Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supporting Information

Origin of Dual Emission in σ Bridged Donor-Acceptor TADF Compounds

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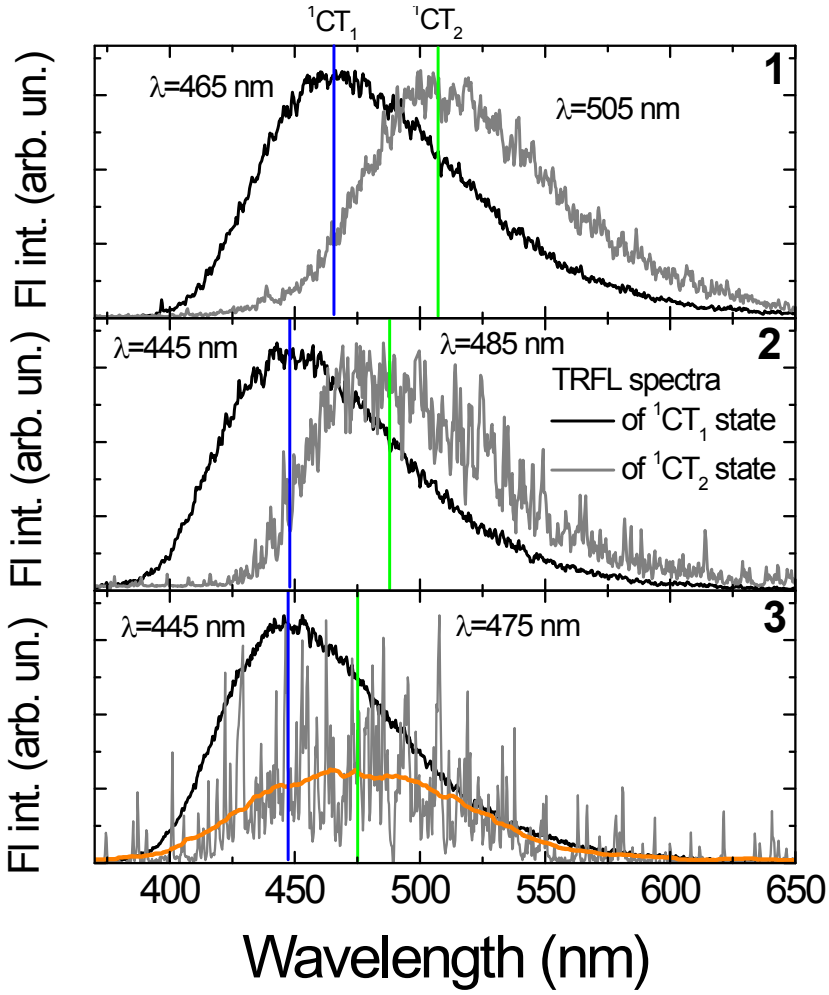

Fig. S1 Normalized time-resolved fluorescence spectra of donor-σ-acceptor compounds **1**-**3** in oxygen-free toluene. TRFL spectrum of $^1CT_1$ state was obtained after about 30 ns delay and for $^1CT_2$ state – 6 μs (for compounds **1** and **2**) and 800 ns (compound **3**). The averaged TRFL spectrum of $^1CT_2$ state of compound **3** is also shown (orange line).

