

## Supplementary information

### **Ultra-precise photothermal measurement reveal near unity photoluminescence quantum yields of molecular emitters in solution**

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## Section 1

In this section an overview of the origin of formula 1 in the main text will be given [1,2]. When a luminophore is optically excited, the heat it generates can be distinguished in two processes: thermalization of excited electrons to the band edges and non-radiative recombination. The thermal energy generated by thermalization is independent of a luminophores PLQY, but increases linearly with an increase in excitation energy. The probability of non-radiative recombination to occur is defined by the PLQY, while the generated heat for such an event is (generally) independent of excitation energy. The thermal energy produced by a non-radiative recombination event is equal to the average emission energy, which will be denoted by  $E_{PL}$ , and can be determined by performing an emission measurement using a spectrometer. Expressing the measured photoluminescent emission flux as  $\phi_{PL}(E)$ , in units of relative amount of emitted photons per square meter per second per electronvolt ( $\frac{\# \text{photons}}{sm^2 eV}$ ), we can obtain the average emission energy via:

$$E_{PL} = \frac{\int_0^{+\infty} \phi_{PL}(E) E dE}{\int_0^{+\infty} \phi_{PL}(E) dE}.$$

Note that in order to obtain  $E_{PL}$  no absolute spectrum is required, only a relative spectrum in terms of emission photon energy  $E$ .

When an absorbed photon leads to non-radiative recombination, all of its energy will be converted to thermal energy, and the generated thermal energy can be seen as the sum of both thermalization and non-radiative recombination:

$$E_{th} = (E_{exc} - E_{PL}) + E_{PL} = E_{exc}$$

While an absorbed photon leading to a luminescent event only produces heat due to thermalization, the remaining energy is re-emitted, with an average photon energy of  $E_{PL}$ :

$$E_{th} = E_{exc} - E_{PL}$$

The probability for a luminescent event to occur is defined by the PLQY.

When an absorbed photon doesn't lead to a luminescent event, non-radiative recombination occurs with a probability  $1 - PLQY$ . Thus, for an average photon the produced thermal energy is:

$$E_{th} = (1 - PLQY)E_{exc} + PLQY(E_{exc} - E_{PL}) = E_{exc} - PLQY * E_{PL}$$

In the experiments the assumption will be made that  $\eta$  is independent of excitation energy within the measurement regime, which will be further rationalized later.

In order to quantify the relative thermal energy produced as a thermal signal both photo-thermal deflection spectroscopy (PDS) and thermal lensing spectroscopy (TLS) techniques are used. For the sake of convenience, this thermal signal will be denoted by ' $TS$ '. The thermal signal depends on the amount of photons absorbed, denoted by  $A$  and dependent on excitation energy, as well as the produced thermal energy:

$$TS(E_{exc}) = c_1 A(E_{exc})(E_{exc} - PLQY * E_{PL})$$

For some constant  $c_1$ , independent of excitation energy.

In order to quantify the amount of absorbed photons, relative to the excitation energy, a photoluminescence excitation, denoted by ' $PLx$ ', experiment is performed. It measures the relative intensity of the emitted light. It is proportional to the amount of absorbed photons:

$$PLx(E_{exc}) = c_2 * PLQY * A(E_{exc})$$

For some constant  $c_2$ , independent of excitation energy.

When dividing both formulas one obtains:

$$\frac{TS(E_{exc})}{PLx(E_{exc})} = c_0(E_{exc} - PLQY * E_{PL}), \text{ with } c_0 = \frac{c_1}{c_2 * PLQY}$$

This equation show the relative increase in thermal energy per absorbed photon, which behaves linearly in function of excitation energy. The constant  $c_0$  depends on several set-up parameters, but is not required to be known for the determination of the PLQY. The equation can be evaluated for different excitation energies, allowing one to solve it for PLQY. Looking at many different excitation energies significantly increases the accuracy with which one can determine PLQY. A visually pleasant way to determine PLQY this way is to look at

the excitation energy where no net thermal energy will be produced. This excitation energy will be denoted as  $E_T$ , here the thermal signal is equal to zero:

$$\frac{PDS(E_T)}{PLx(E_T)} = 0 = E_T - PLQY * E_{PL}$$

Now PLQY easily drops out:

