Supporting Information

Kinetic Modelling of Transient Photoluminescence from Thermally Activated Delayed Fluorescence

Nils Haase*[a,b], Andrew Danos*[c], Christof Pflumm[b] , Antonia Morherr[b], Patrycja Stachelek[c], Amel Mekic[b,d], Wolfgang Brütting[a], and Andrew P. Monkman[c]

[a] Institute of Physics, Experimental Physics IV, University of Augsburg, Universitätsstr. 1, 86135 Augsburg, Germany

[b] Merck KGaA, Performance materials - Display Solutions, Frankfurter Straße 250, 64293 Darmstadt, Germany

[c] Department of Physics, Durham University, South Road, DH1 3LE, UK

[d] Institute of Organic Chemistry, University of Regensburg, Universitätsstr. 31, 93053 Regensburg, Germany

*Email: nils.haase@external.merckgroup.com

*Email: andrew.danos@durham.ac.uk

Fitting model implementation

Finding the kinetic parameters that give the best agreement between model curves and experimental data is challenging for TADF emission decays. This is due to the large range of intensities recorded in the decay curve, often spanning five or more decades on a logarithmic intensity axis. In this work the challenge is further heightened as we wish to fit both the prompt and delayed intensity simultaneously.

The standard optimization method of minimizing squared residuals was found to immediately fail when used for our model parameters. This is because the size of each residual in the fitting is roughly proportional to the height of the data, which causes the optimization to prioritize good fitting in the larger prompt region and ignore the smaller delayed region. An example of the typical output of this kind of “linear fit” (ie: minimizing $\sum_t (I_{exp} - I_{fit})^2$, where data and model are of the form $I(t)$) is shown in Figure S1 in orange. While good fits using linear optimization could be found if the parameter starting values were finely tuned, this requirement is unsatisfactory for a general fitting procedure.

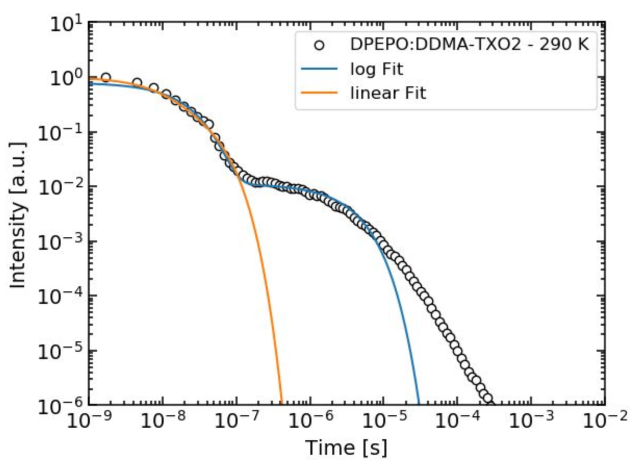

Figure S1: Comparison of linear (unrestricted dataset) and log (restricted dataset) fits to decay data, using same initial parameter values.

In contrast to linear fitting, logarithmic fitting (ie, minimizing $\sum_t (\log(I_{exp}) - \log(I_{fit}))^2$ optimizes the fit parameters based on the ratio of data to model, rather than their difference. This kind of optimization gives roughly equal weight to every datapoint regardless of their actual value, which allows the fitting routine to appropriately take the lower intensity delayed emission into consideration as well. An example of logarithmic fitting is shown in Figure S1 in blue, however this optimization method is not without its own drawbacks. Indeed, precisely because logarithmic fitting gives all datapoints equal weight, it was also routinely found to fail when applied to TADF decay data. This is because the long tail of the decay is considered just as important as the prompt and delayed regions. Examples of typical poor logarithmic fits to decay data are shown in Figure S2.