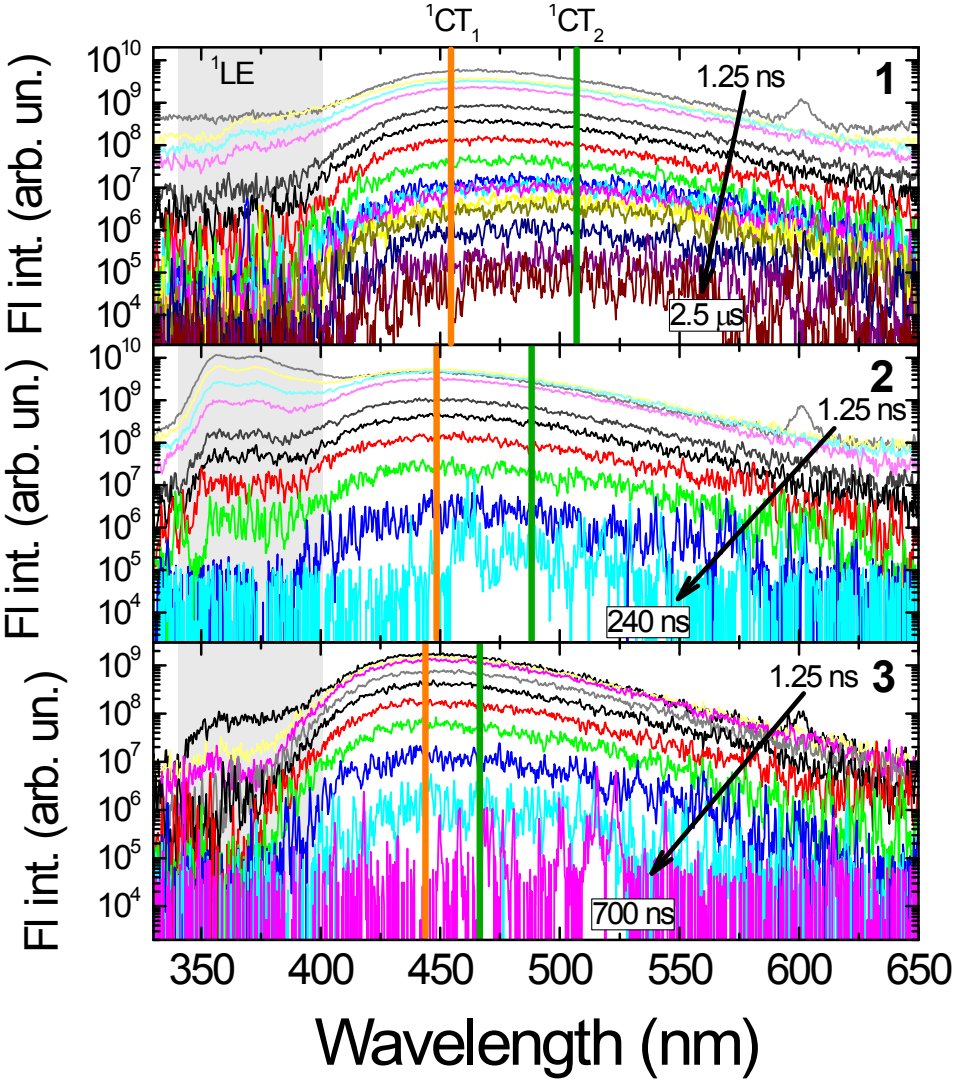

Fig. S2 Time-resolved fluorescence spectra of donor-σ-acceptor compounds **1**-**3** in oxygen-saturated toluene. Numbers in picture denotes initial and final delay times.