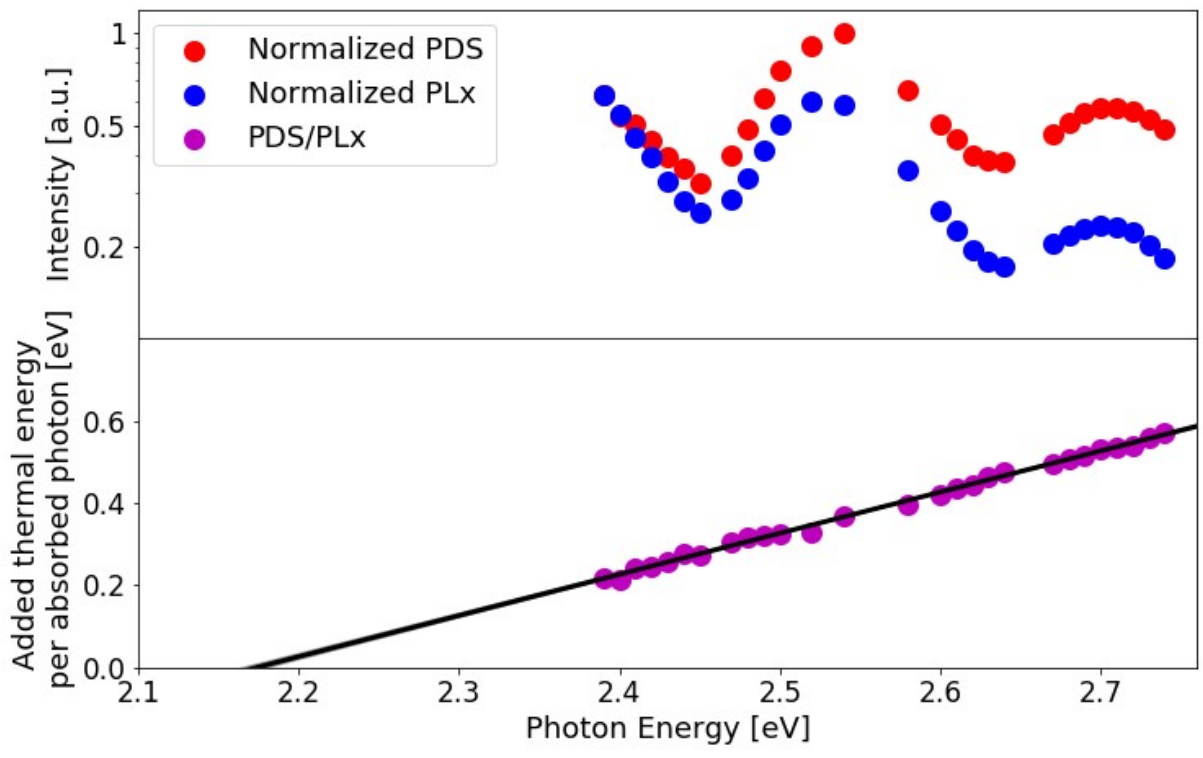
$$PLQY = \frac{E_T}{E_{PL}}$$

Since generally  $E_T$  is below the absorption band of the luminophore, very little absorption occurs at  $E_T$  making it very difficult to directly measure it experimentally. However, one can obtain a very accurate estimate on  $E_T$  based on the extrapolation of measurements done at higher excitation energy.

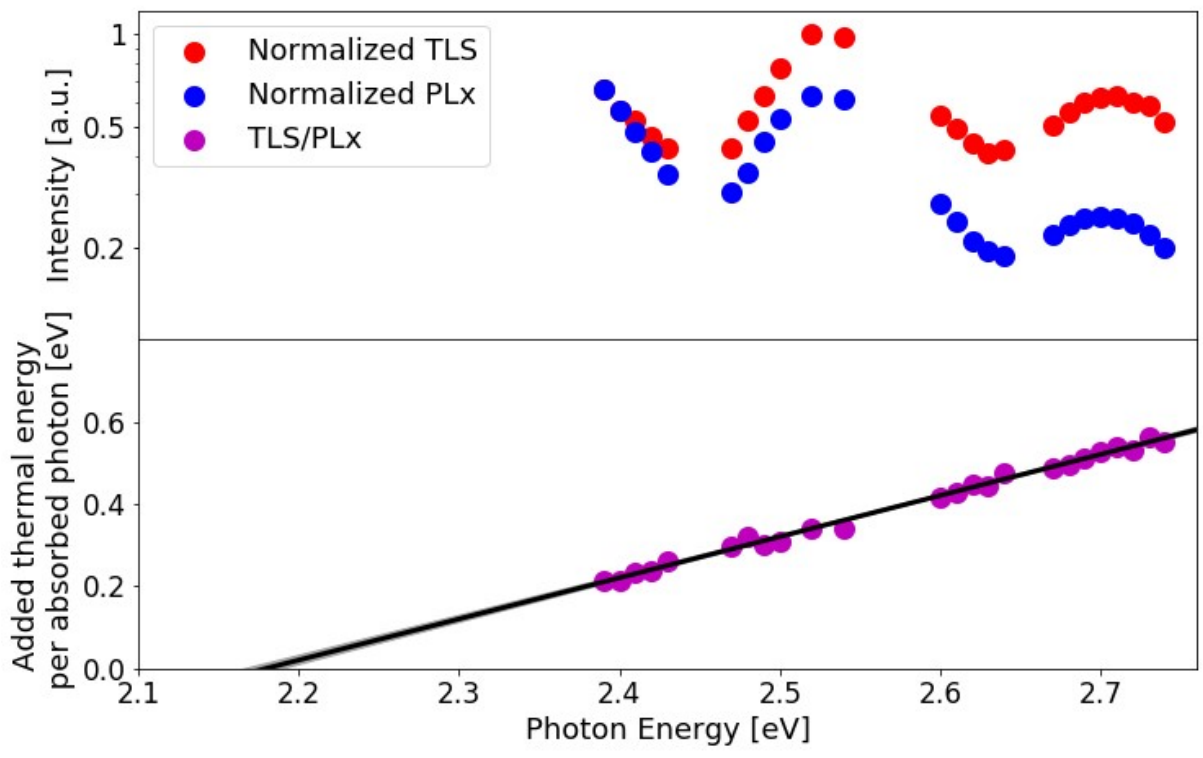
## Section 2

In this section figures originating from the data obtained by the thermal measurements (PDS, TLS) and PLx-measurements will be given. For each emitter-solution combination, the thermal signal divided by the laser intensity is normalized to unity and represented by red dots (each point represents the average of 60 measurements). The PLx signal, also divided by the laser intensity, is represented by the blue dots and is normalized such that the PLx spectrum overlaps with the thermal signal for the lowest excitation photon energy. The division of the thermal signal with the PLx signal is given by the purple dots in the graph below, the black line represents the linear regression line and the 95%-confidence area is represented by the grey area.

