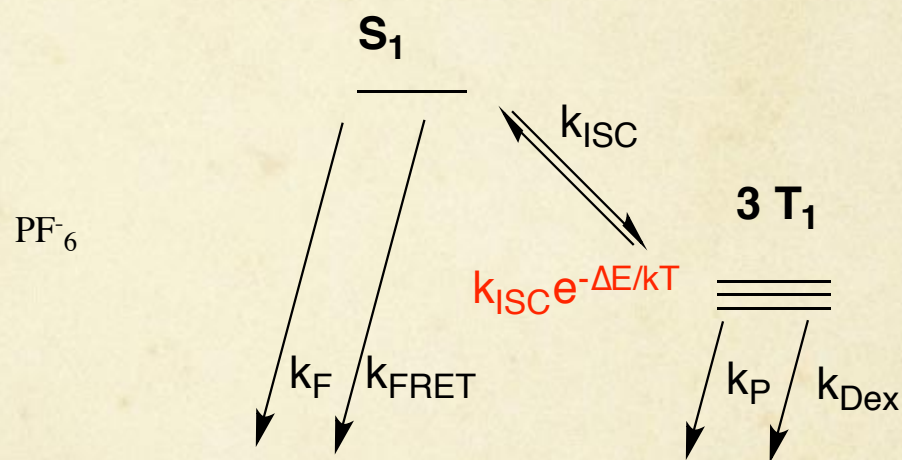
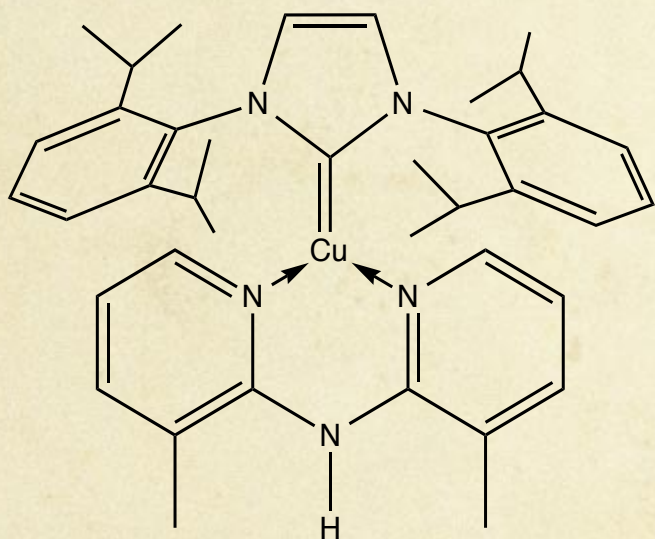


On the temperature
dependence of the
quenching in TADF solids

Zhengyu Zhang,^a Arnaud Brosseau,^a Margaux Elie,^b
Aurelie Stallivieri,^b Matthieu Hamel,^c Sylvain Gaillard
^b and Robert B. Pansu

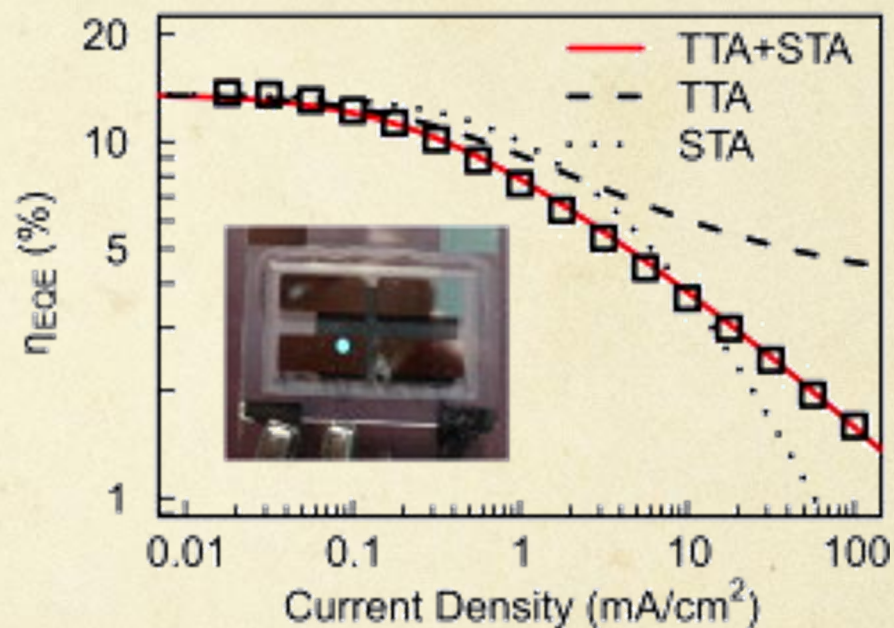
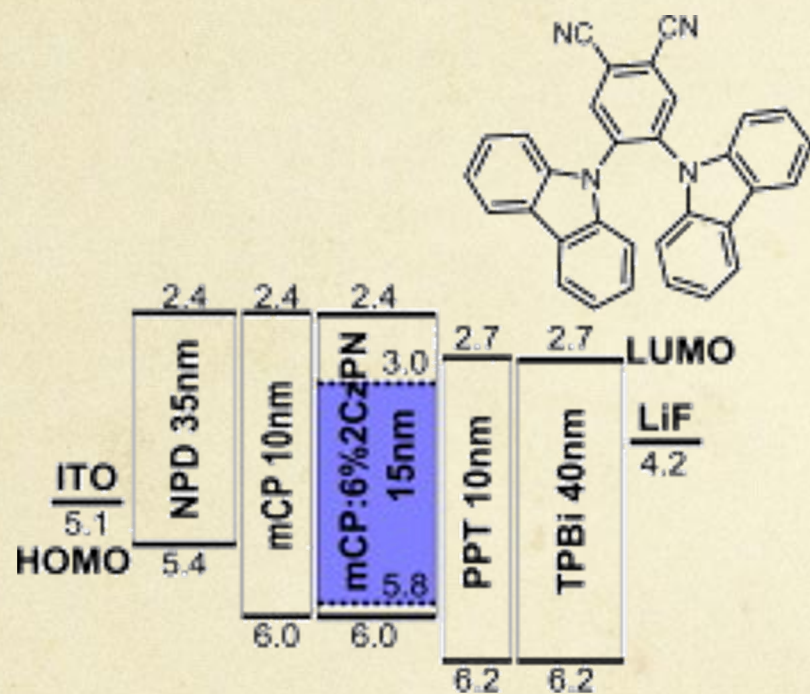
TADF

