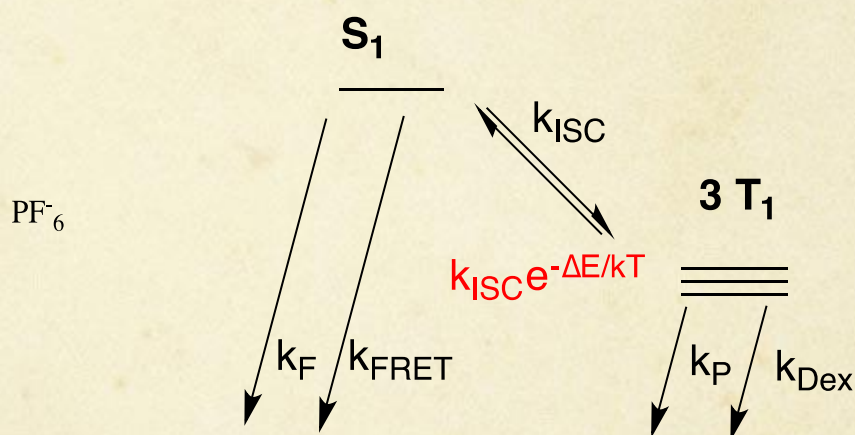
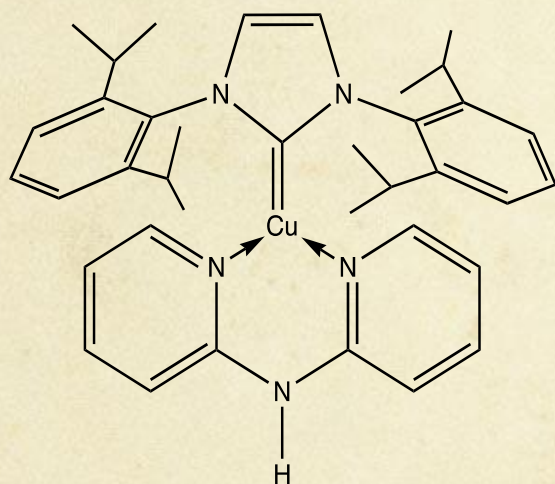
- TADF for neutron detection by scintillator
- Analysis of complex solid state decays
- Many Quencher per exciton : the Perrin Model
- Model free analysis
- No model ?
- Conclusion

TADF for Neutron detection



TADF

An efficient phosphorescence that increases OLED efficiency without Iridium



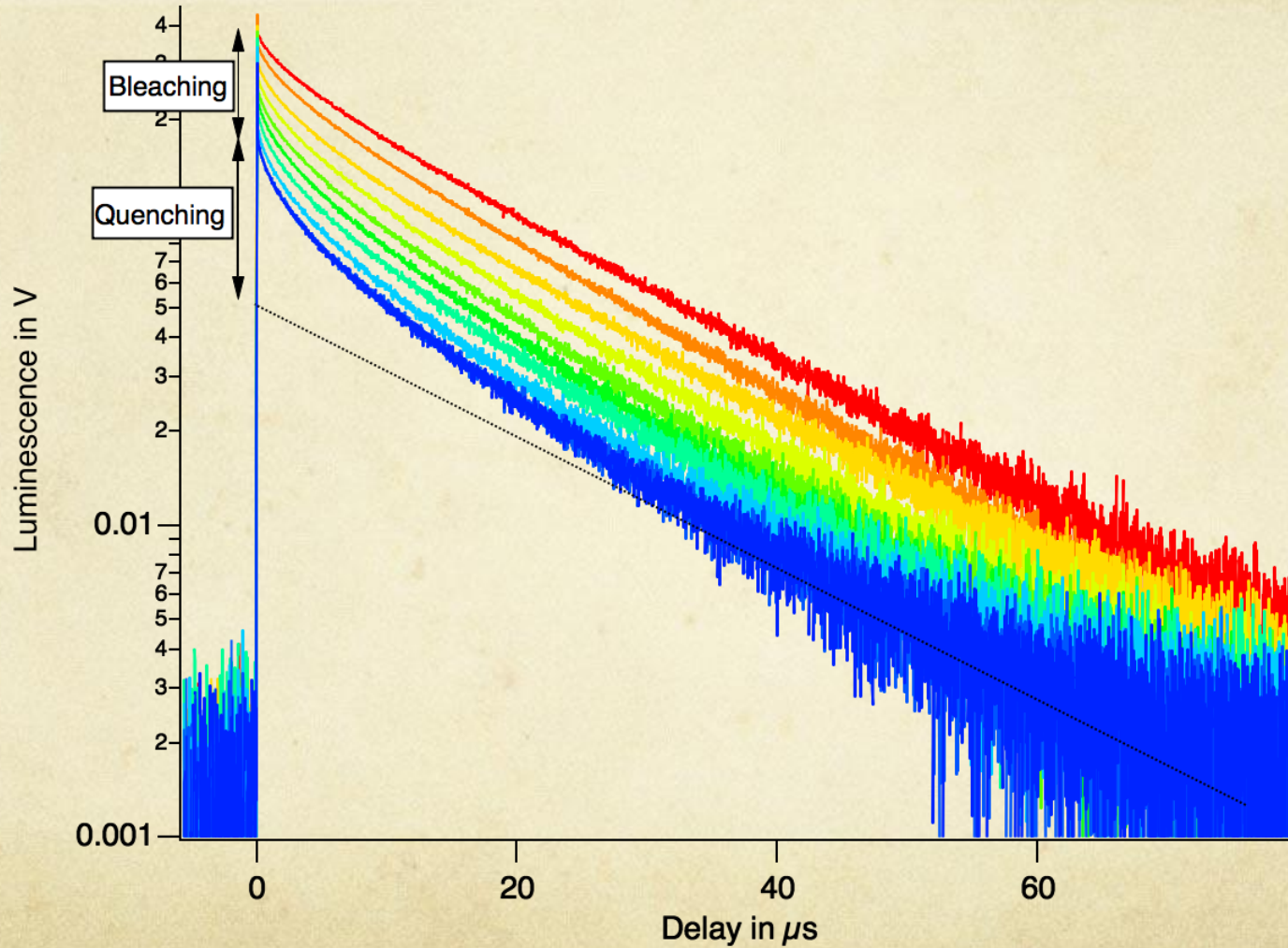
Gaillard S. et al (2016) *ACS App. Mat. & Interf.* 8(23), 14678-91.

(2017) *Chem. Eur. J.*,23(64), 16328-16337.

