

Electronic supporting information

NIR Phosphorescence from decatungstate anions allows the conclusive characterization of its elusive excited triplet behaviour and kinetics

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Synthesis of $\text{Na}_4[\text{W}_{10}\text{O}_{32}]$, NaDT

Sodium tungstate dihydrate (15 g, 45.5 mmol) was dissolved in deionised water (85 ml) and heated to 95 °C while stirring. Then hot (95 °C) 1M HCl was poured into sodium tungstate dihydrate solution, and the reaction mixture was stirred at 95 °C for 1 min. The yellowish solution was poured into a pre-cooled 1 L Erlenmeyer flask and left in an ice bath for cooling for 10 min under stirring. After the mixture cooled to 10 °C, sodium chloride (60 g) was added. The mixture was stirred in an ice bath for 1 h and the white suspension was formed. The suspension was filtered under vacuum using a coarse-pore glass frit, the solid was washed with cold deionized water (20 mL), ethanol (20 mL), and diethyl ether (20 mL) and dried for 30 min under air. Sodium decatungstate was obtained (7.512 g).¹

Reversal of triethyl amine quenching

Triethyl amine is an excellent quencher of ${}^3\text{DT}^*$ (Figure 3 and Table 2), but the process is readily reversed by addition of a strong acid, capable of protonating the amine.

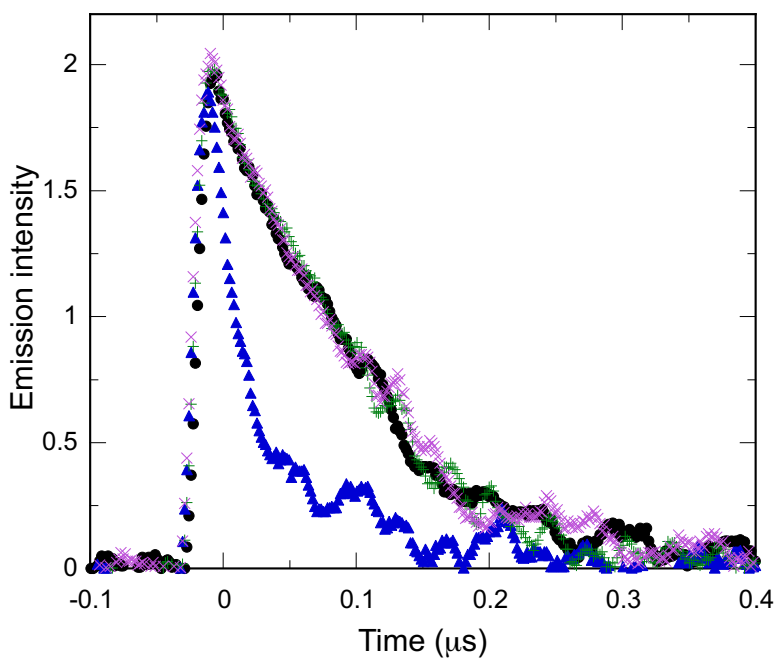


Figure S1: Quenching of ${}^3\text{DT}^*$ from TBADT by 33 mM triethylamine (TEA) followed by two additions of trifluoroacetic acid (TFA) reaching a final concentration of 100 mM. The sample was 33 mM TBADT in acetonitrile excited at 355 nm with the phosphorescence monitored at 1330 nm. The original decay is shown in black, the decay after TEA addition on blue, addition of 50 mM TFA in green and addition of 100 mM TFA in purple.

DT emission following sensitization by Rose Bengal

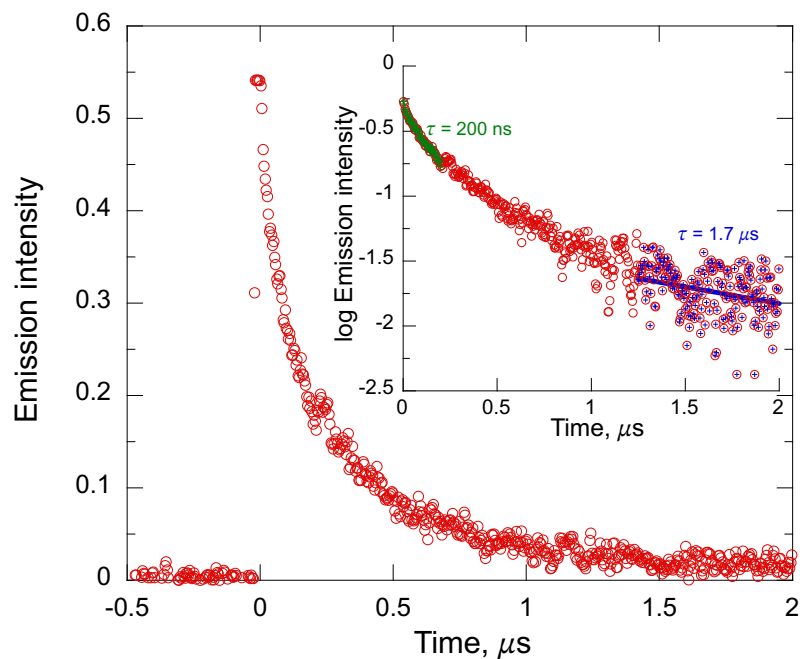


Figure S2: Quenching of the RB triplet state in acetonitrile under argon by TBADT, irradiated at 532 nm and monitored at 610 nm. Note that the decay is much longer than the lifetime of $^3\text{DT}^*$ in acetonitrile; this is due to sensitization that is prolonged as long as the RB triplet (the lives microseconds) is available. The inset shows a semilog plot of the NIR emission showing an early lifetime of around 200 ns and a tail lifetime of ~ 1.7 μs. The decay is not monoexponential.