An efficient phosphorescence that increases OLED efficiency without Iridium



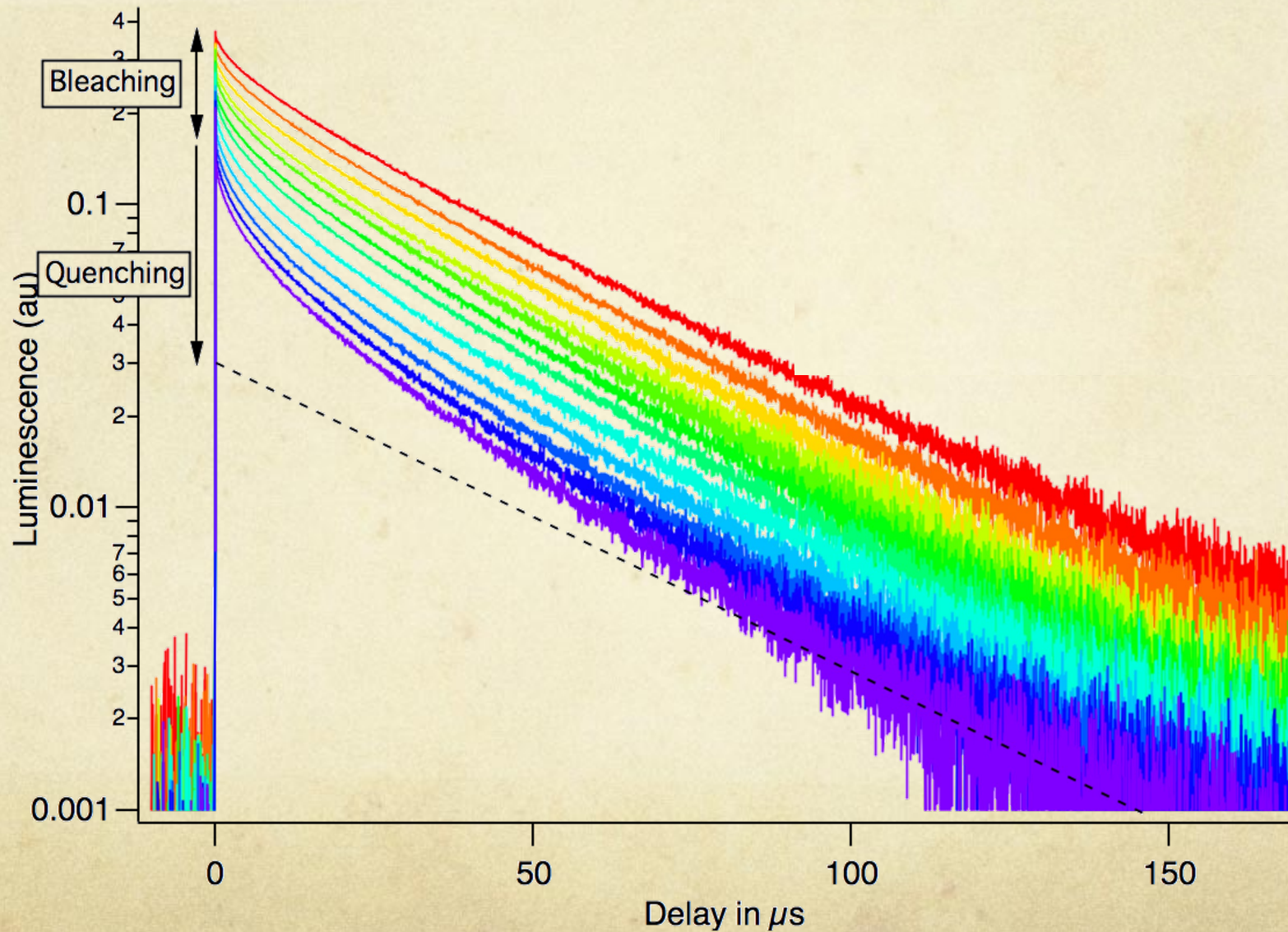
Elie M., Pansu R. B., Hamel M., Gaillard S. (2016). ACS Applied Materials & Interfaces in press.
ANR NESSYNE

Exciton Quenching kills Brightness



Kensuke Masui, et al. Organic Electronics, (2013), 2721–2726.
<http://dx.doi.org/10.1016/j.orgel.2013.07.010>

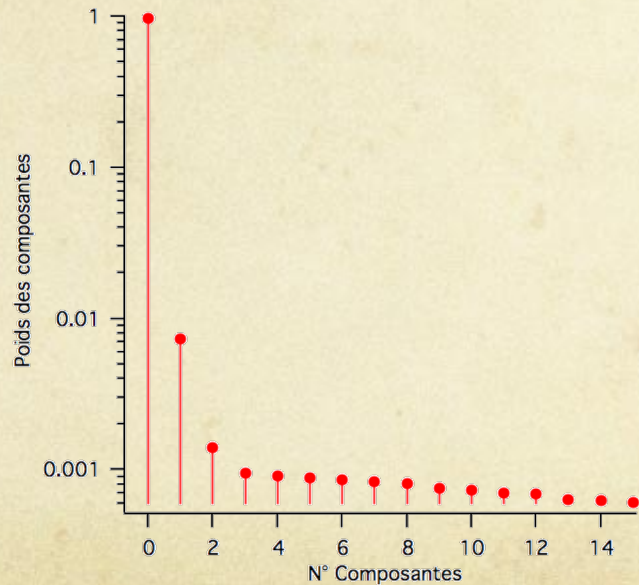
Create defects to study quenching



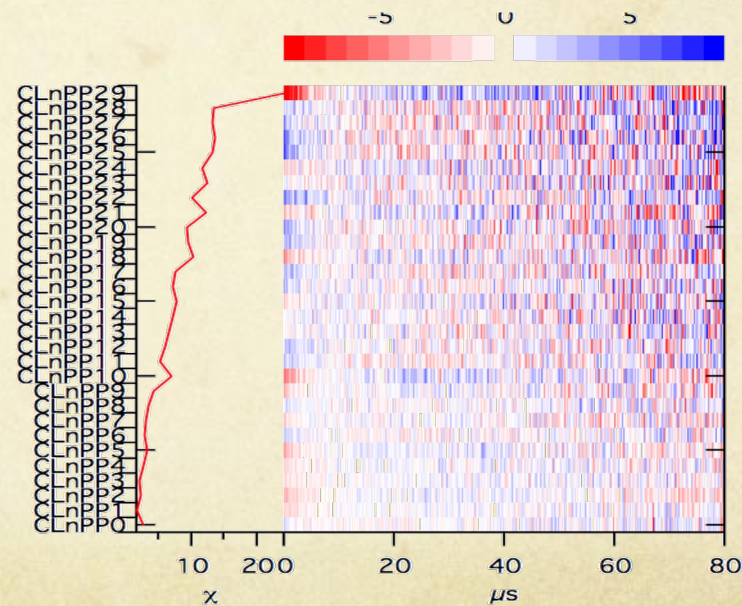
Linearity in the space of reaction rates