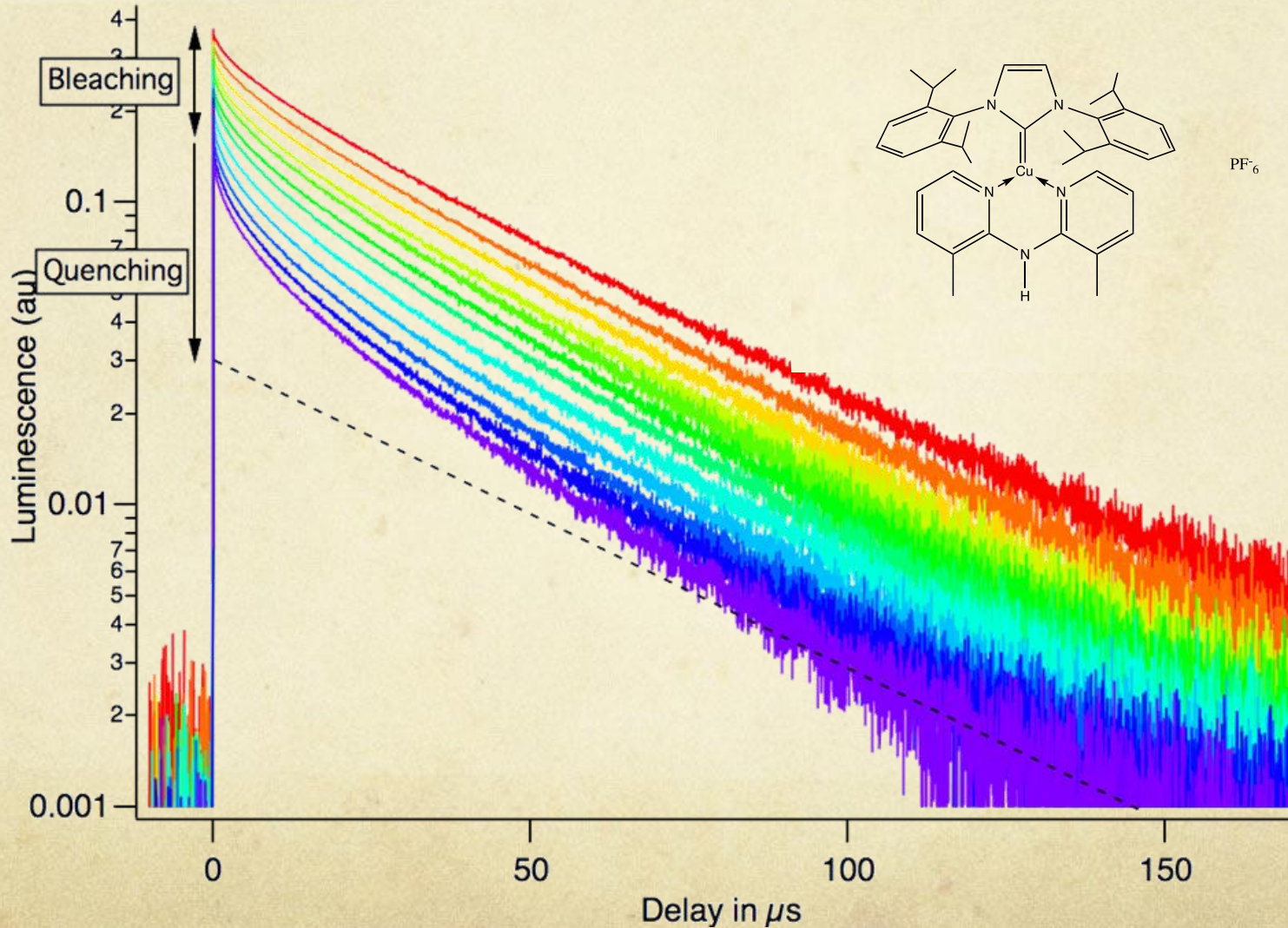
ANR NESSYNED



Create defects to study quenching



A second example

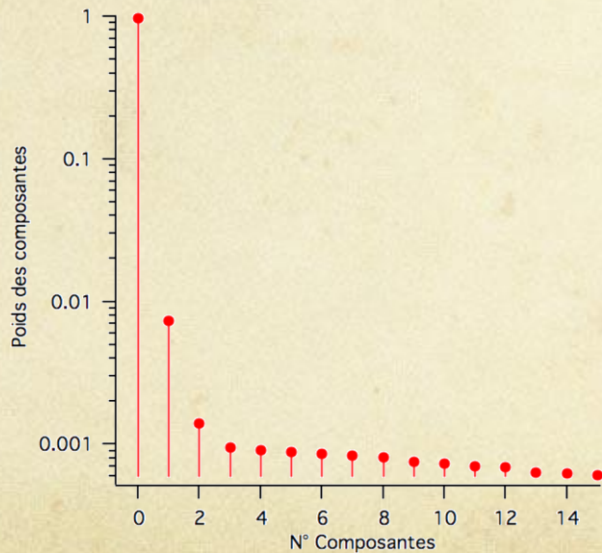


Linearity in the space of reaction rates

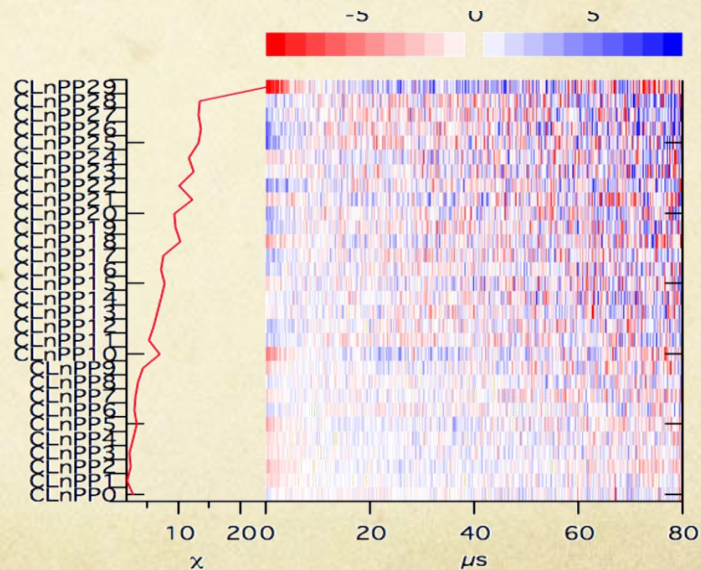
$$\frac{d[S]}{dt} = -k_S[S] - k_Q(t)[S][Q]$$

$$\ln([S]/[S]_0) = -k_S t - [Q] \int_0^t k_Q(t) dt$$

Berberan-Santos, M. N. Chem. Phys. 2005, 315, 171-182.