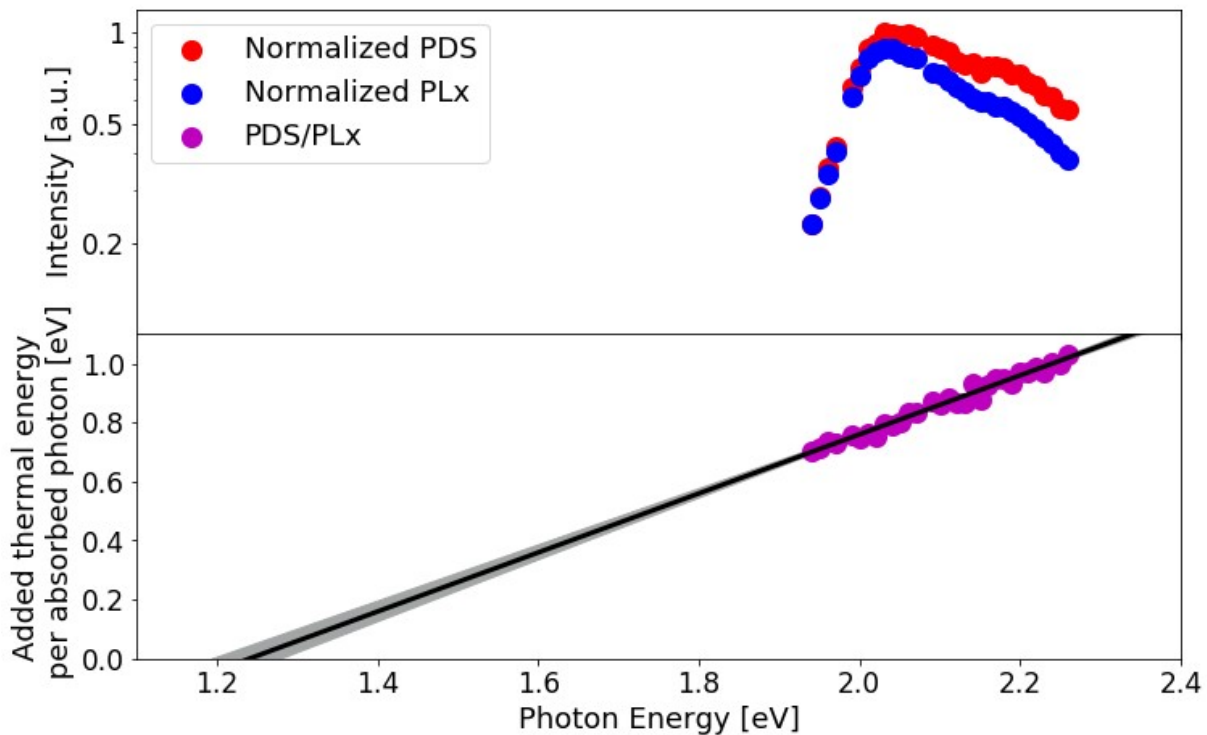
Before each measurement a threshold thermal signal value was chosen such that the thermal signal is in the linear regime. A PID-controller adjusts the excitation laser intensity such that the preset thermal signal value is attained. However, when the excitation laser intensity is too high or too low, the desired thermal signal value can't be attained. High thermal signal measurement values fall in a non-linear regime and low thermal signal values have a poor signal/noise ratio, therefore the values obtained are discarded by the algorithm in both cases. Since the intensity of the tunable laser for a certain wavelength is quite unpredictable and the entire process is automated this unfortunately can lead to "gaps" in the measurement data. Measurement points for excitation energies between 2.28 and 2.38 eV are also lacking due to technical constraints of our laser.



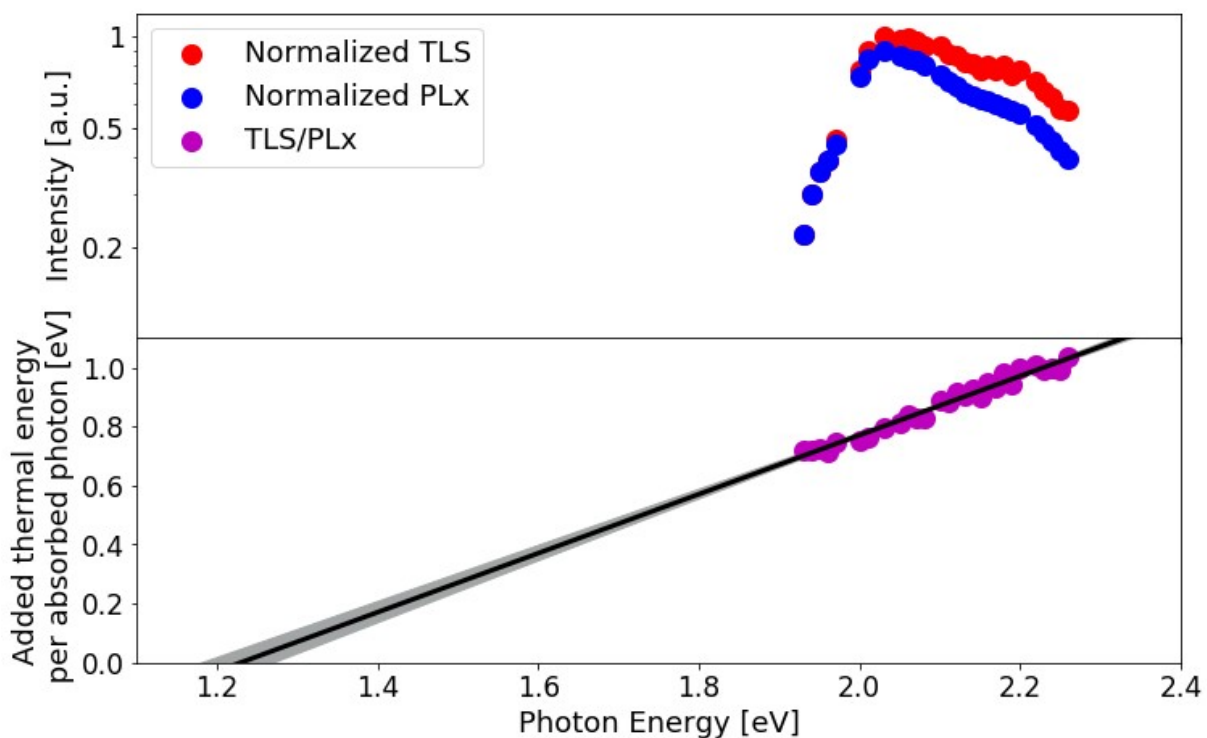
**Figure 1A.** Perylene Orange in chloroform (PDS).