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

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

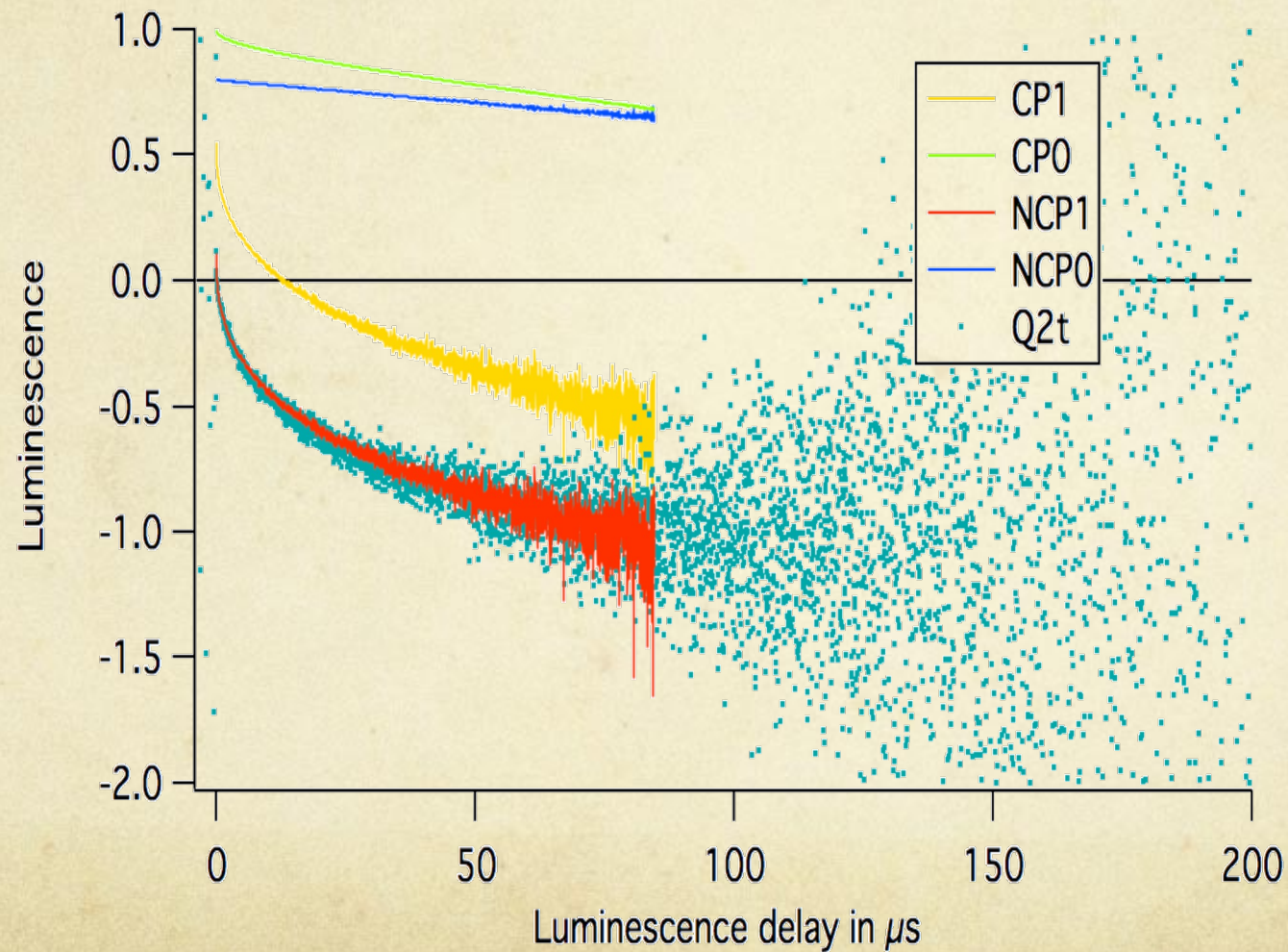


2 linear components PCA analysis

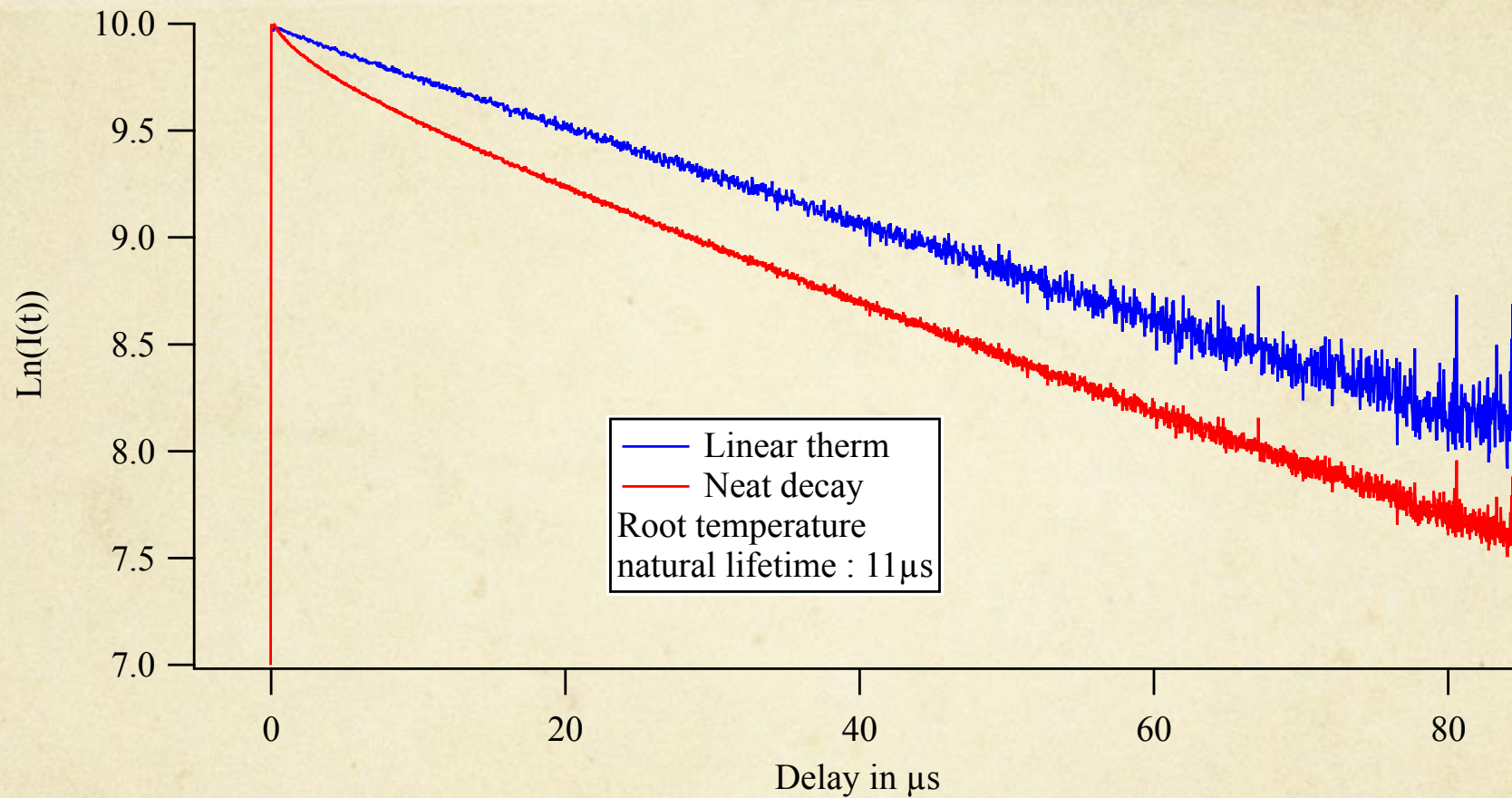


Good description of the data

Building the kinetics

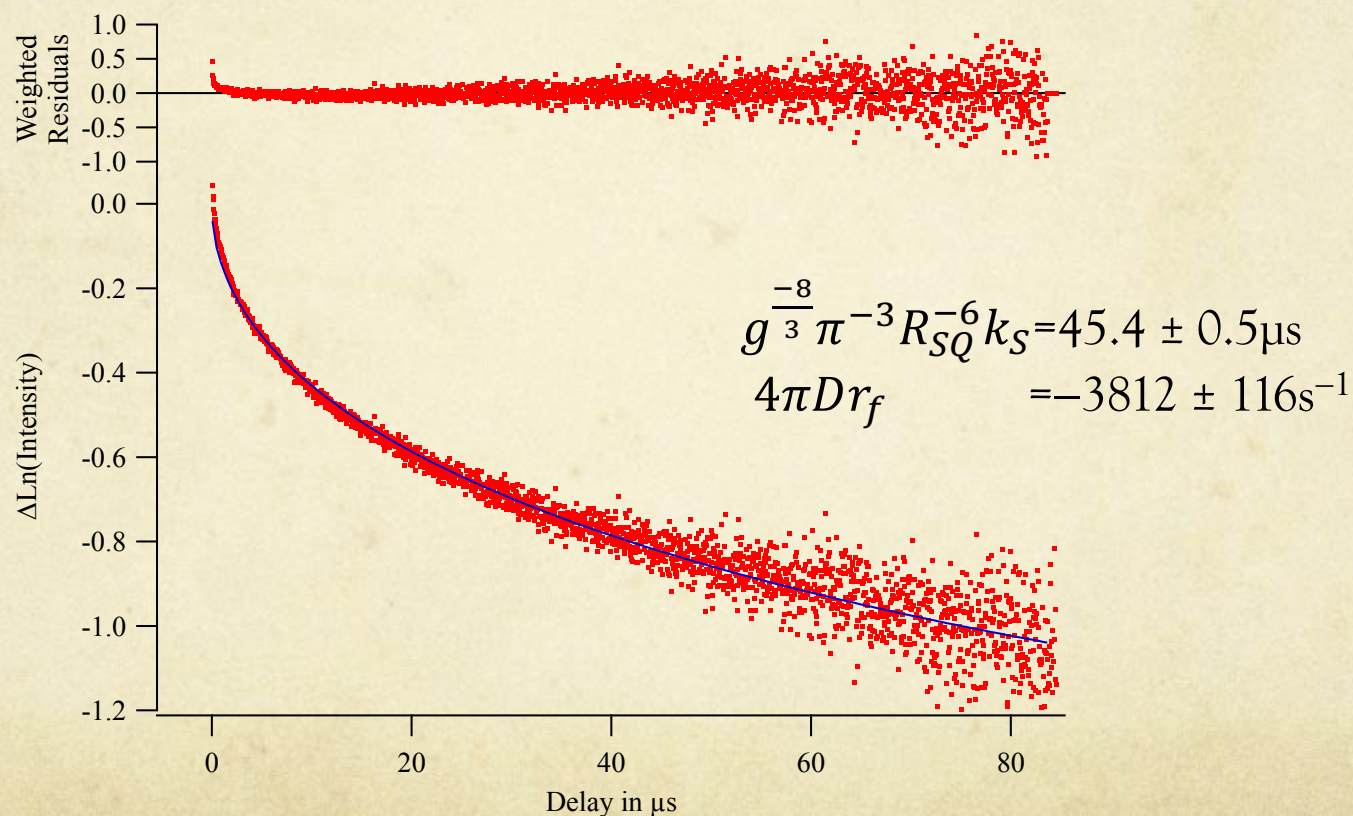


Decays spoiled by defects

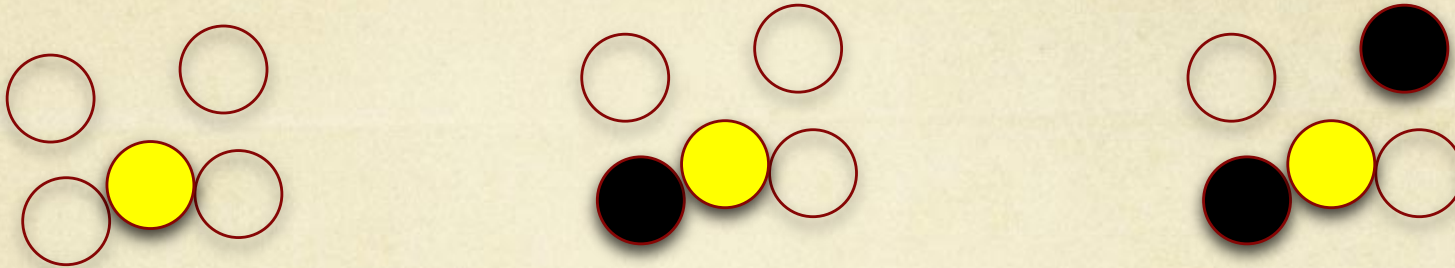


The Usual Fit

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