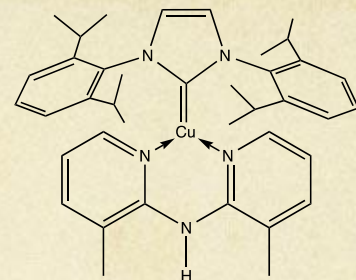
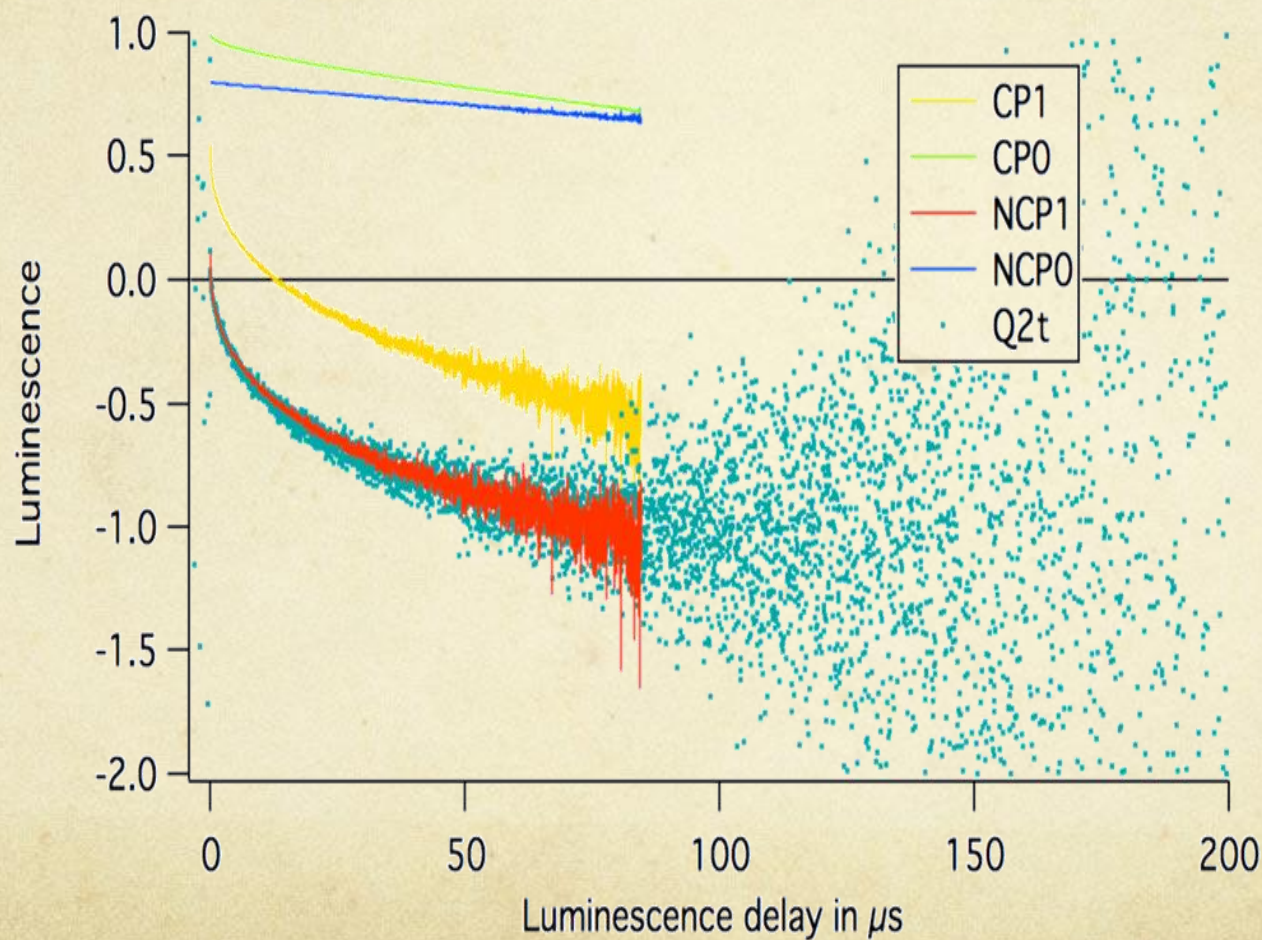