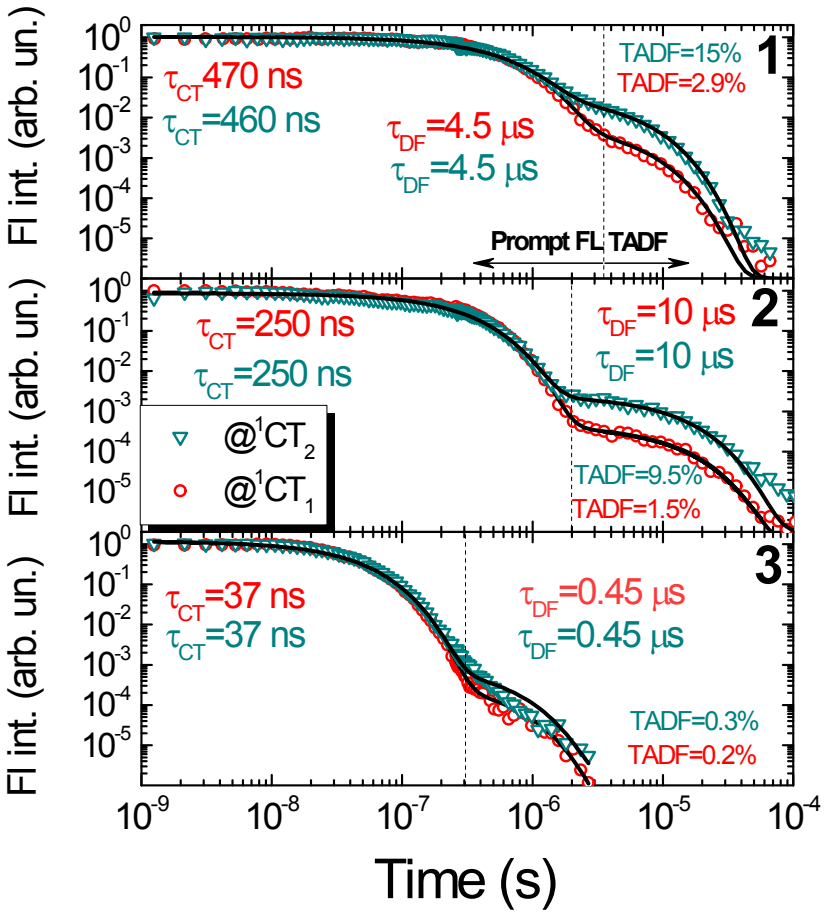

Fig. S3 Normalized fluorescence decay transients of donor-σ-acceptor compounds **1**-**3** in oxygen-deficient toluene at ^{1}CT1 (red figures) and ^{1}CT2 (dark green figures) peak positions. Black curves are bi-exponential fits.

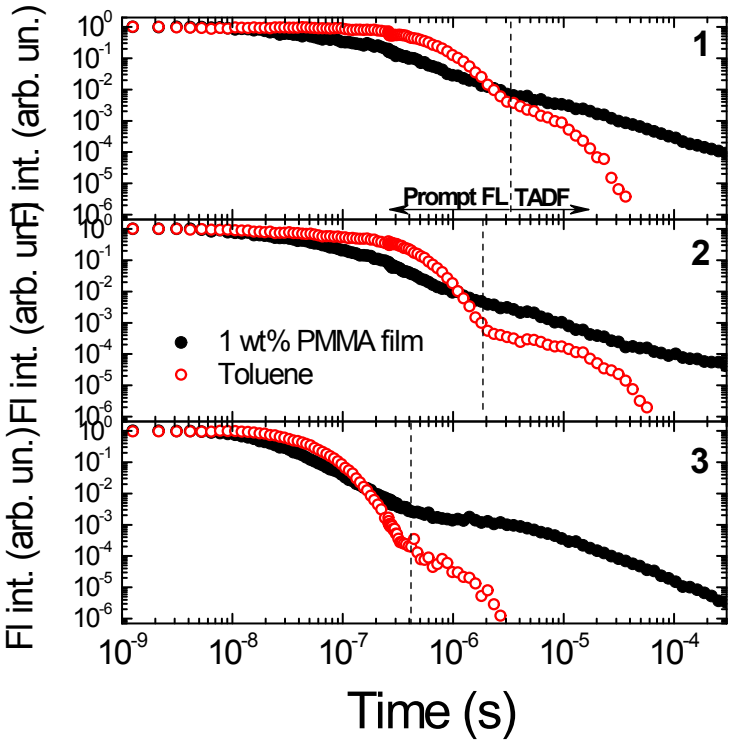

Fig. S4 Normalized fluorescence decay transients of donor-σ-acceptor compounds **1**-**3** in dilute toluene (red figures) and 1 wt% PMMA films (black figures), estimated at emission peak.