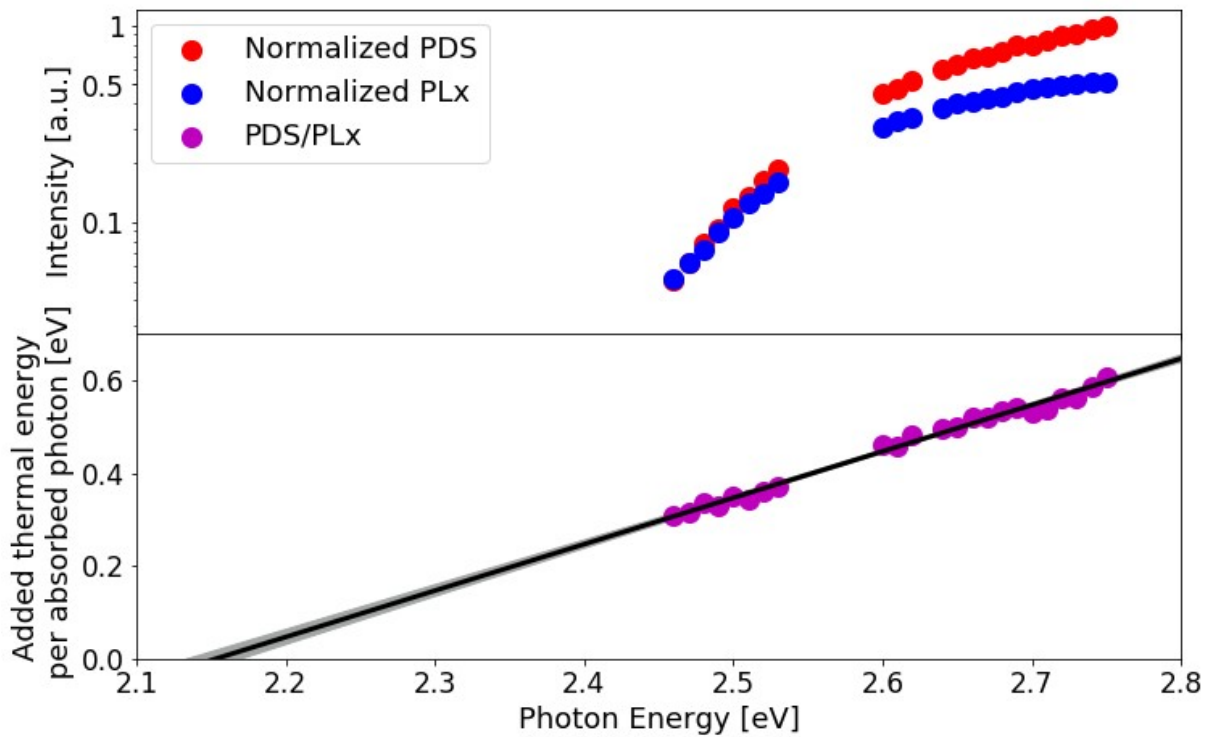
**Figure 1B.** Perylene Orange in chloroform (TLS).



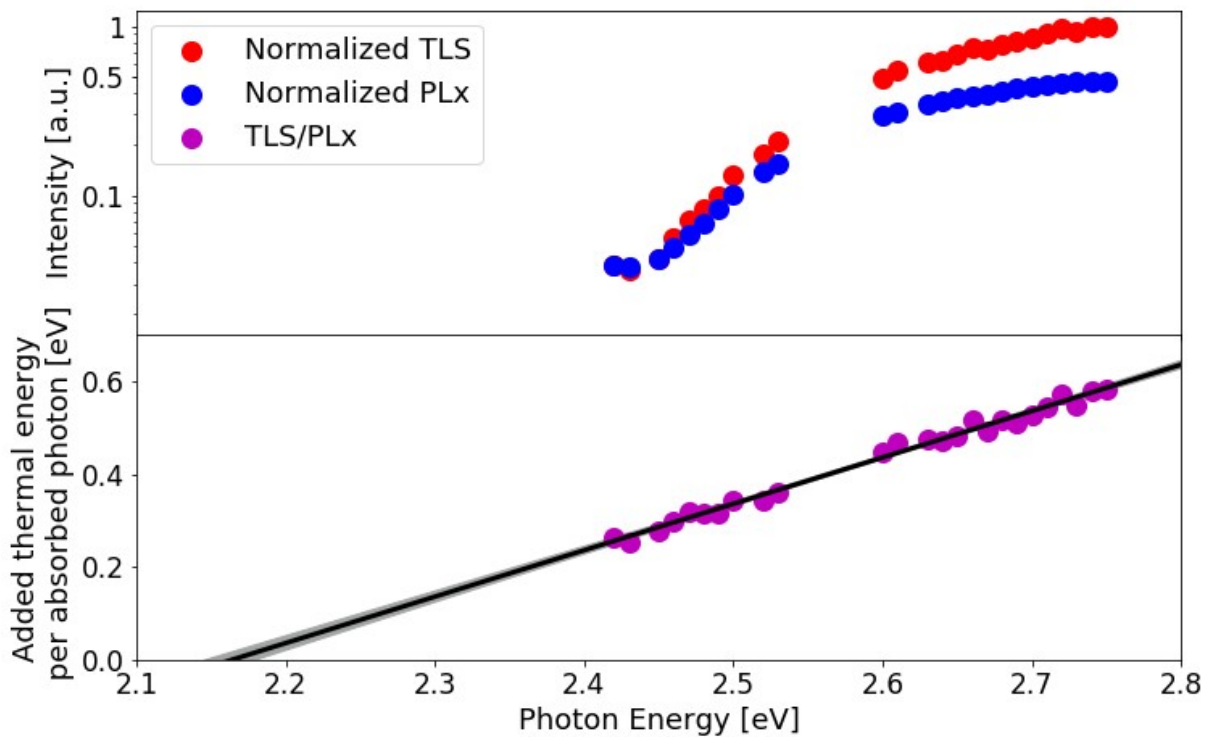
**Figure 2A.** Oxazine 170 Perchlorate in chloroform (PDS).