The Perrin Model



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.

The Förster Energy transfer

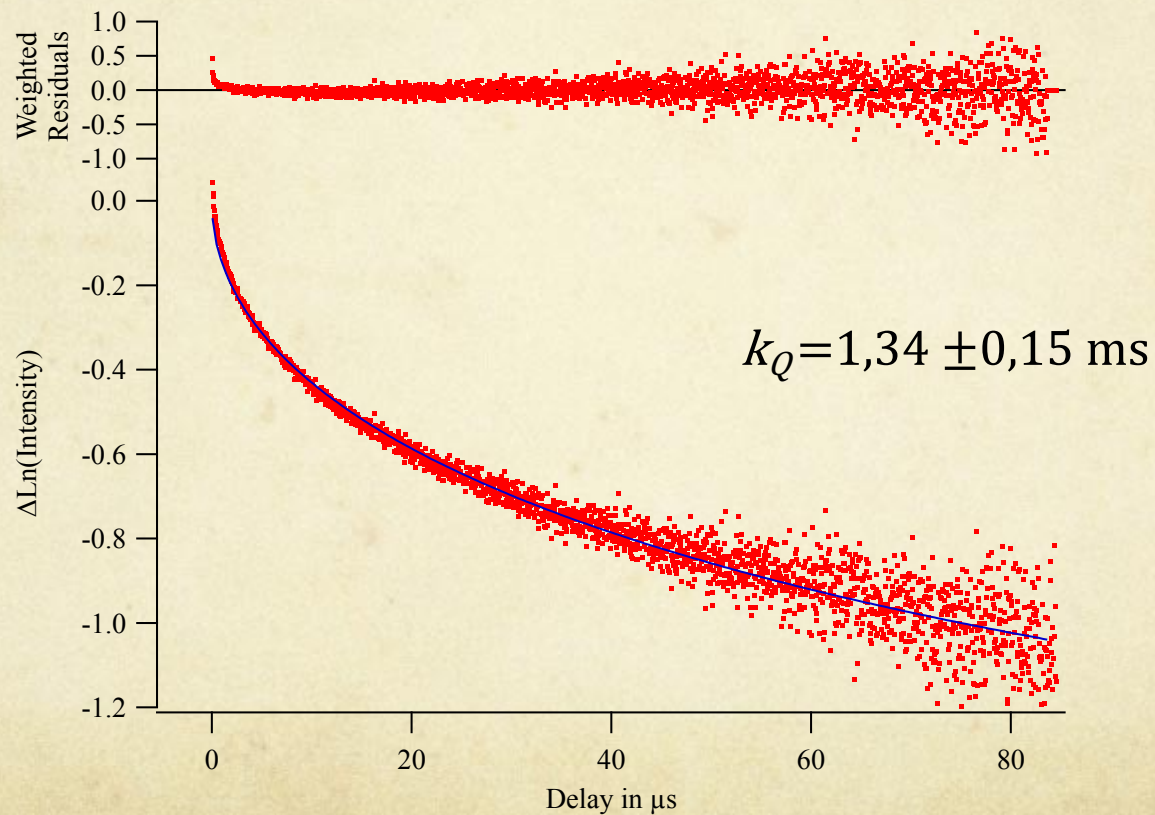
$$\rho_{FRET1Q}(t) = -\sqrt{\pi} \left(\frac{Ro}{g}\right)^3 \sqrt{k_F \langle \kappa^2 \rangle t} + \left(\frac{Ro}{g}\right)^6 k_F \langle \kappa^2 \rangle t + O(t^2)$$

merged :

$$\ln \left(\frac{I(t)}{I_0} \right) = -k_F t + [Q] V_{FRET} \left\{ \exp \left(-\sqrt{\pi k_Q t} + k_Q t \right) - 1 \right\}$$