2 linear components PCA analysis



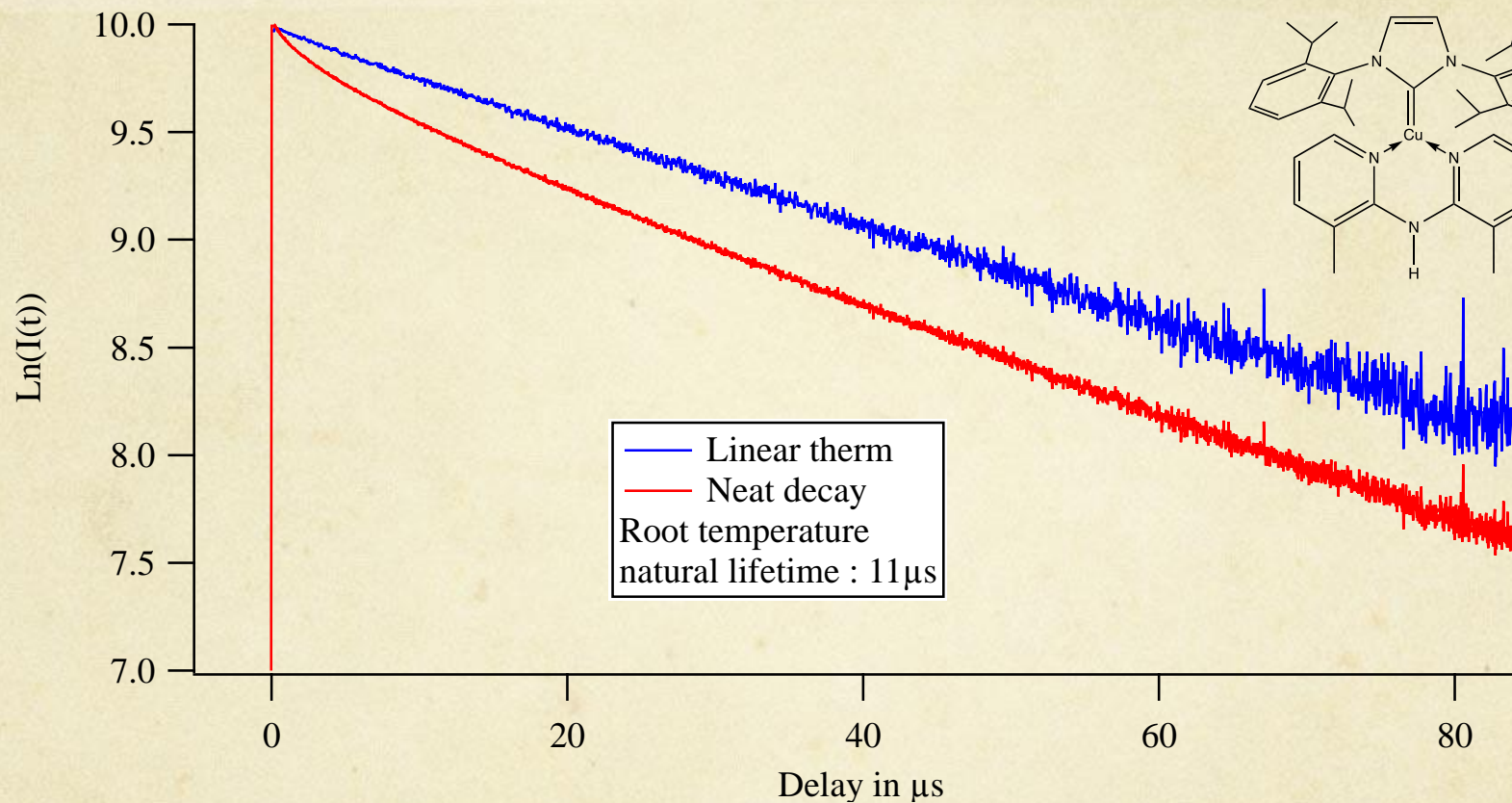
Good description of the data

Building the kinetics

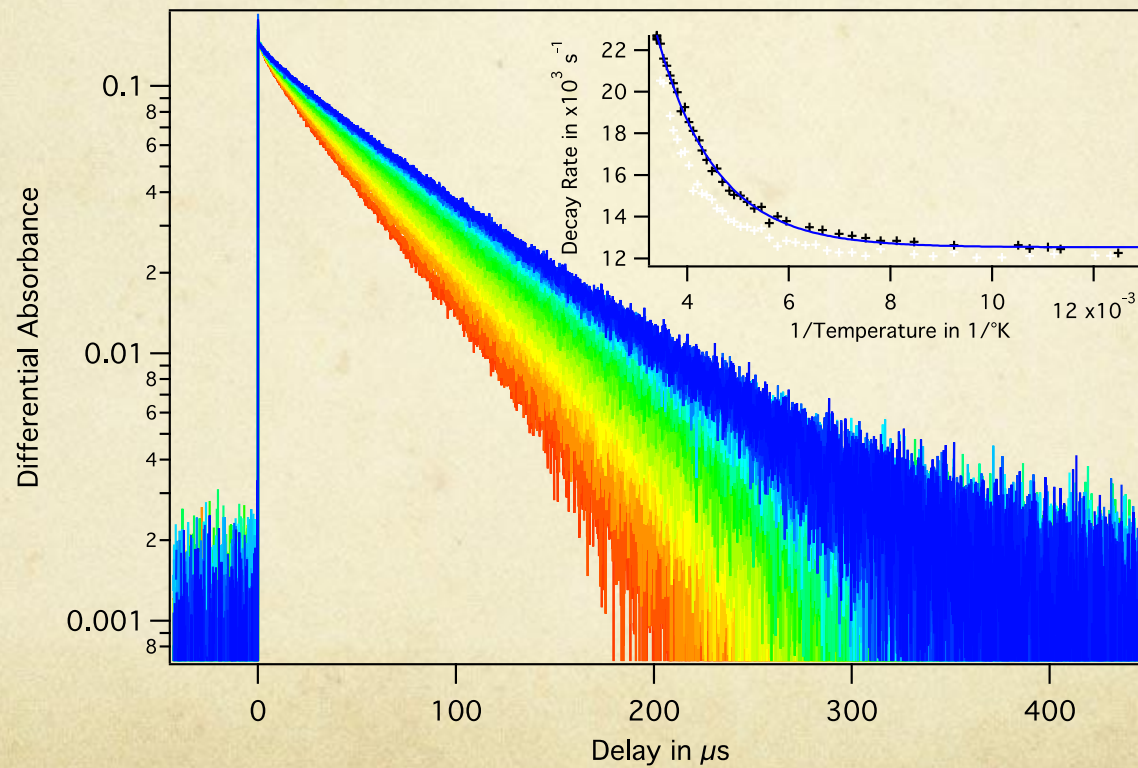
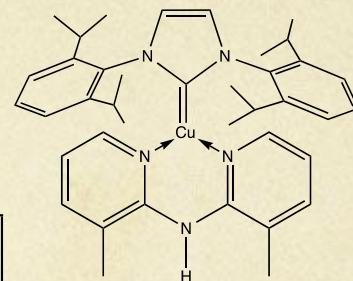


PF₆⁻

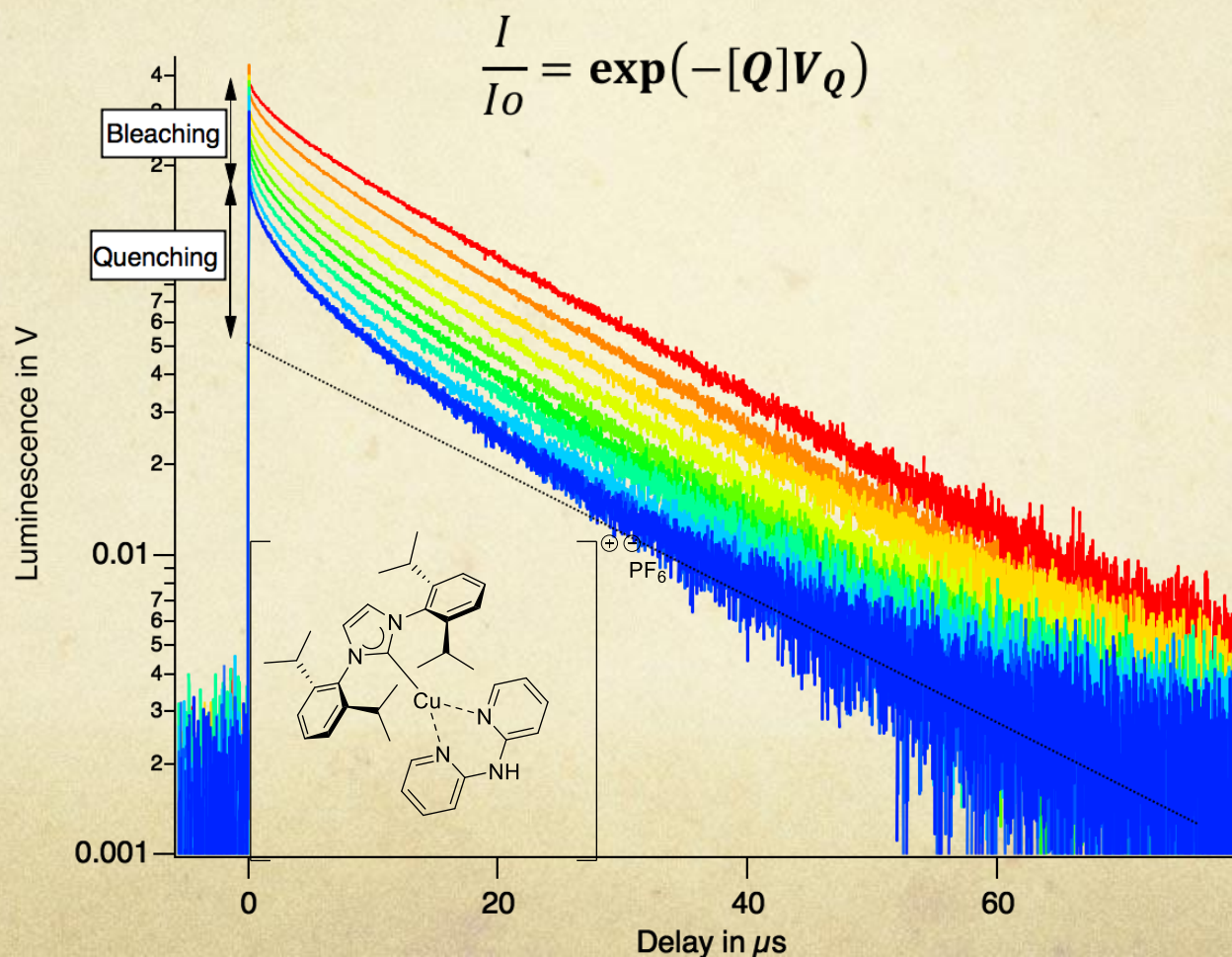
Decays spoiled by defects



Improved samples !



Quenching amplitude gives quencher concentration (Perrin)



Quenching by a distribution of quenchers

A few quenchers : Perrin, F., C.R. Acad. Sci. (1924), 178, 1978-1980.

In solids : Blumen, A., Il Nuovo Cimento Soc. Ital. Fis., B (1981), 63, 50-58.

In micelles : Murata, S.; Tachiya, M., Chem. Phys. Lett. (1992), 194, 347-350.

Model Free : Hartmann L., et al. ACS Nano 6 (2012): 9033-9041.