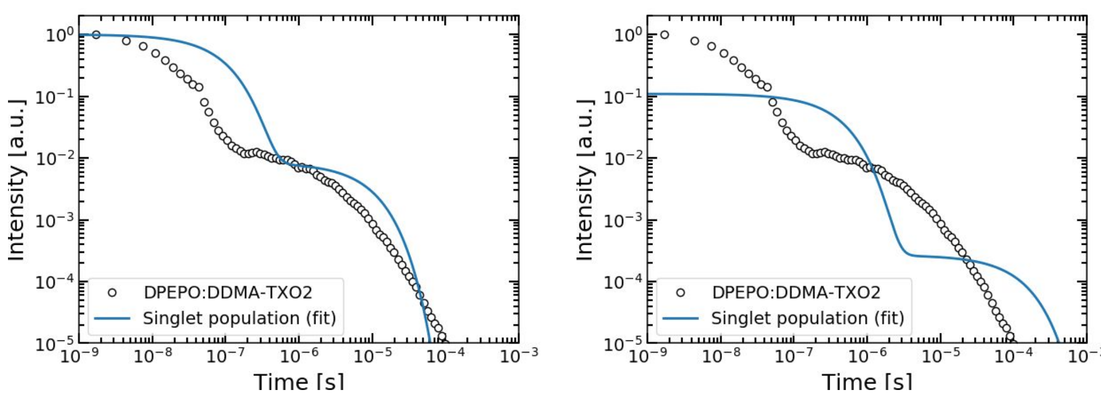

Figure S2: Examples of poor fitting using logarithmic fits on unrestricted datasets.

Ultimately a suitable compromise was found. In datasets where the tail is excluded (ie restricted datasets) the logarithmic fitting routine was found to reproducibly generate good fits that were insensitive to parameter initial values (which were set at $[S_1](t=0) = 0.8$, $k_F = 10^6$, $k_{ISC} = 10^6$, $k_{rISC} = 10^4$). For each decay a maximum dataset size could be found, above which the logarithmic fitting procedure began to fail. This maximal restricted dataset was used with logarithmic optimization to generate the fits presented in the main text. In the main paper figures the restricted datasets are plotted in solid color, while the excluded data points are greyed out.

However, arbitrarily excluding the tail of the decay without sounds justification is undesirable. Therefore, to check that use of the restricted dataset (and exclusion of the decay tail) did not unduly impact the fitting parameters, we return to the linear optimization method. By using the optimized parameter values from the log fitting as initial values for the linear fitting (except for $[S_1](t=0)$), good fits could be found for the unrestricted dataset without significant changes to the initial values. The parameter values found by both optimization methods are shown in Table S1, while an example of the subsequent fits is shown in Figure S3. In contrast to the other fitting parameters we found that $[S_1](t=0)$ had to be fixed at its initial (log fitted) value, as when it was allowed to vary the linear fitting would raise it to once again improve the fitting in the prompt at the expense of the delayed region (similar to Figure S1). Nonetheless, the agreement of the other fitting parameters in both optimization methods confirmed that the fitted parameter values found by the restricted log fitting corresponded to a true minimum of the residual function, even with later data points excluded.

We note that while the values of the fit parameters agree well for both log and linear optimization methods, the reported errors for the linear fits are much larger. As parameter errors from non-linear fitting procedures are usually determined from partial derivatives of the error function with respect to that parameter, it makes sense that the errors from the linear fitting would be larger than those for the logarithmic fitting. Once again, as the logarithmic fitting only considers the relative size of the residuals (ie, deviation of the data/model ratio from 1), the parameter errors it reports are not inappropriately magnified by the large absolute values of the residuals in the prompt region.

Table S1: Fitted rate constants for restricted dataset logarithmic optimisation, and subsequent unrestricted linear optimisation with transferred initial values and fixed $[S_1](t=0)$.

DPEPO:DDMA-TXO2(13%)

temp. [K]	Fit	$[S_1](t=0)$[%]	k_F [10^6 s^{-1}]	k_{ISC} [10^6 s^{-1}]	k_{rISC} [10^5 s^{-1}]
290	Log	78.4 ± 0.1	15.0 ± 0.3	32.4 ± 1.2	9.8 ± 0.3
	Linear	-	15.5 ± 10.3	34.2 ± 38.6	1.2 ± 1.4
230	Log	83.6 ± 5.5	14.4 ± 0.8	31.5 ± 1.2	9.3 ± 0.4
	Linear	-	14.0 ± 121.7	33.0 ± 155.9	9.3 ± 3.5
180	Log	80.6 ± 5.6	18.4 ± 1.0	26.7 ± 1.0	7.1 ± 0.3
	Linear	-	18.0 ± 72.5	27.4 ± 41.2	5.8 ± 22.9
130	Log	78.3 ± 4.6	26.0 ± 1.1	20.6 ± 0.7	4.9 ± 0.2
	Linear	-	23.0 ± 154.3	23.6 ± 157.8	2.7 ± 1.7