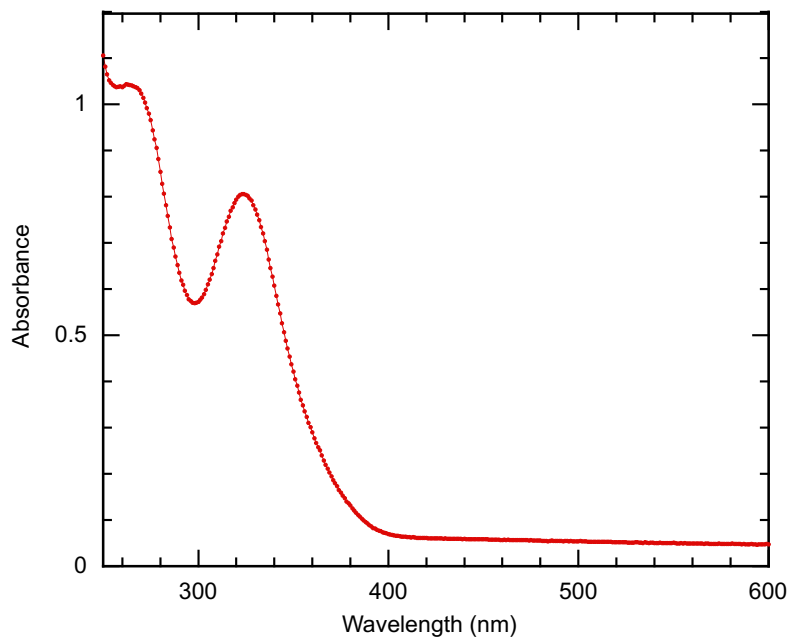


Figure S3: Spectrum for TBADT 0.05 mM in acetonitrile

DT emission at 77K

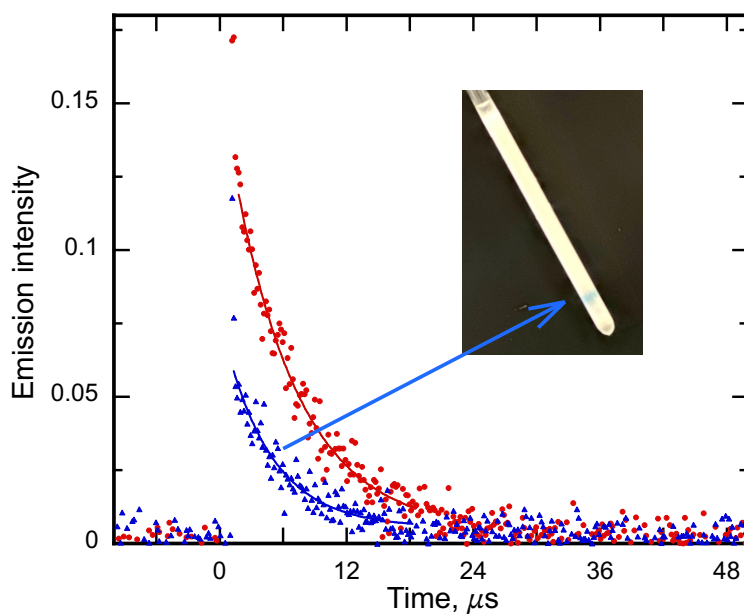
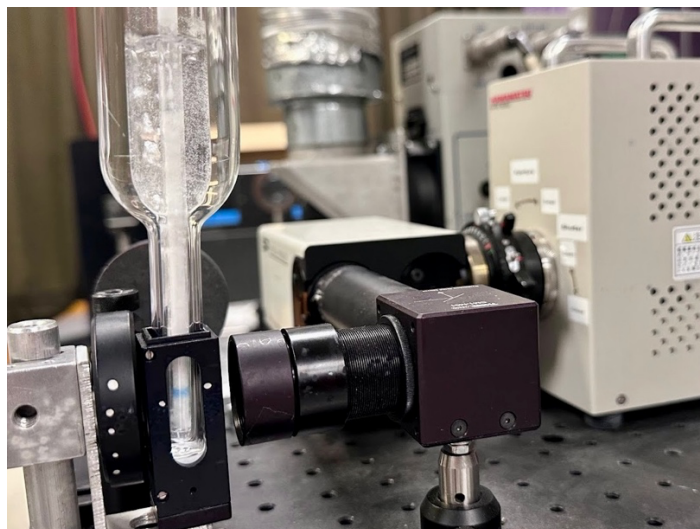


Figure S4: *Top*: Experimental low temperature set up for NIR kinetics. *Below*: Decay kinetics at 77K monitored at 1330 nm for a fresh sample (red) and for a sample exposed to ~200 laser pulses at 355 nm. Note that the signal is reduced by more than 50% and that some blue (due to DTH•) is formed. It appears that even at 77K $^3\text{DT}^*$ has some reactivity. The lifetime is 6.8 μs .

References

1. P. J. Sarver, V. Bacauanu, D. M. Schultz, D. A. DiRocco, Y.-h. Lam, E. C. Sherer and D. W. C. MacMillan, The merger of decatungstate and copper catalysis to enable aliphatic C(sp³)–H trifluoromethylation, *Nature Chem.*, 2020, 12, 459-467.