**Figure 2B.** Oxazine 170 Perchlorate in chloroform (TLS).

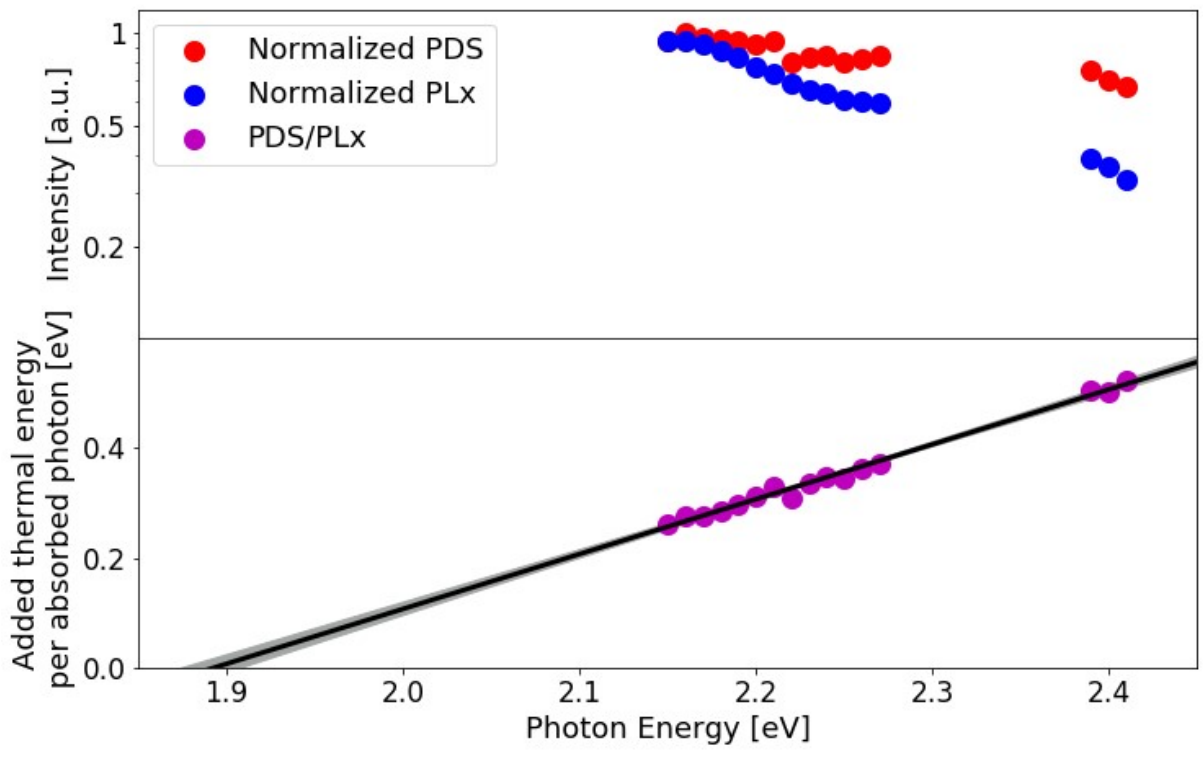


**Figure 3A.** SuperYellow in chloroform (PDS).

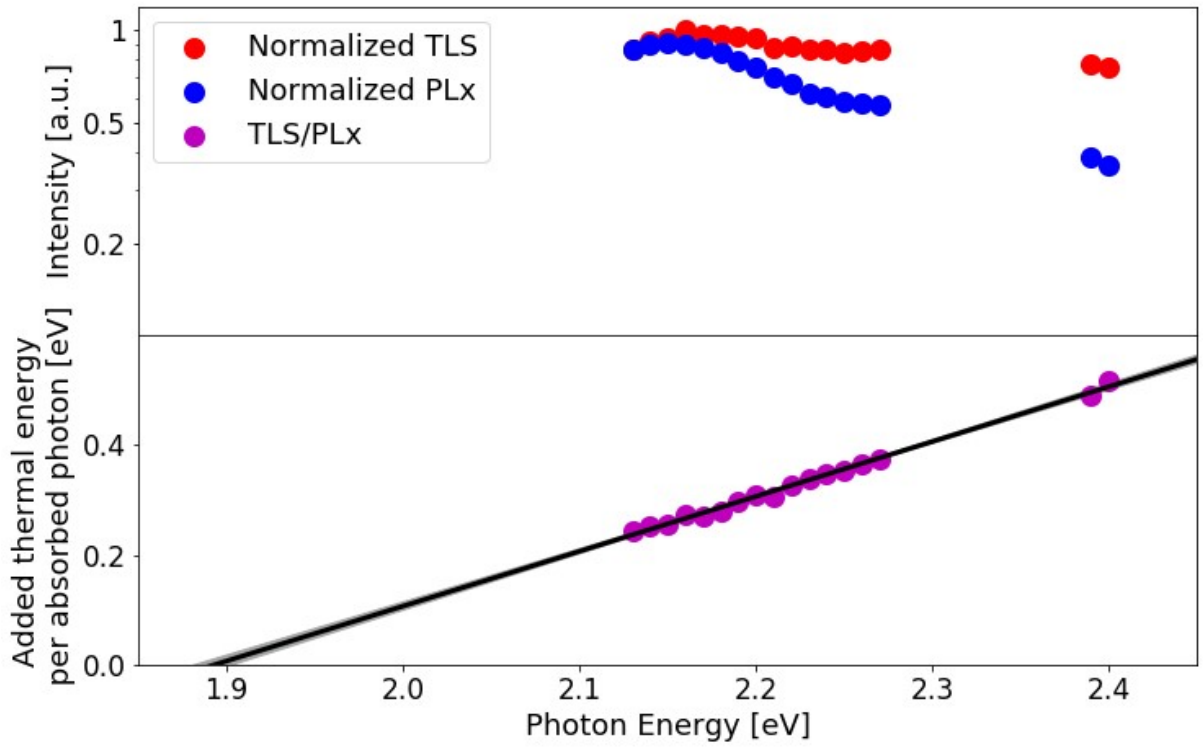


**Figure 3B.** SuperYellow in chloroform (TLS).