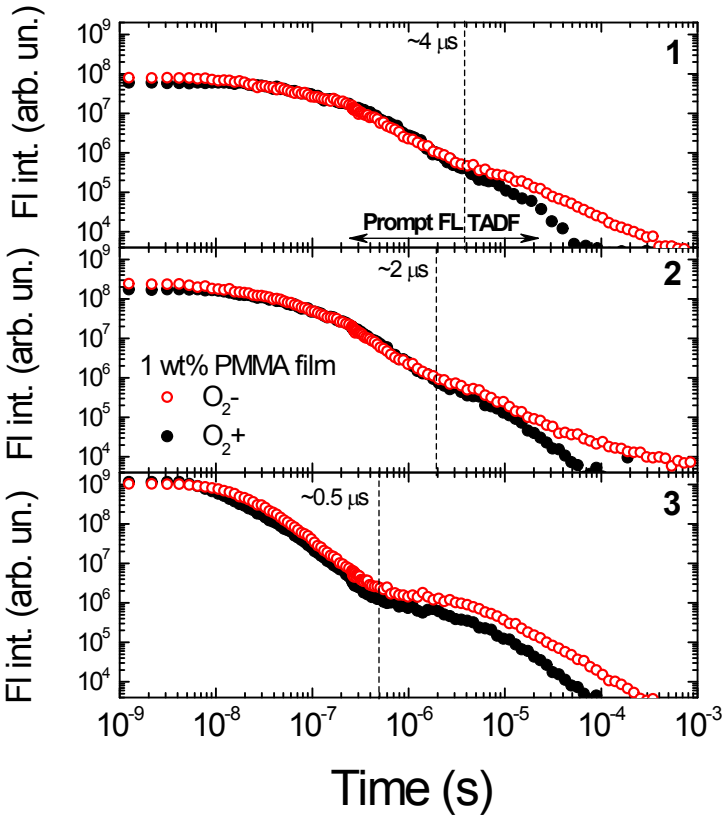

Fig. S5 Fluorescence decay transients of donor-σ-acceptor compounds **1**-**3** in oxygen-deficient toluene solutions (red figures) and 1 wt% PMMA films (black figures), estimated at emission peak.

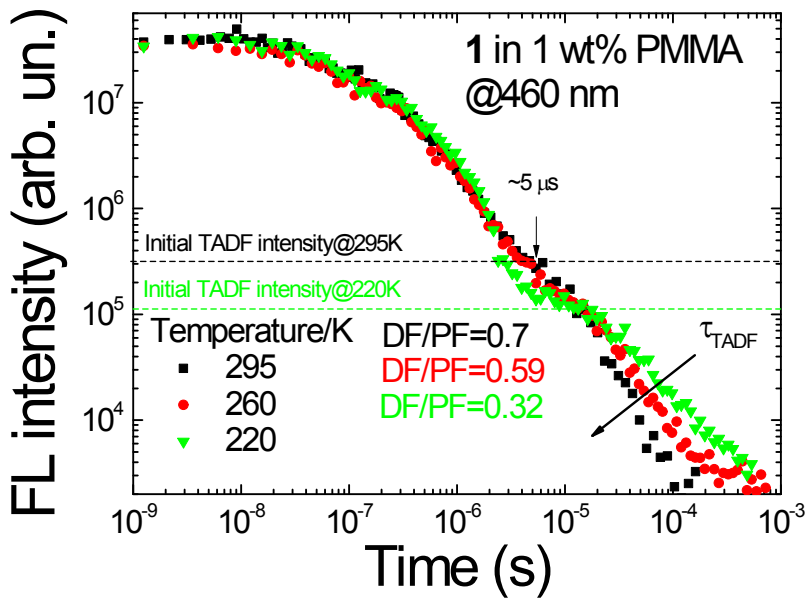

Fig. S6 Fluorescence decay transients of 1 wt% PMMA film of donor-σ-acceptor compound **1** in oxygen-deficient conditions at 295K (black figures) 260K (red figures) and 220 K (green figures) temperatures, estimated at emission peak.