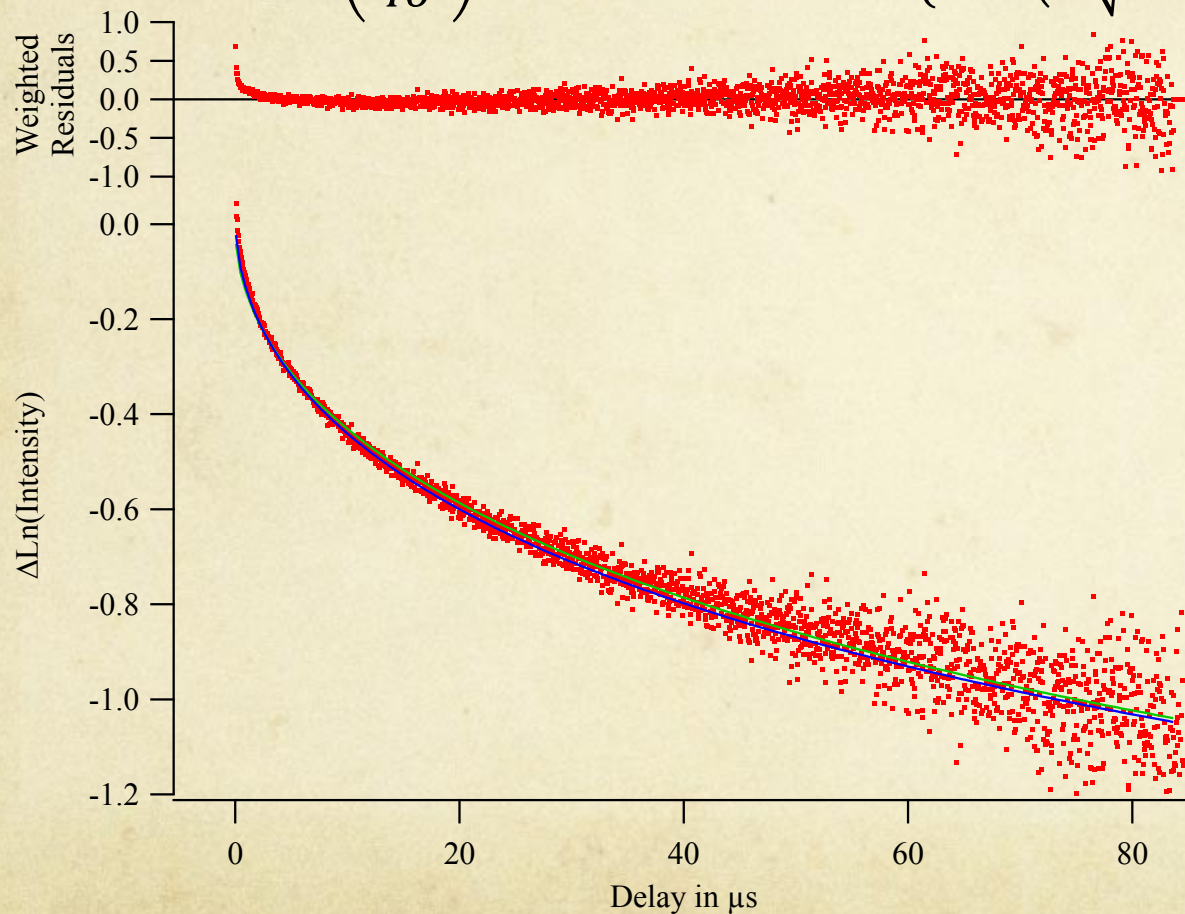
Perrin-Förster Model

$$\ln\left(\frac{I(t)}{I_0}\right) = -k_F t - [Q]V_{FRET} \left\{ \exp\left(-\sqrt{\pi k_Q t} + k_Q t\right) - 1 \right\}$$



Both Model fits

$$\ln\left(\frac{I(t)}{I_0}\right) = -k_F t - [Q]V_{FRET} \left\{ \exp\left(-\sqrt{\pi k_Q t} + k_Q t\right) - 1 \right\}$$



$$\left(\frac{R_{SQ}}{g}\right)^6 k_F \langle \kappa^2 \rangle = 1,34 \pm 0,15 \text{ ms}$$

$$\frac{g^{-8}}{4\pi D r_f} \pi^{-3} R_{SQ}^{-6} k_F = 45.4 \pm 0.5 \mu\text{s}$$

$$= -3812 \pm 116 \text{ s}^{-1}$$

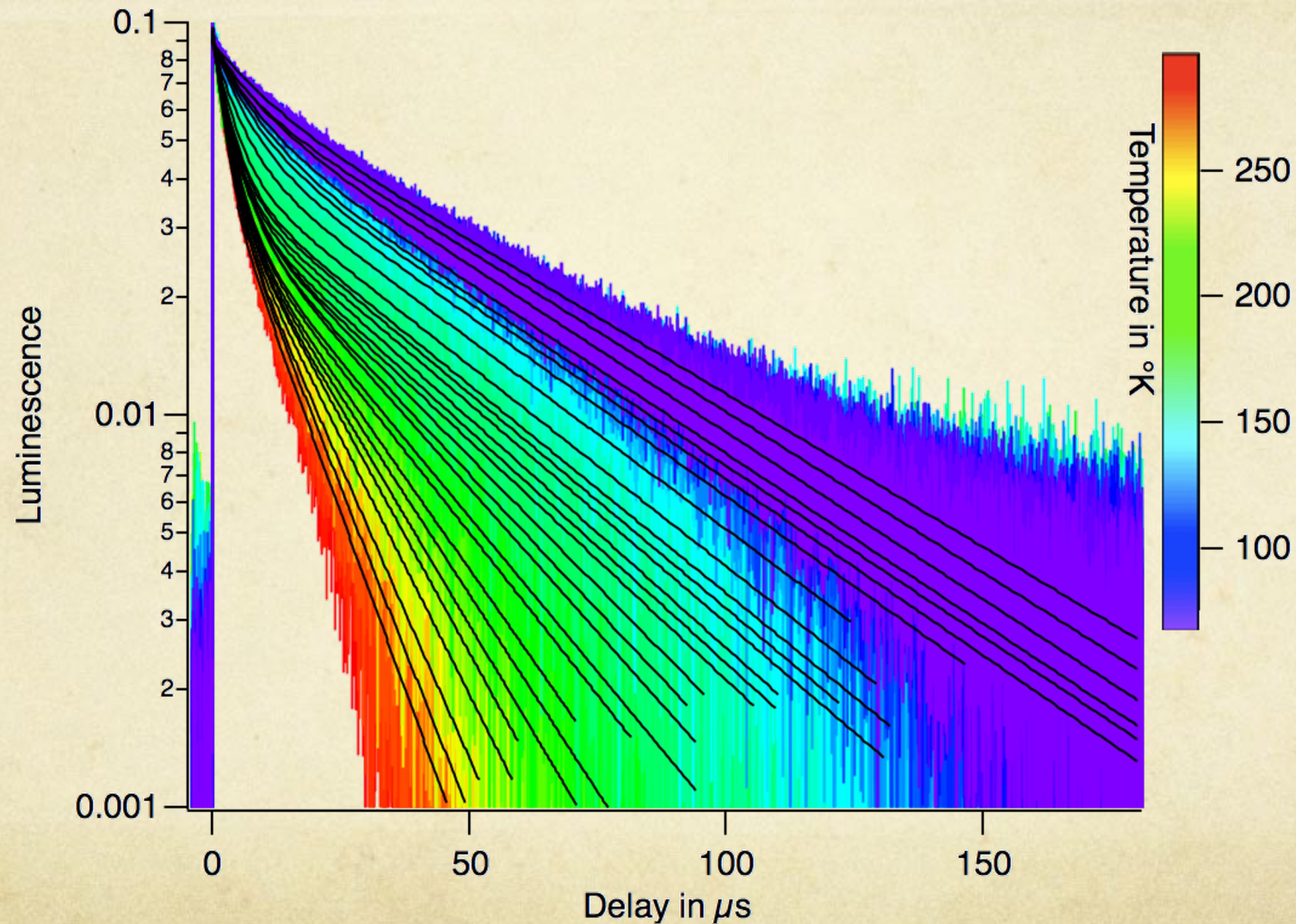
Conclusions

- The Usual equation does not fit.
- The Blumen equation was subjected to a too strong approximation. We recommend :

$$\text{Ln} \left(\frac{I(t)}{I_0} \right) = -k_F t - [Q] V_{FRET} \left\{ \exp \left(-\sqrt{\pi k_Q t + k_Q t} \right) - 1 \right\}$$

