

## Supporting Information for:

### Fluorescence Delayed is Fluorescence Denied

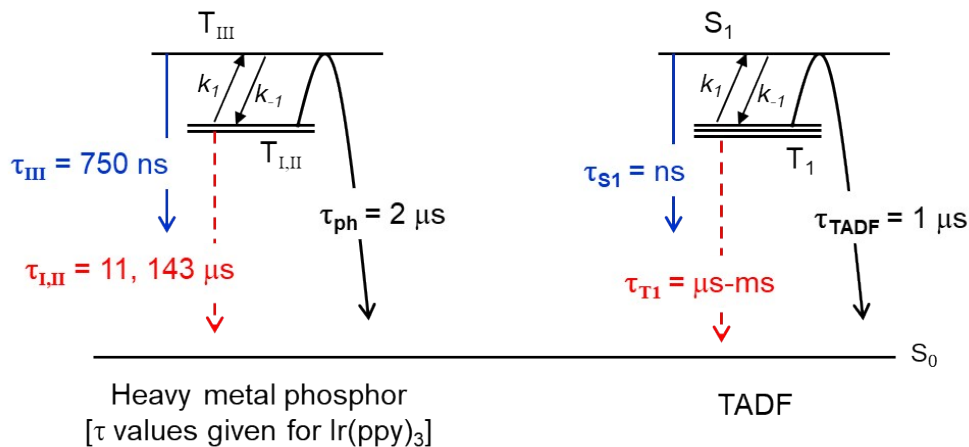
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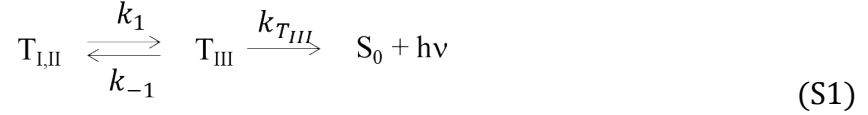
#### 1. Analysis for emission from molecular heavy metal based phosphors

As we discussed in the text, the model presented for Case 2 TADF materials (materials where  $k_{ISC} \gg k_{S1}$ ) can also be used for heavy metal complexes. The kinetic scheme for high efficiency emitters of either molecular heavy metal based phosphorescent or TADF compounds is shown in Figure S1. Yersin has shown that the scheme illustrated here is common for heavy metal phosphors, where the upper triplet has a markedly higher emission rate than the lower two levels.<sup>1, 2</sup> The lifetimes for the triplet sublevels and the overall phosphorescence lifetime for the heavy metal scheme shown here are for *facial*-tris(2-phenylpyridinato-C2,N)iridium.<sup>3</sup> Note that the principal differences in the schemes are that the phosphor case emits from an upper *triplet* level (not a *singlet*) and the lower level is comprised of two triplet sublevels rather than three. The emission



**Figure S1:** Kinetic schemes for heavy metal-based phosphors and organic TADF emitters. Note that the assumption here is that the emission takes place with a luminescence efficiency approaching 100% in both cases, so nonradiative pathways are not considered.

in both cases involves thermal population of a higher lying, short lived state from a long-lived triplet. The thermally assisted emission process dramatically outcompetes emission (phosphorescence) from the lower triplet sublevels. Thus, equations 1-3 used to describe TADF emission are S1-S3 for a heavy metal based phosphor (assuming that the  $k_{ISC} \gg k_{T_{III}}$ ).



$$\frac{d(h\nu)}{dt} = \frac{k_1 k_{T_{III}}}{k_{-1} + k_{T_{III}}} [T_1] \quad (S2)$$

$$\frac{d(h\nu)}{dt} = \frac{k_1 k_{T_{III}}}{k_{-1}} [T_{I,II}] = K_{eq} k_{T_{III}} [T_1] \Rightarrow \tau_{ph} = \tau_{T_{III}} / K_{eq} \quad (S3)$$

The energy spacing between the upper  $T_{III}$  and lower  $T_I, T_{II}$  levels is the zero field splitting (ZFS) energy, which is analogous to  $\Delta E_{ST}$  for TADF emitters. Thus, the same sort of thermal activation described for TADF based emission is seen for molecular heavy metal phosphors. This energy difference sets up the same sort of equilibrium between the lower (long-lived) and upper (emissive) states as seen in TADF. An analogous expression to equation 4 for TADF is given in equation S4, which relates the ZFS energy to the equilibrium constant between the triplet sublevels ( $T_{I,II} \rightleftharpoons T_{III}$ ). Here the factor of 2 account for the doubly degenerate lower triplet sublevels.