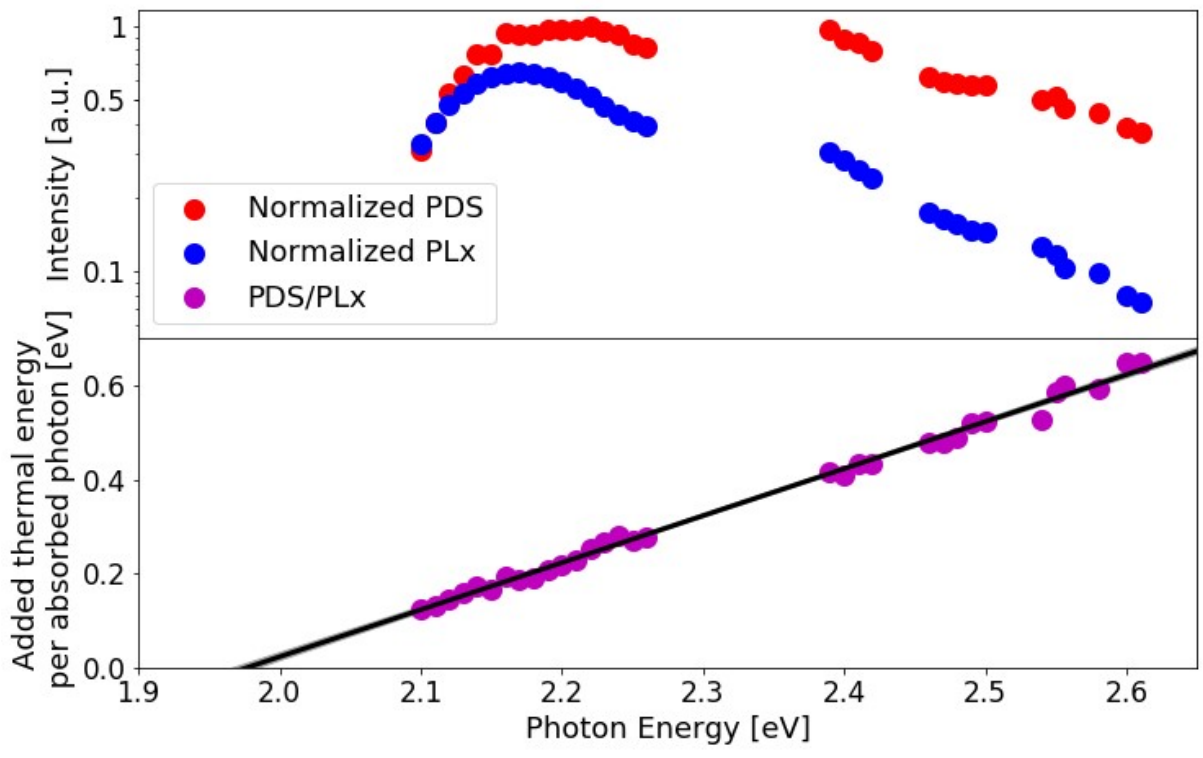




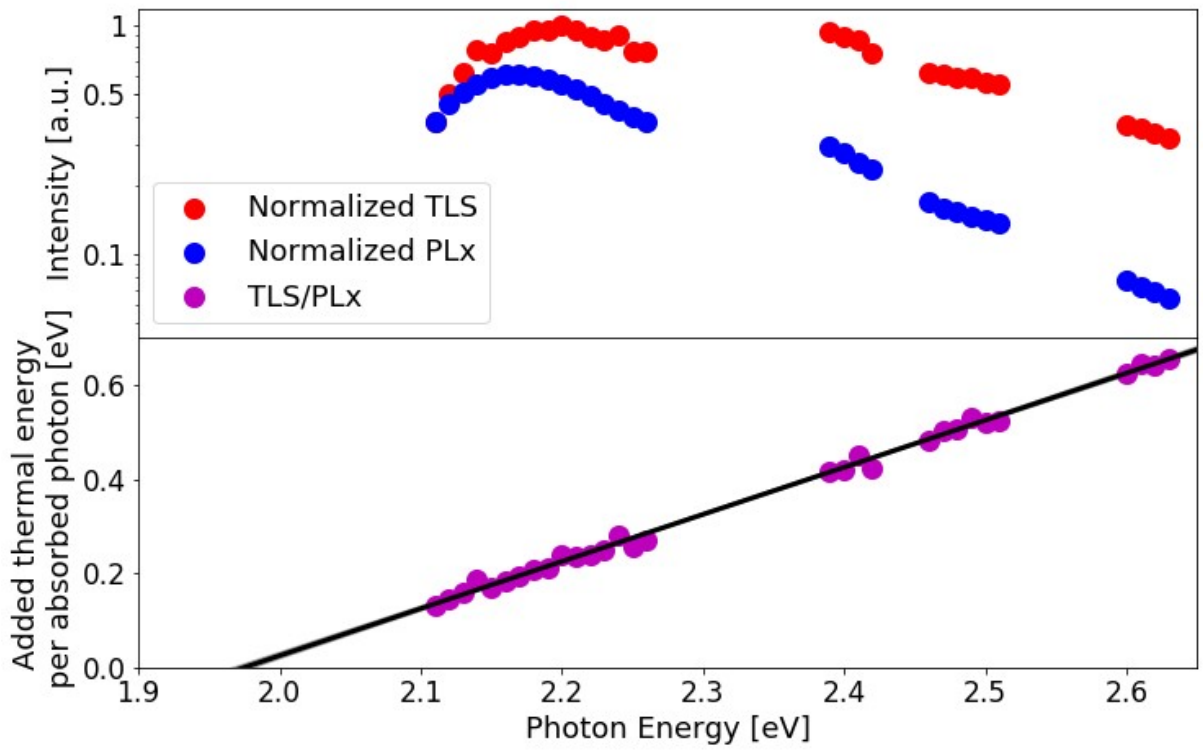
**Figure 4A.** Perylene Red in chloroform (PDS).



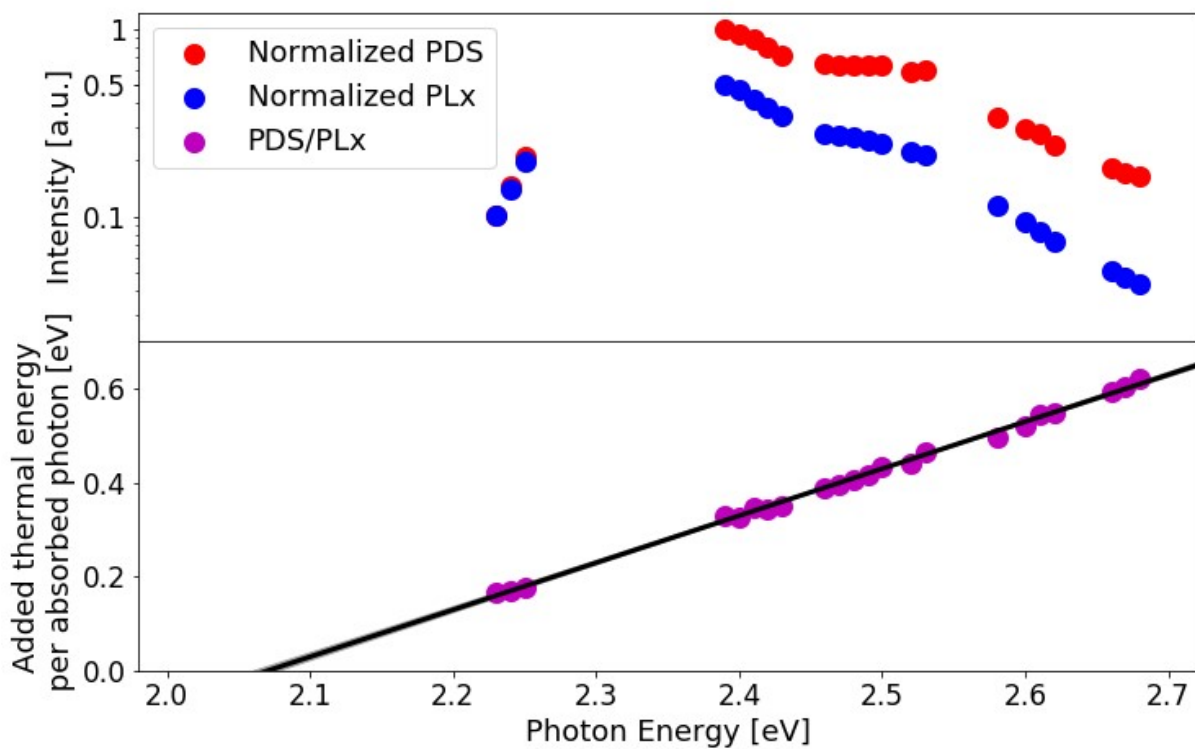
**Figure 4B.** Perylene Red in chloroform (TLS).