CBP:DPTZ-DBTO2(10%)

temp. [K]	Fit	$[S_1](t=0)$[%]	k_F [10^6 s^{-1}]	k_{ISC} [10^6 s^{-1}]	k_{rISC} [10^5 s^{-1}]
298	Log	43.1 ± 5.1	4.0 ± 0.5	33.4 ± 3.2	19.3 ± 2.0
	Linear	-	4.9 ± 19.4	32.4 ± 133.7	28.6 ± 342.6
220	Log	40.7 ± 4.1	6.1 ± 0.7	34.3 ± 2.4	12.6 ± 1.0
	Linear	-	5.9 ± 21.1	42.2 ± 121.0	17.0 ± 57.7
160	Log	44.1 ± 3.6	8.8 ± 0.9	20.7 ± 1.1	4.1 ± 0.3
	Linear	-	10.1 ± 107.8	23.3 ± 132.0	5.2 ± 260.1

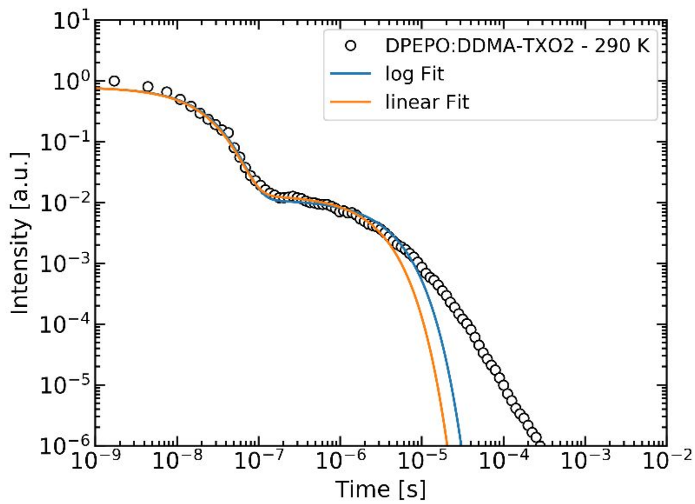

Figure S3: Comparison of log fit (restricted dataset, default starting parameters) and linear fit (unrestricted dataset, starting parameters preceding log fit).

Transient absorption measurements

Measurements of transient absorption (TA) of the TADF materials were performed as follows. Films of DPEPO:DDMA-TXO2(20%) or CBP:DPTZ-DBTO2(20%) were evaporated onto glass or quartz substrates and mounted in an evacuated cryostat with quartz windows. The output of an Energetiq laser driven light source (EQ-99X) was focused to a spot of ~4mm diameter on the sample as probe, and overlapped quasi-colinearly with the output of an EKSPLA 355nm Nd:YAG laser as pump. The laser output was between 60 and 120uJ per pulse, and operated at 500 Hz repetition rate. The time resolved transmission of the probe light was collected using a Bentham TMc300 monochromator, Femto HCA-S-200M-Si photoreceiver, and Agilent DSO6052A oscilloscope triggered by the pump laser and averaged over 4096 shots. The background emission due to the pump was measured similarly with the probe beam blocked and identical oscilloscope settings.

Transmission data was processed into absorption as follows. The diode offset and pump induced emission were simultaneously accounted for by subtracting the pump only measurement from the probe transmission measurement. The signal level before the pump was taken to represent the CW transmission (T), while changes from this signal level gave ΔT. Changes in absorption could then be calculated using $\Delta A(t) = -\log\left(\frac{\Delta T(t)}{T} + 1\right)$, and was measured independently at each wavelength. The zero time of each measurement was taken from the maximum of the pump induced emission data, and the $\Delta A(t)$ data was normalized to its value at this time.