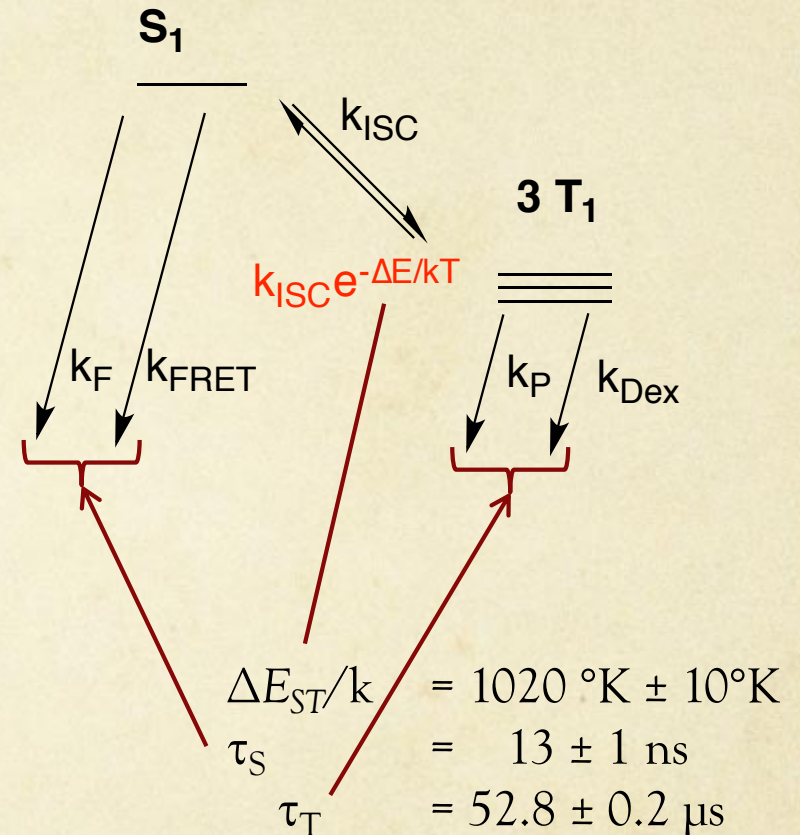
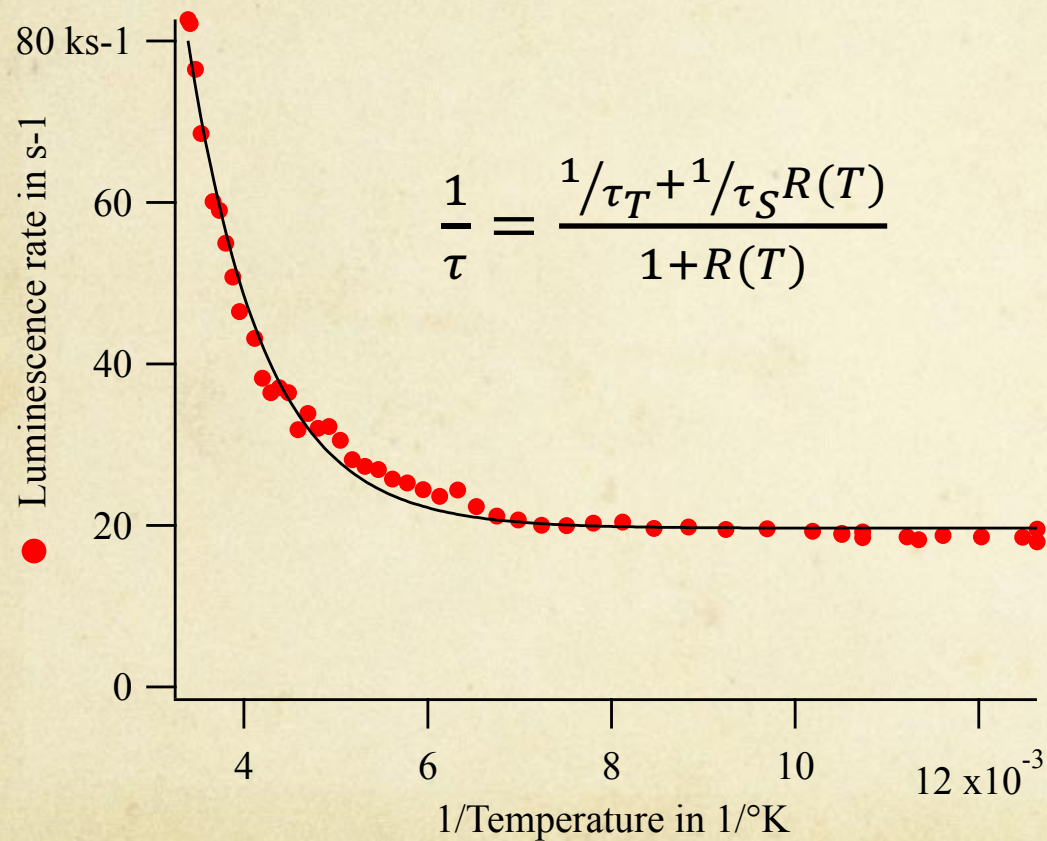
- The exciton of these copper complexes is trapped as shown by this burning experiment.
- We can extract from the data the number of defect in the Förster volum.