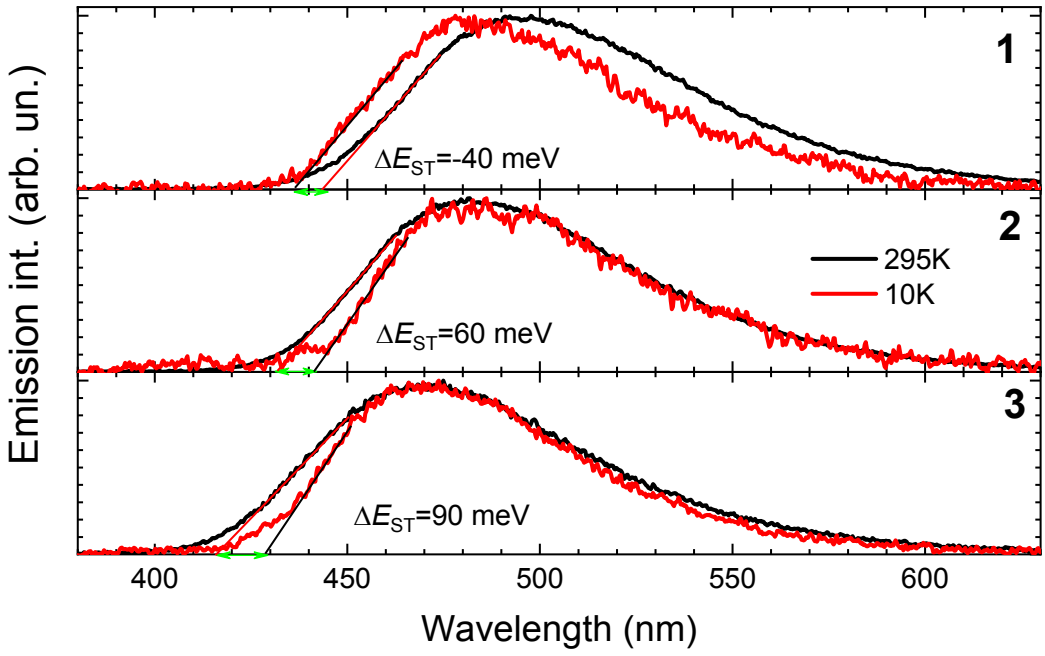

Fig. S7 Normalized fluorescence and phosphorescence spectra of neat films of compounds **1**-**3** at room temperature (black lines) and 10K (red lines). ΔE_{ST} gaps are shown for every compound.