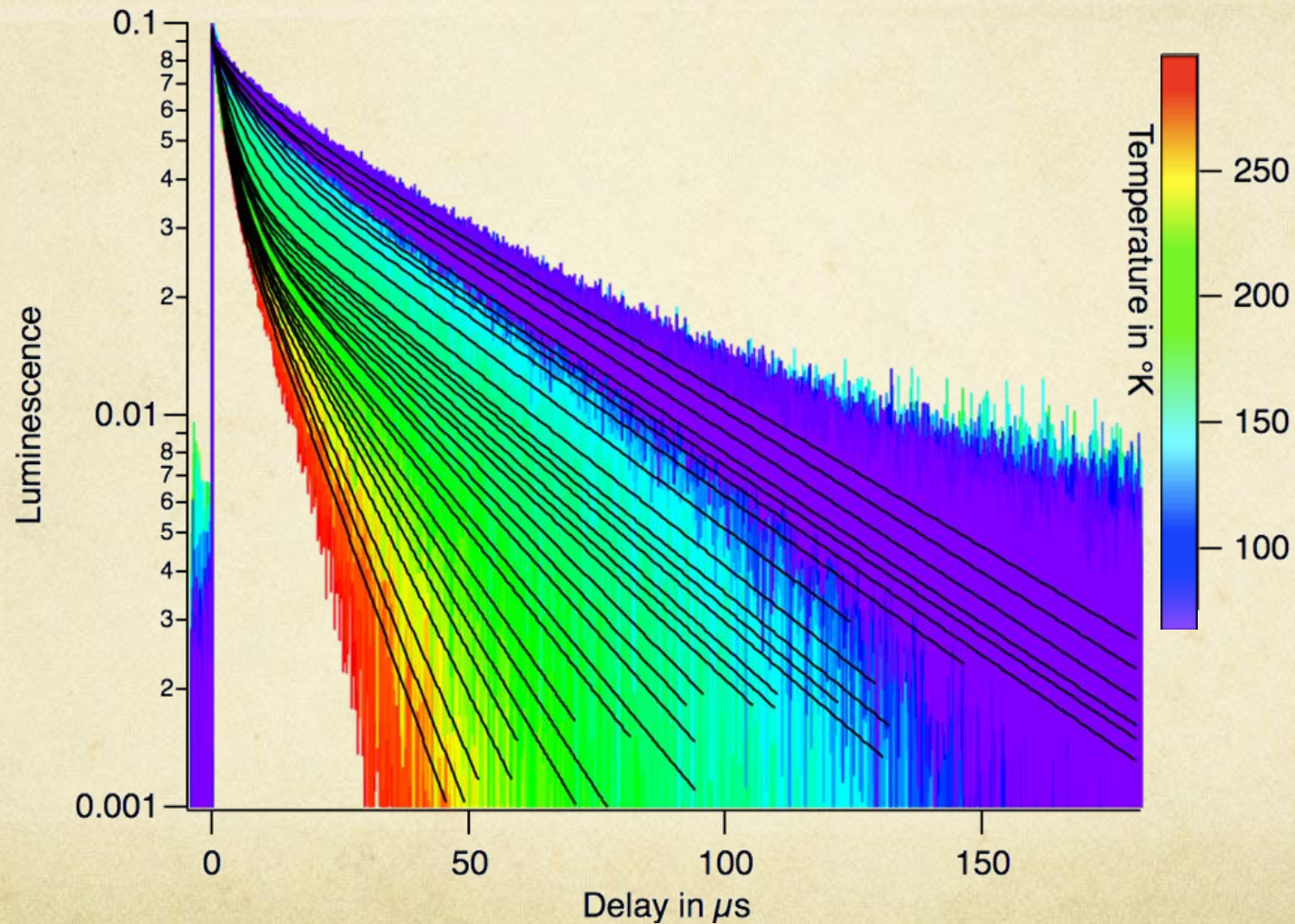
$$\ln\left(\frac{I_f(t)}{I_f(0)}\right) \rightarrow -k_f t + mp \left\{ \exp\left(-\int_0^t k_Q(u) du\right) - 1 \right\} \quad \text{as } p \rightarrow 0$$

Where $\exp\left(-\int_0^t k_Q(u) du\right)$ is the decay of a hypothetical sample where there is only one quencher per excited state.

As $t \rightarrow \infty$ the quenching term tends to $-mp$

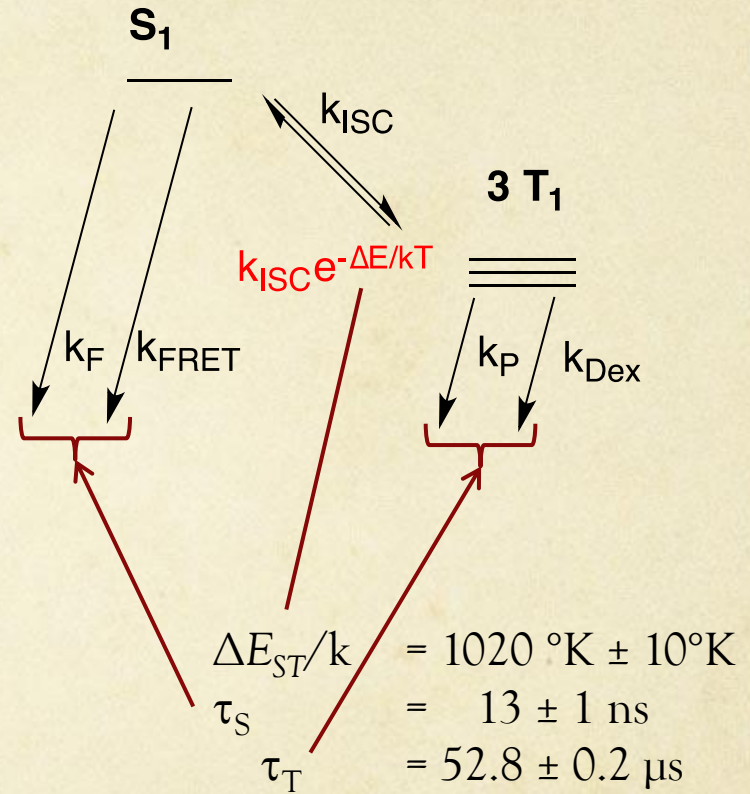
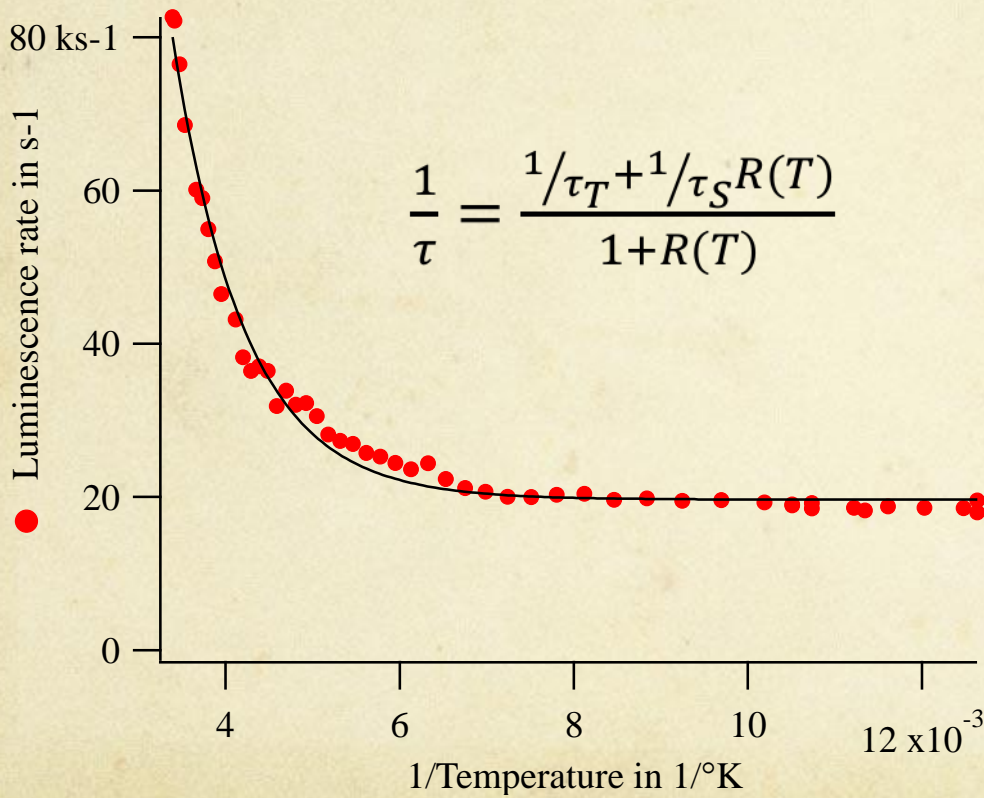