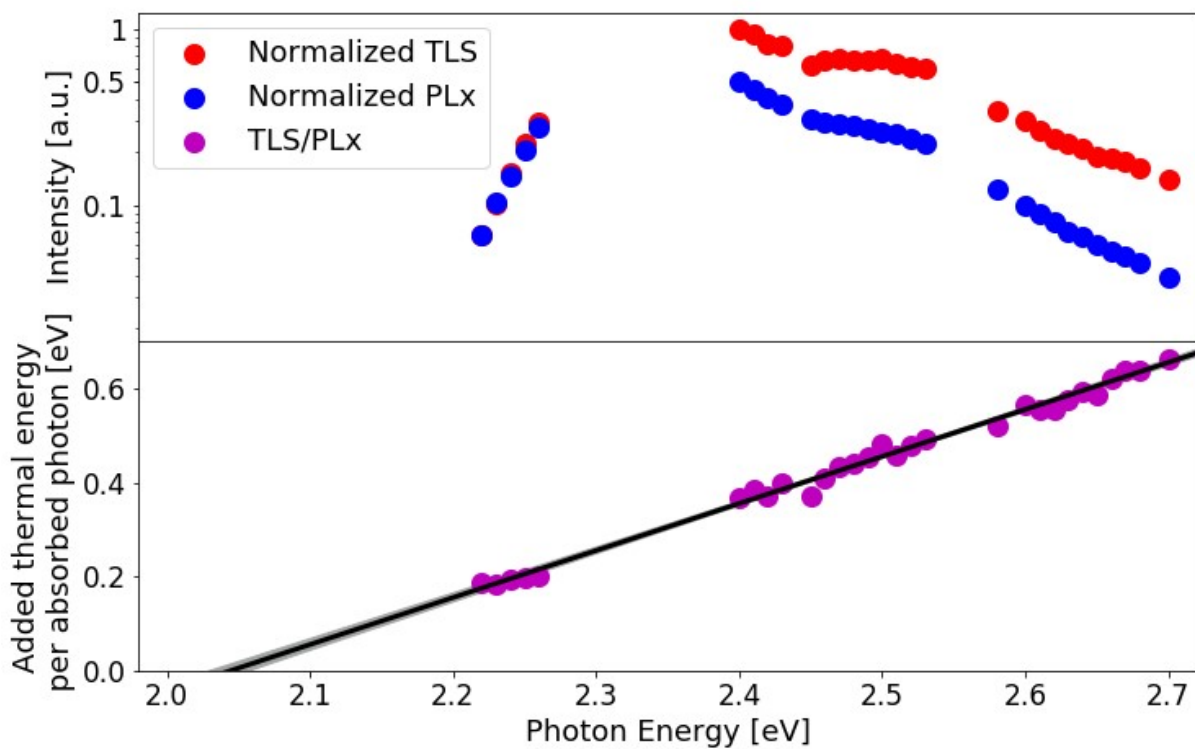
**Figure 5A.** Perylene Red in carbon tetra chloride (PDS).



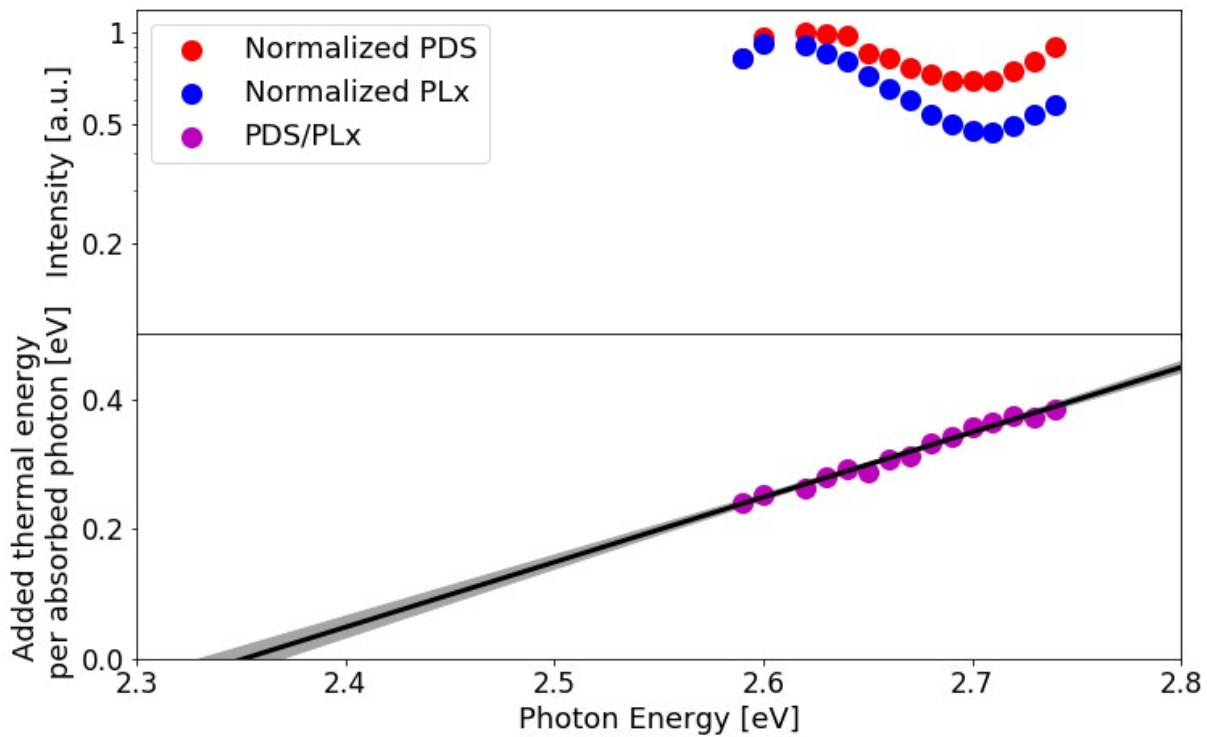
**Figure 5B.** Perylene Red in carbon tetra chloride (TLS).