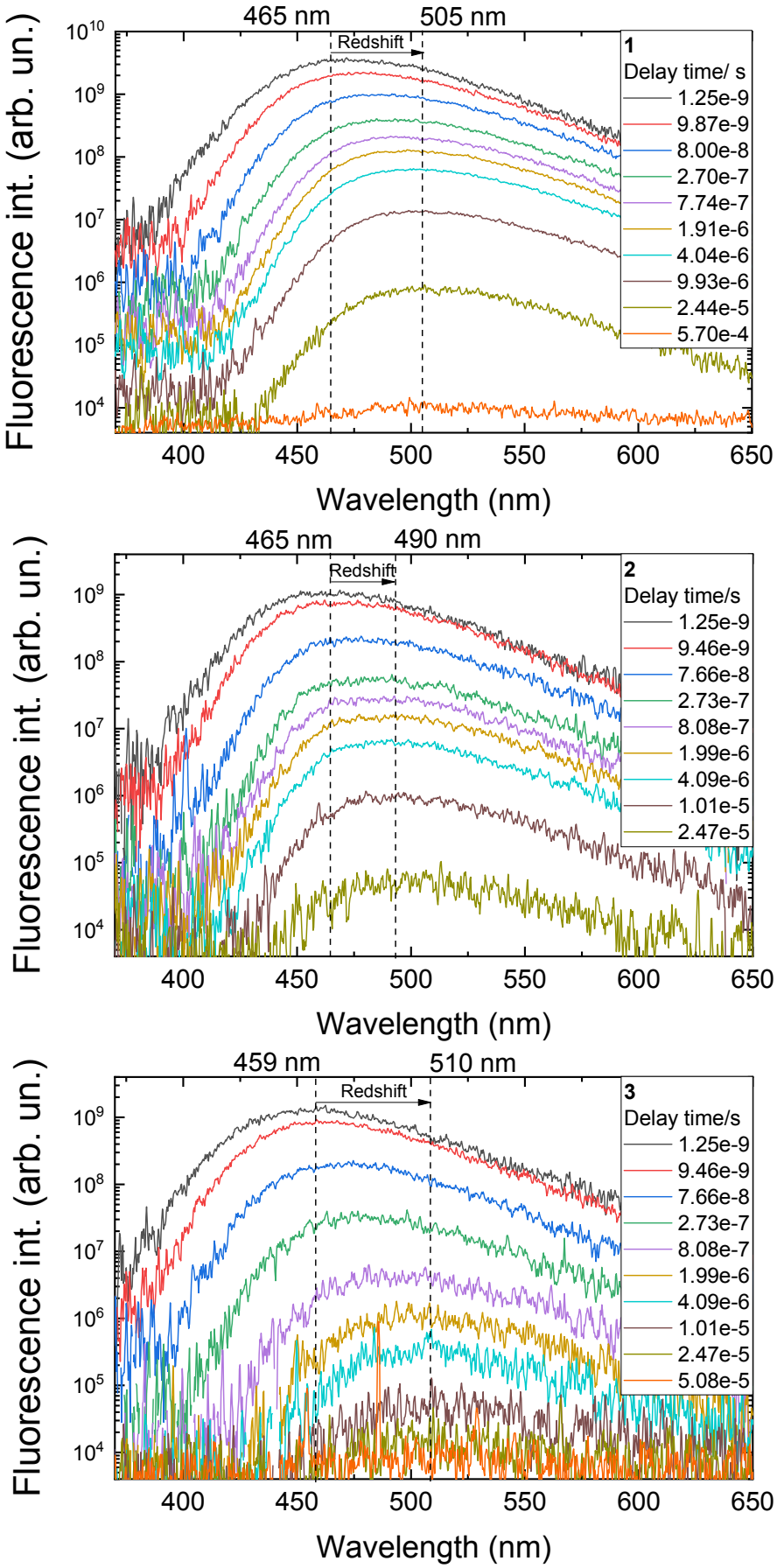

Fig. S8 Time resolved fluorescence spectra of neat films of compounds **1**-**3**.

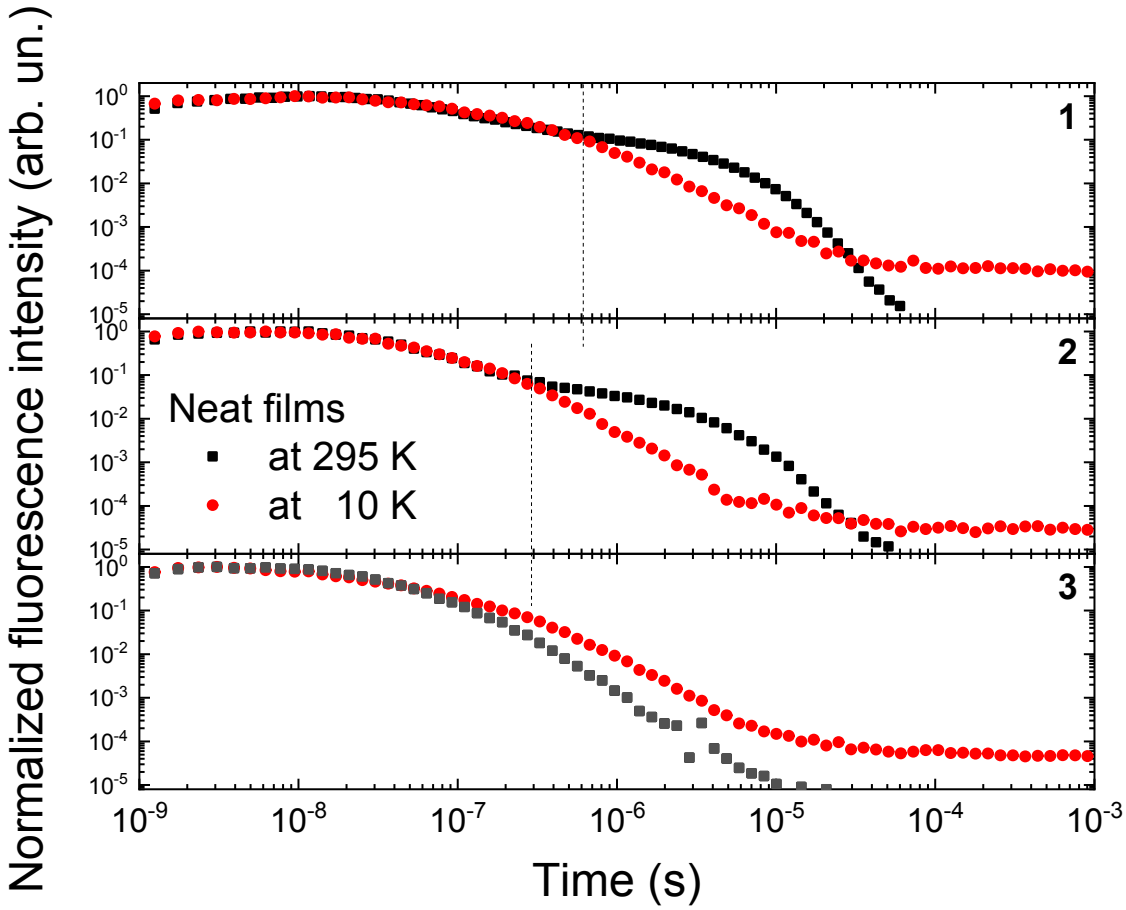

Fig. S9 Normalized fluorescence decay transients of neat films of compounds **1**-**3** at room temperature (black squares) and 10K (red dots) in oxygen-free environment at emission peak.