Luminescence Lifetime vs Temperature

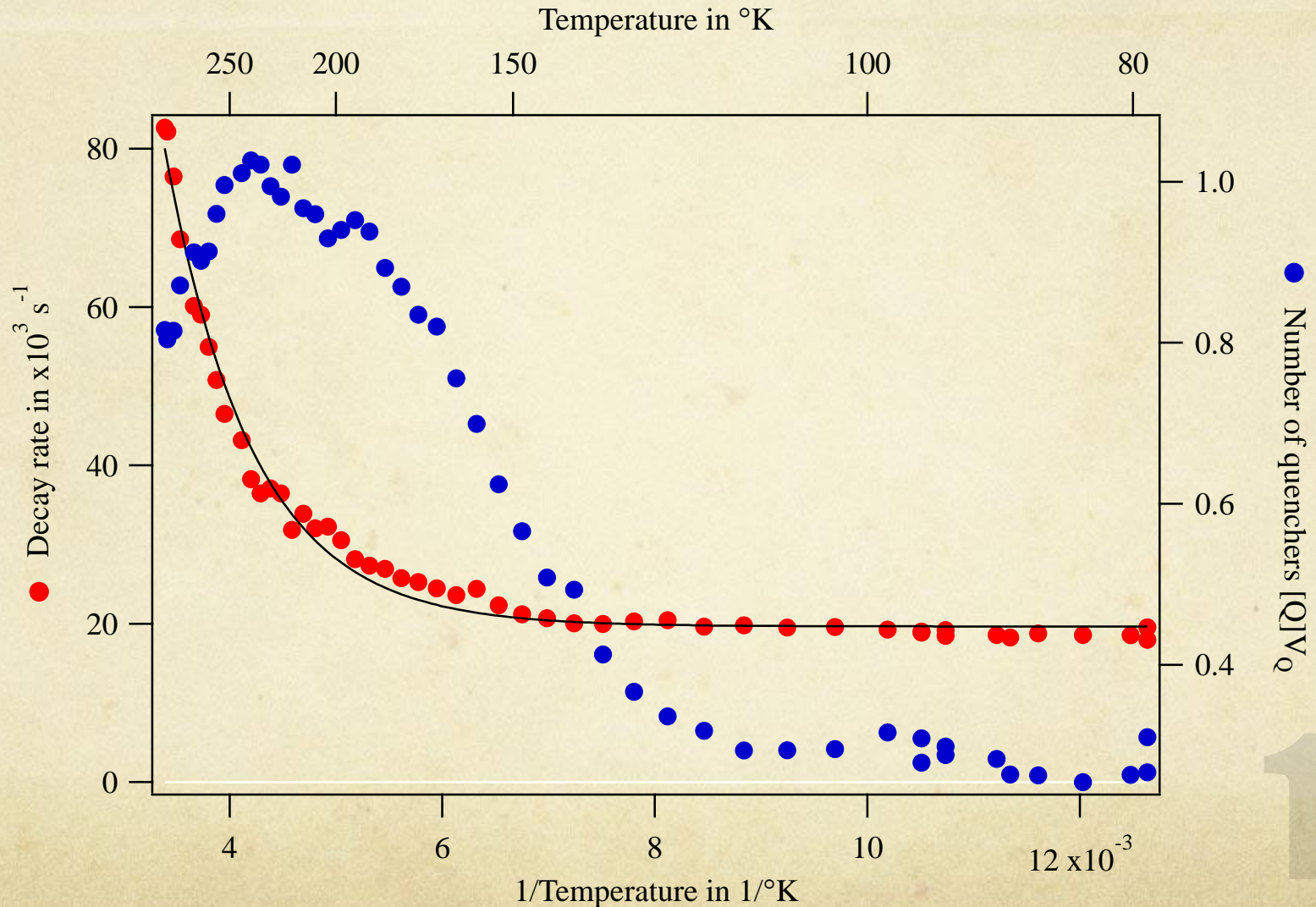


S ⇌ T equilibrium

Non quenched decay rate



Singlet and triplet quenching



Quenching of the triplet through Förster

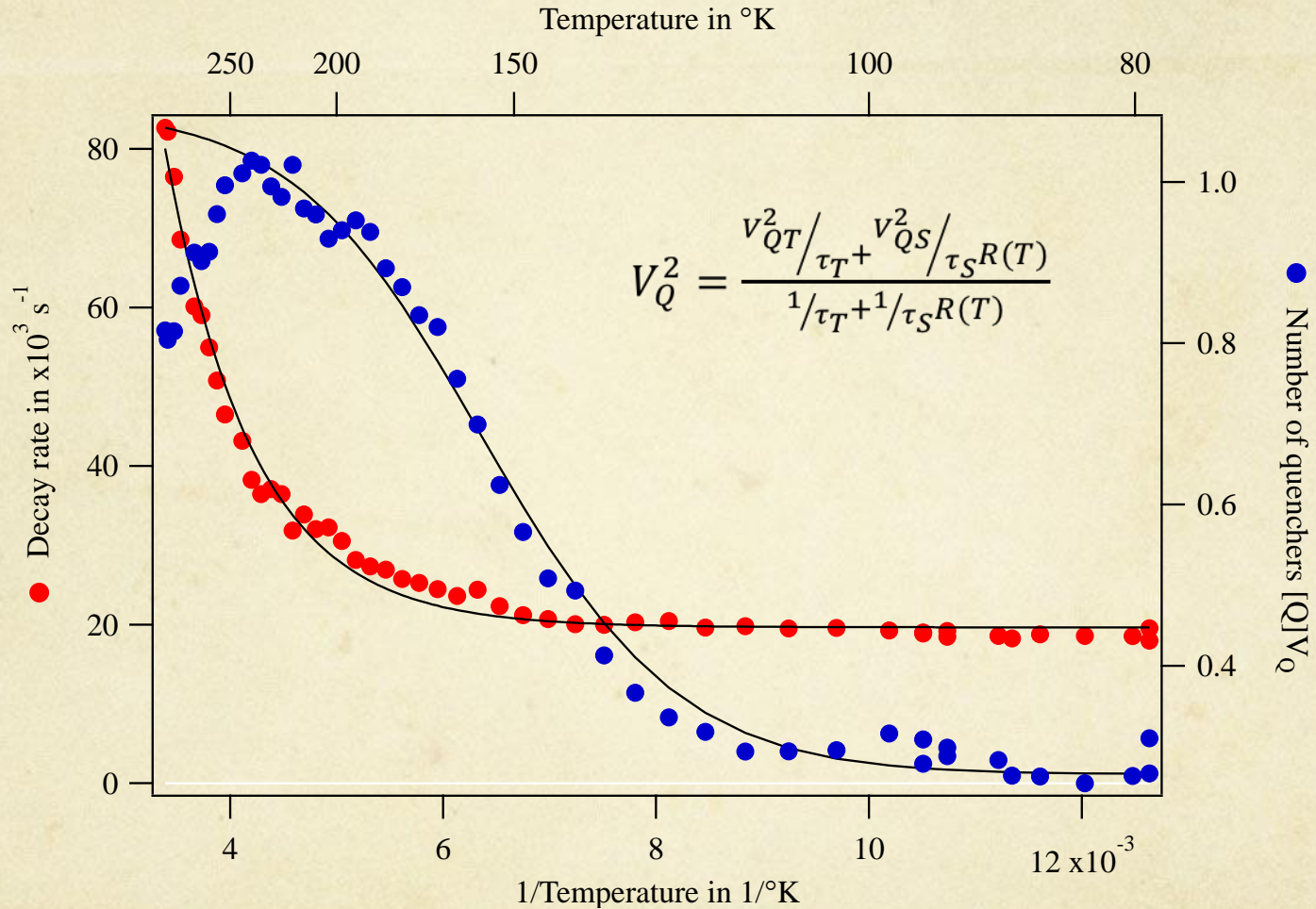
Let define the quenching volume V_Q as that where the quenching rates exceed the decay rate.