Luminescence Lifetime vs Temperature

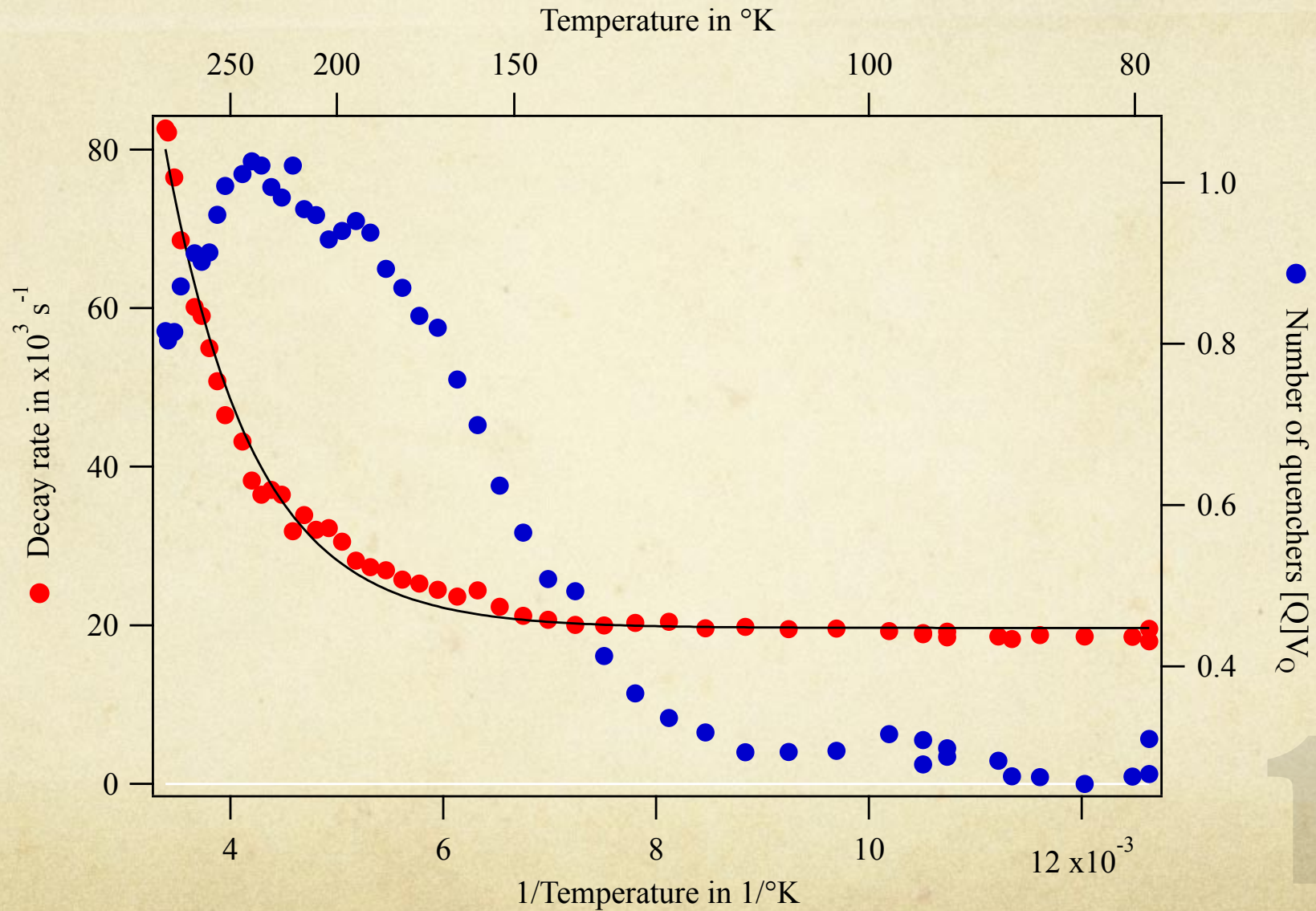


S \rightleftharpoons T equilibrium

Non quenched decay rate



Singlet and triplet quenching



Quenching of the triplet through Förster

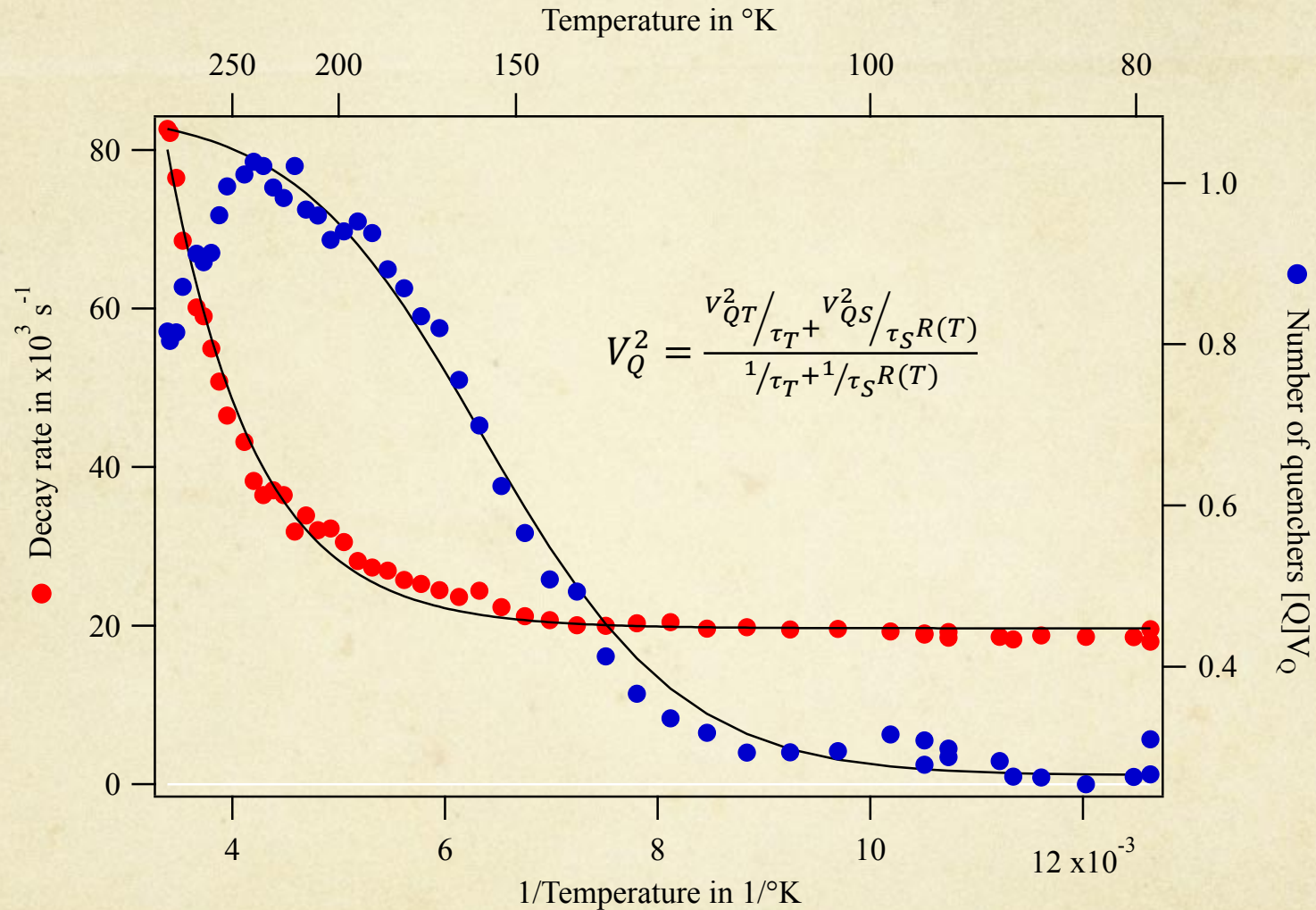
Let define the quenching volume V_Q as that where the quenching rates exceed the decay rate.

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

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

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

Singlet and triplet quenching



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

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

Conclusion

Our Copper Carbene 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.

Both Singlet and Triplet are quenched through FRET.

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

Perspective

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

Team and Collaboration:

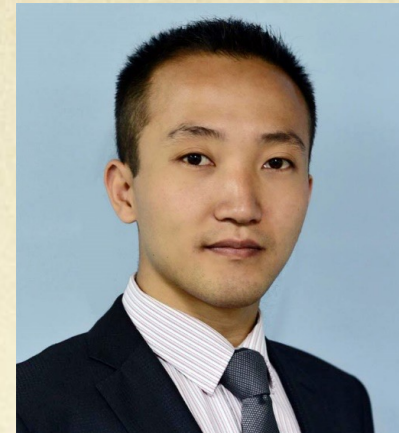
Transient luminescence

PPSM, UMR8531, CNRS,ENS Paris Saclay

Zhengyu Zhang

Arnaud Brosseau

Isabelle Leray



Zhengyu Zhang

Molecules

LCMT, Normandie Univ., CNRS, UMR 6507

Sylvain Gaillard

Margaux Elie

Aurélie Stallivieri,

Solid scintillators

LCAE, LIST, CEA,

Mathieu Hamel

Eva Montbarbon

Funding :

ANR Grant NESSYNED

The Perrin Model

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

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

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

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.

Decay of a single quencher population

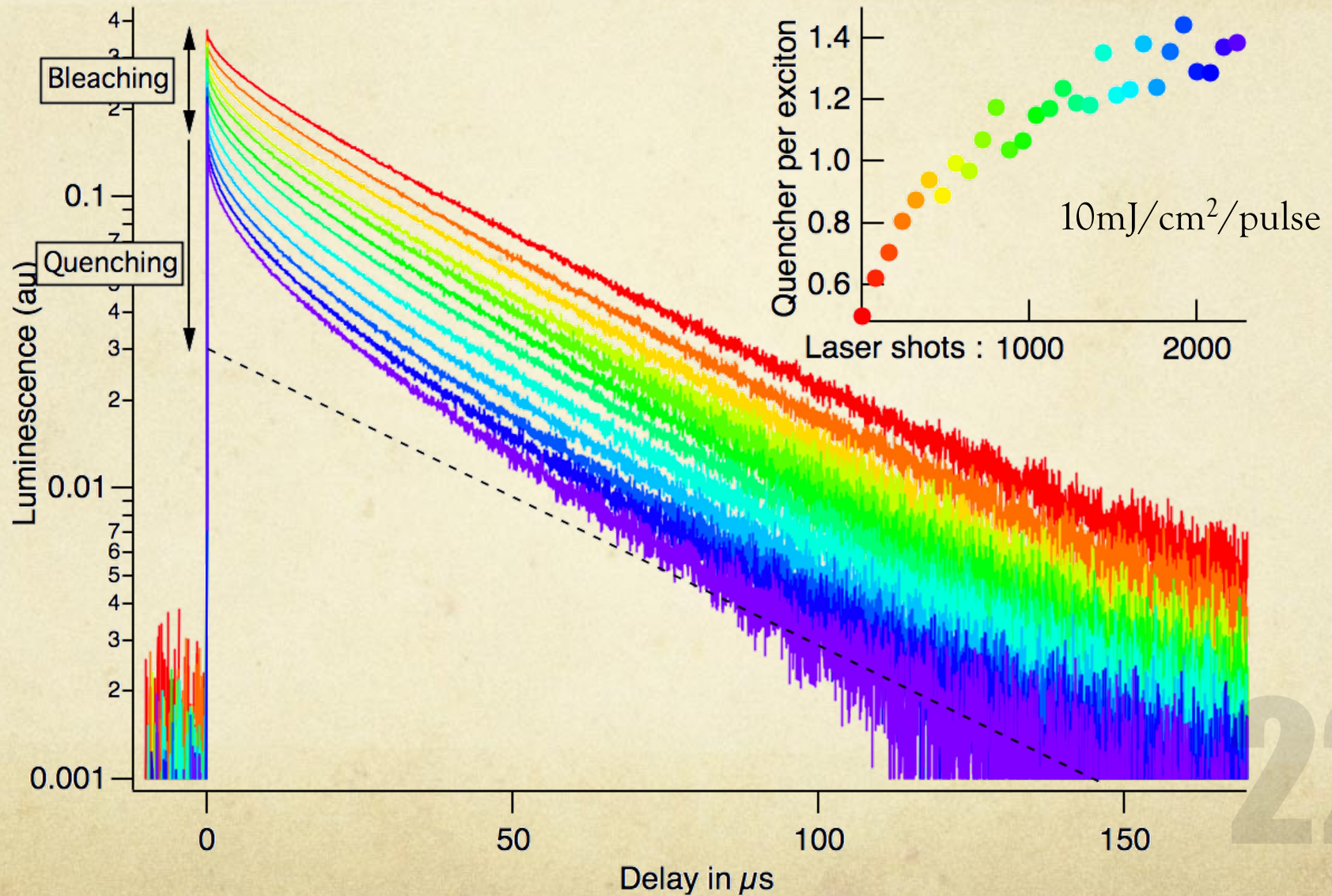
$$\rho_{FRET1Q}(t) = \lim_{L \rightarrow \infty} \int_g^L \exp\left(-k_F \langle \kappa^2 \rangle \left(\frac{Ro}{r}\right)^6 t\right) Q r^2 dr$$

$$Q = \frac{3}{4\pi r^3} \quad ; \quad \frac{1}{u^2} = k_F \langle \kappa^2 \rangle \left(\frac{Ro}{r}\right)^6 t$$