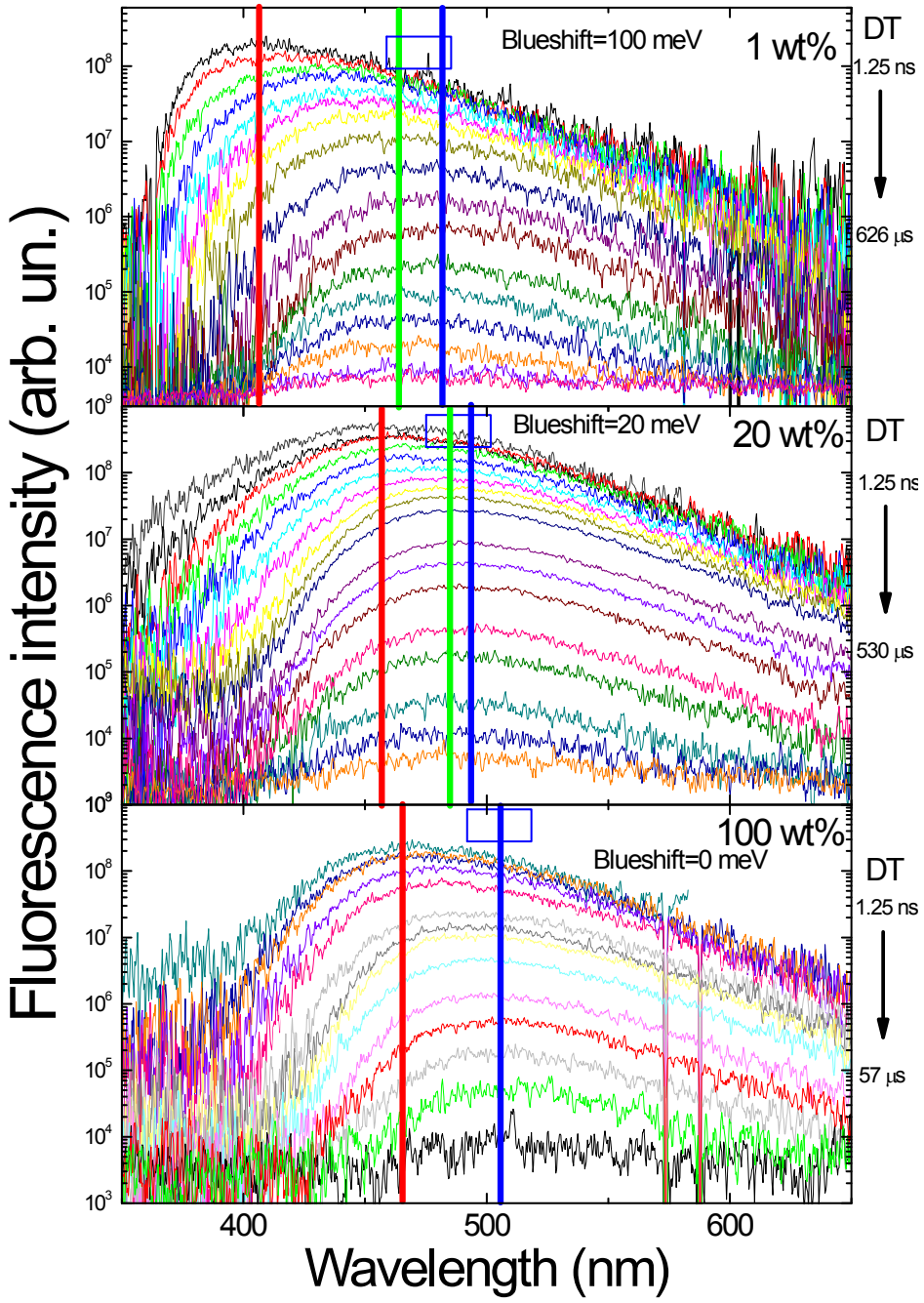

Fig. S10 Fluorescence decay transients of compound **1** embed in PMMA matrix at 1 wt% concentration (upper picture), 20 wt% concentration (middle picture) and at 100 wt% concentration (lower picture). Delay time (DT) intervals are denoted for every film. Red line represent the peak wavelength of the initial conformers, blue line represent the peak wavelength of the conformers with the lowest energy while the green line represent the peaks of the latest conformers. Lower blueshift of delayed emission is observed at the larger doping concentration due to the stronger quenching.