$$k_{FRET} = k_f \left(\frac{R_0}{R}\right)^6 = k_f \left(\frac{V_0}{V}\right)^2$$

$$\frac{1/\tau_T (V_{QT}/V_Q)^2}{1+R(T)} + \frac{1/\tau_S (V_{QS}/V_Q)^2 R(T)}{1+R(T)} = \frac{1}{\tau} = \frac{1/\tau_T + 1/\tau_S R(T)}{1+R(T)}$$

$$V_Q^2 = \frac{V_{QT}^2/\tau_T + V_{QS}^2/\tau_S R(T)}{1/\tau_T + 1/\tau_S R(T)}$$

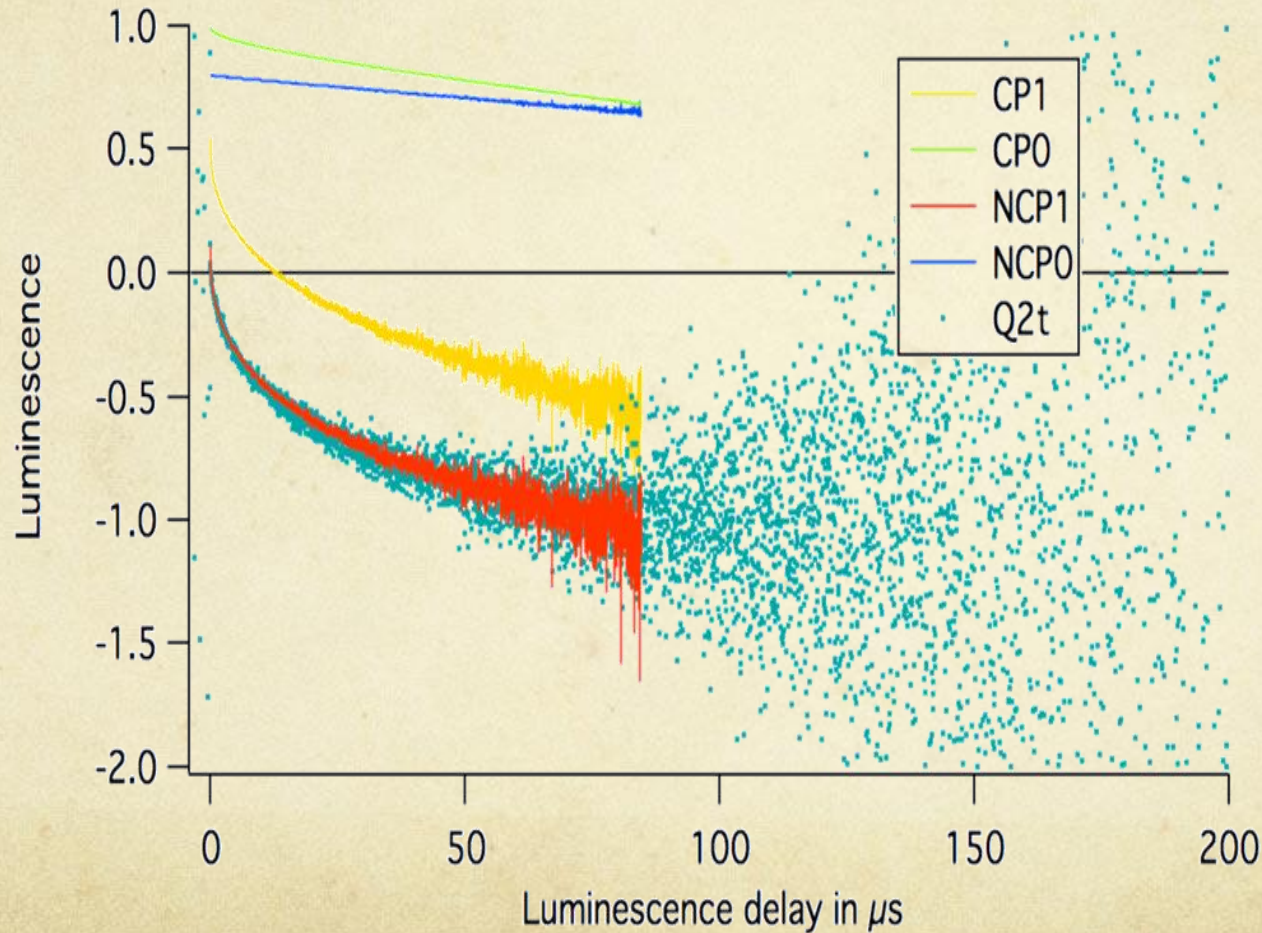
Singlet and triplet quenching



$$\Delta E_{ST}/k = 1020 \text{ }^\circ\text{K} \pm 10^\circ\text{K} \quad \tau_S = 13 \pm 1 \text{ ns} \quad V_{QT}/V_{QS} = 0,52$$