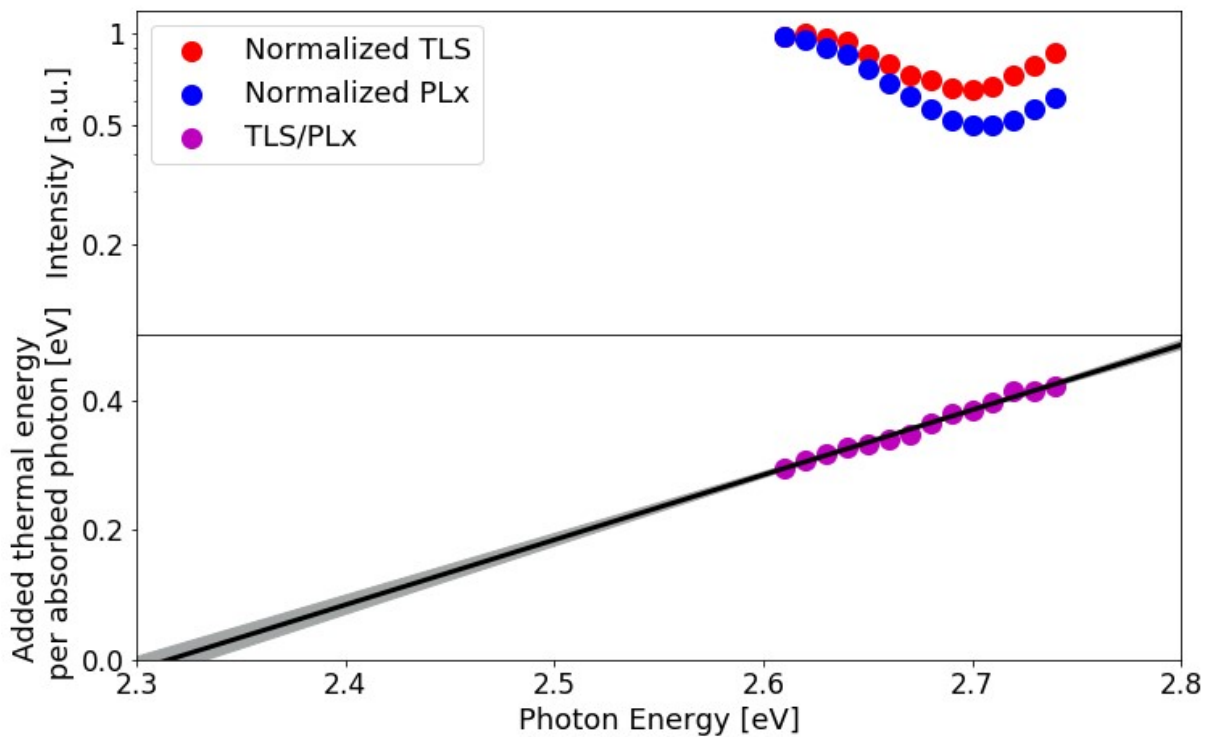
**Figure 6A.** Rhodamine 6G in Ethanol (PDS).



**Figure 6B.** Rhodamine 6G in Ethanol (TLS).



**Figure 7A.** Perylene Yellow in Chloroform (PDS).



**Figure 7B.** Perylene Yellow in Chloroform (TLS).

		PDS			TLS			Average Emission Energy
		Lower bound	Mean	Upper bound	Lower bound	Mean	Upper bound	
Perylene Red CCL4	Threshold Energy	1.968eV	1.977eV	1.986eV	1.968eV	1.975eV	1.982eV	1.987eV
	PLQY	0.990	0.995	0.999	0.990	0.994	0.997	
Perylene Orange CHCL3	Threshold Energy	2.165eV	2.174eV	2.181eV	2.167eV	2.179eV	2.191eV	2.202eV
	PLQY	0.983	0.987	0.991	0.984	0.990	0.995	
Perylene Red CHCL3	Threshold Energy	1.876eV	1.893eV	1.909eV	1.882eV	1.894eV	1.904eV	1.940eV
	PLQY	0.967	0.976	0.984	0.970	0.976	0.981	
Perylene Yellow CHCL3	Threshold Energy	2.331eV	2.351eV	2.370eV	2.292eV	2.316eV	2.337eV	2.398eV
	PLQY	0.972	0.981	0.988	0.956	0.966	0.974	
Super Yellow CHCL3	Threshold Energy	2.135eV	2.153eV	2.171eV	2.147eV	2.164eV	2.180eV	2.280eV
	PLQY	0.936	0.944	0.952	0.942	0.949	0.956	
Rhodamine 6G ETOH	Threshold Energy	2.062eV	2.071eV	2.079eV	2.049eV	2.062eV	2.072eV	2.187eV
	PLQY	0.943	0.947	0.951	0.937	0.943	0.947	
Oxazine CHCL3	Threshold Energy	1.196eV	1.240eV	1.281eV	1.182eV	1.229eV	1.273eV	1.791eV
	PLQY	0.668	0.693	0.715	0.660	0.686	0.711	

**Table 1.** The threshold energy (mean) as determined by PDS/Plx and TLS/Plx measurements for each emitter-solution pair, the lowerbound and upperbound of the 95%-confidence interval are shown to the left and right respectively. Below each value is the corresponding PLQY-value, based on the average emission energy determined from an emission spectrum (show at the far right).

**Comment [SM]:** Should I make a nicer looking Table?

## References

1. D. A. Hanifi, N. D. Bronstein, B. A. Koscher, Z. Nett, J. K. Swabeck, K. Takano, A. M. Schwartzberg, L. Maserati, K. Vandewal, Y. Van De Burgt, A. Salleo, A. P. Alivisatos, 2019, **363**, 1199-1202.
2. B. Couch, A. Meyer, B. Heller, S. L. Johnson, *Methods and Applications in Fluorescence*, 2018, **7**, 015004.