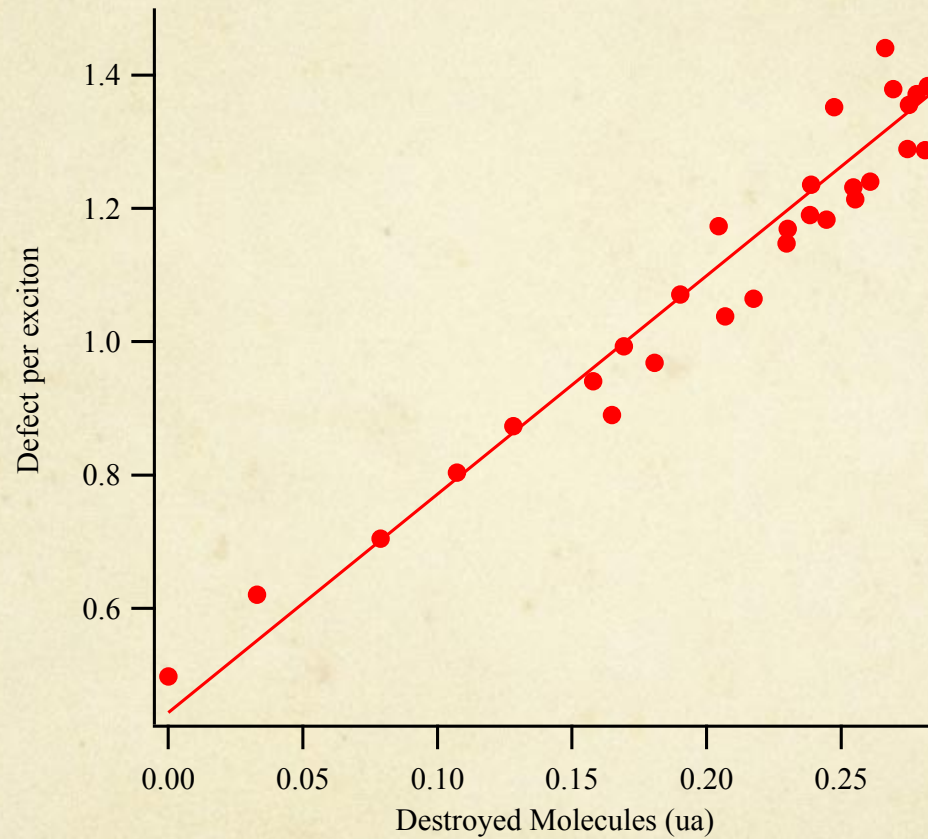
$$\rho_{FRET1Q}(t) = \lim_{L \rightarrow \infty} \frac{1}{\lambda} \int_{\lambda_0}^{\lambda} \exp\left(-\frac{1}{u^2}\right) du = \lim_{L \rightarrow \infty} \left[\exp\left(-\frac{1}{\lambda^2}\right) - \sqrt{\pi} \frac{\text{erfc}(1/\lambda)}{\lambda} \right]_{\lambda_0}^{\lambda}$$

$$\rho_{FRET1Q}(t) = -\sqrt{\pi} \left(\frac{Ro}{g}\right)^3 \sqrt{k_F \langle \kappa^2 \rangle t} + \left(\frac{Ro}{g}\right)^6 k_F \langle \kappa^2 \rangle t + O(t^2)$$

Quantification of defects

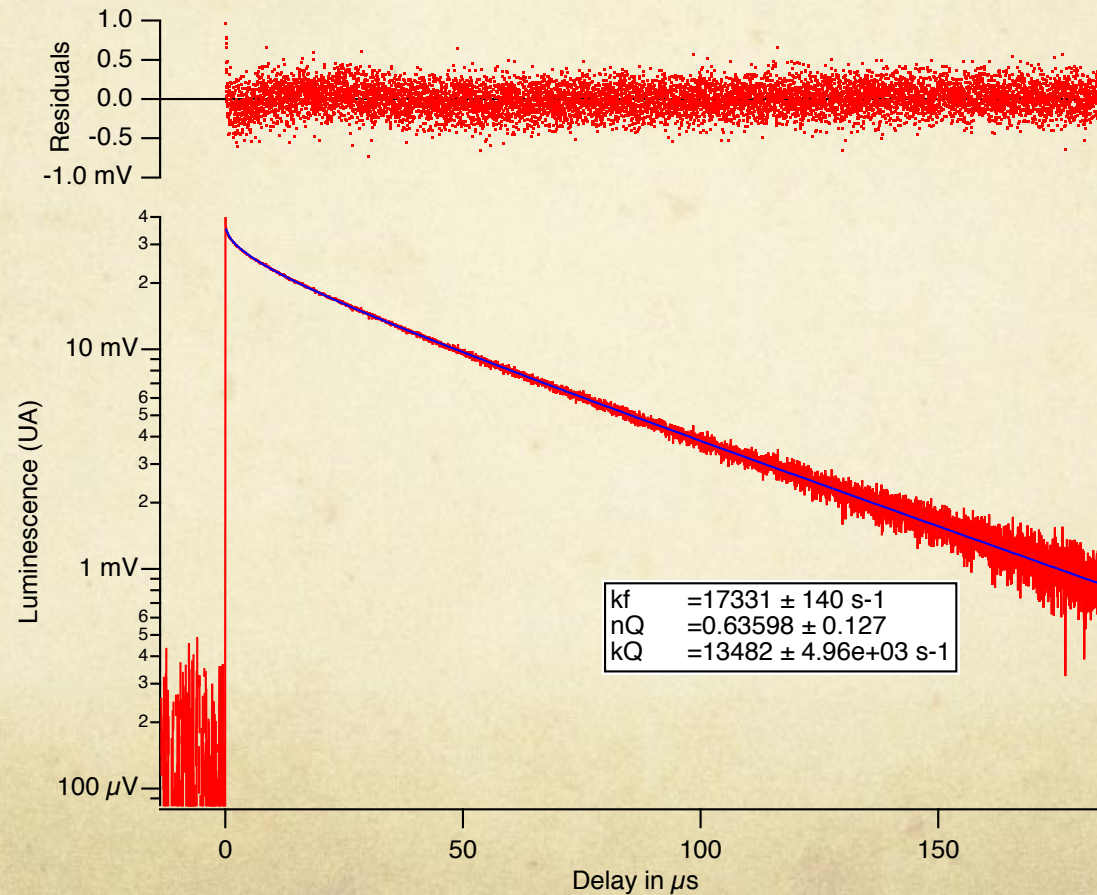


Defect Production Yield



Förster fit for $T < 100^\circ\text{K}$

$$\ln\left(\frac{I(t)}{I_0}\right) = -k_F t - [Q]V_{FRET} \left\{ \exp\left(-\sqrt{\pi k_Q t} + k_Q t\right) - 1 \right\}$$



Förster fit at 300°K

$$\ln\left(\frac{I(t)}{I_0}\right) = -k_F t - [Q]V_{FRET} \left\{ \exp\left(-\sqrt{\pi k_Q t} + k_Q t\right) - 1 \right\}$$