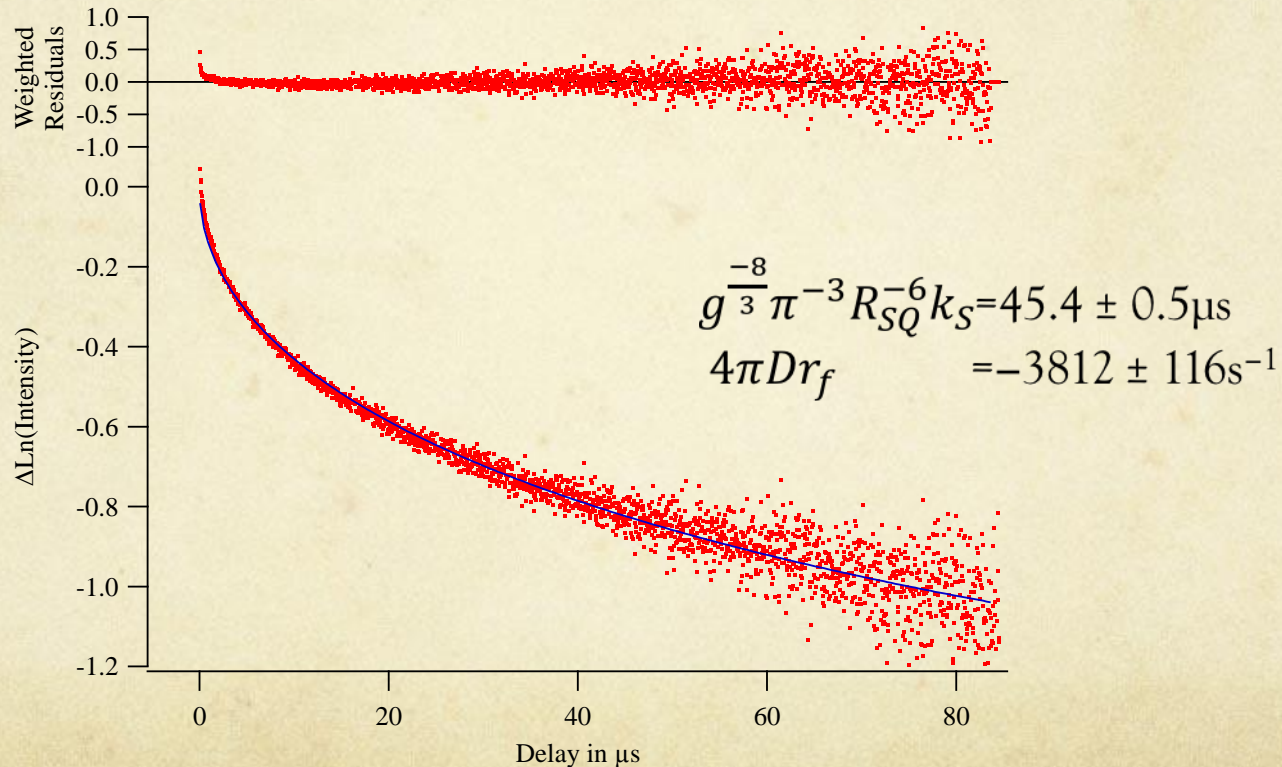
$$\tau_T = 52.8 \pm 0.2 \text{ } \mu\text{s}$$

Building the kinetics



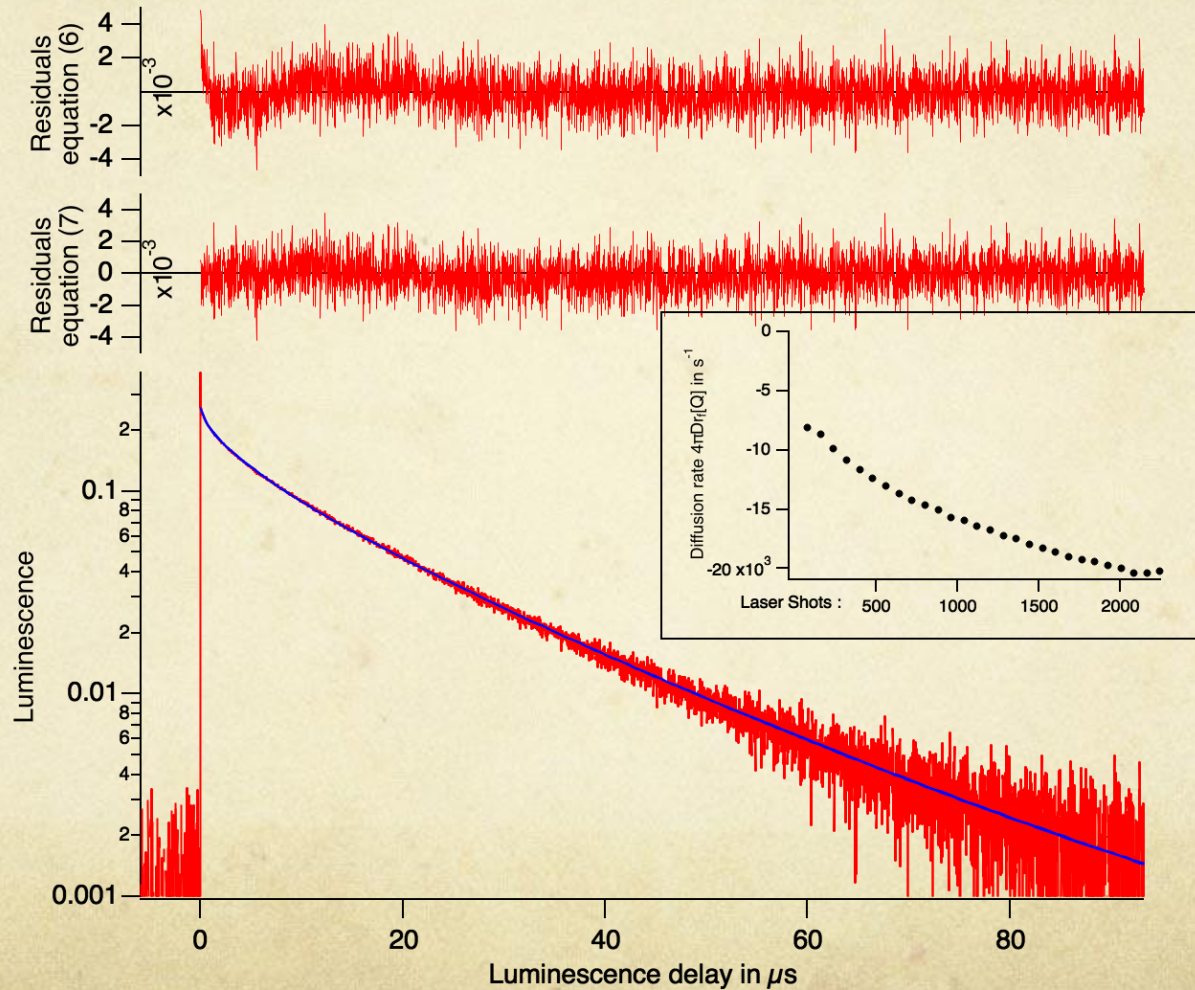
The FRET does not fit

$$\ln\left(\frac{I(t)}{I_0}\right) = -k_s t - [Q]\left\{4\pi D r_f t + g^{\frac{4}{3}} \pi^{\frac{3}{2}} R_{SQ}^3 \sqrt{k_s t}\right\}$$



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Same using global fit



Conclusion

Our Copper Carben complexes are TADF molecules with a 1020°K splitting.

At low temperature the lifetime increases as the molecule spends more time as a Triplet.

At low temperature the quenching volume decreases as the molecule spends more time as a Triplet.

At room temperature Singlet are responsible of 75% of the quenching even if they are only 2% of the population.

The excited state is trapped as shown by the burning experiment.

Conclusions

- Check for the linearity in the reaction rate space
- If you can extract the non quenched population, you will measure a density of defects
- We need theory !

Perspective

- We can determine the concentration and the quenching efficiency of unknown species :
 - detection of polarons in OLED
 - SSA, STA, TTA in scintillators