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{1}{2} \exp\left(-\frac{\Delta E_{ST}}{k_B T}\right) \Rightarrow \Delta E_{ST} = -k_B T \cdot \ln(2K_{eq}) \quad (S4)$$

## 2. Derivation of Equation 11 in the text

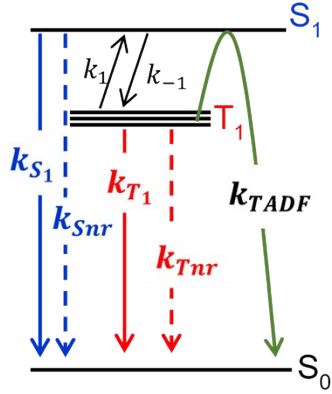


Figure S2: Full kinetic scheme for TADF emitters.

For the kinetic scheme shown in Figure S2, using only the assumption that the three triplet sublevels are degenerate, the rate expression can be written as<sup>4</sup>:

$$k_{TADF} = \frac{k_1 k_{-1} \Phi_p}{k_p \Phi_{TADF}} \quad \#(S4)$$

where,  $k_p$  and  $k_{TADF}$  are the prompt and delayed fluorescence rates while  $\Phi_p$  and  $\Phi_{TADF}$  are the quantum yields of prompt and delayed emission respectively.

$$\text{Substituting } k_1 = \frac{k_{-1}}{3} e^{-\frac{\Delta E_{S_1-T_1}}{k_B T}} \quad \text{in (S4)}$$

$$\frac{k_{-1}}{3} e^{-\frac{\Delta E_{S_1-T_1}}{k_B T}} = \frac{k_p k_{TADF} \Phi_{TADF}}{k_{-1} \Phi_p} \quad \#(S5)$$

Replacing  $\Phi_{TADF}$  in terms of the total quantum yield ( $\Phi_{total} = \Phi_{TADF} + \Phi_p$ ) gives (S6)

$$\frac{k_{-1}}{3} e^{-\frac{\Delta E_{S_1-T_1}}{k_B T}} = \frac{k_p k_{TADF} (\Phi_{total} - \Phi_p)}{k_{-1} \Phi_p} \quad \#(S6)$$

Substituting  $\Phi_p = k_{S1} \tau_p$  in (S6)

$$\frac{(k_{-1})^2}{3} e^{-\frac{\Delta E_{S_1-T_1}}{k_B T}} = k_{TADF} \frac{(\Phi_{total} - k_{S1} \tau_p)}{k_{S1} (\tau_p)^2} \quad \#(S7)$$

$$k_{TADF} = \frac{k_{S1} (\tau_p)^2}{(\Phi_{total} - k_{S1} \tau_p)} \frac{(k_{-1})^2}{3} e^{-\frac{\Delta E_{S1-T1}}{k_B T}} \quad \# \text{ (S8)}$$

## References

1. H. Yersin, A. F. Rausch, R. Czerwieniec, T. Hofbeck and T. Fischer, *Coord. Chem. Rev.*, 2011, **255**, 2622-2652.
2. A. F. Rausch, H. H. H. Homeier and H. Yersin, *Organometallic Pt(II) and Ir(III) Triplet Emitters for OLED Applications and the Role of Spin–Orbit Coupling: A Study Based on High-Resolution Optical Spectroscopy*, Springer Berlin Heidelberg, 2010.
3. W. J. Finkenzeller and H. Yersin, *Chem. Phys. Lett.*, 2004, **377**, 299-305.
4. K. Goushi, K. Yoshida, K. Sato and C. Adachi, *Nature Photonics*, 2012, **6**, 253-258.