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# Supplementary Information

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## Unusually Slow Intramolecular Proton Transfer Dynamics of 4′-N,N-Dimethylamino-3-Hydroxyflavone in High n-Alcohols : Involvement of Solvent Relaxation

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**Table ST1:** Fitting parameters for fluorescence time-profiles of DMA3HF at different emission wavelengths in the three n-alcohols ($\lambda_{ex}$ = 375 nm)

| solvent | $\lambda_{em}$ (nm) | $\tau_1$ (ns) | $a_1$ (%) | $\tau_2$ (ns) | $a_2$ (%) | $\tau_3$ (ns) | $a_3$ (%) | $\tau_4$ (ns) | $a_4$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1-Butanol | 400 | 0.07 | 99 | 0.44 | 1 | - | - | - | - |
| | 420 | 0.08 | 95 | 0.30 | 4 | 1.92 | 1 | - | - |
| | 440 | 0.08 | 91 | 0.24 | 6 | 1.89 | 3 | - | - |
| | 450 | 0.09 | 90 | 0.28 | 4 | 1.89 | 6 | - | - |
| | 460 | 0.11 | 89 | 1.89 | 11 | - | - | - | - |
| | 470 | 0.12 | 82 | 1.93 | 18 | - | - | - | - |
| | 480 | 0.13 | 71 | 1.96 | 29 | - | - | - | - |
| | 490 | 0.07 | -19 | 0.13 | 51 | 1.97 | 30 | - | - |
| | 500 | 0.06 | -21 | 0.14 | 36 | 1.99 | 43 | - | - |
| | 515 | 0.06 | -36 | 0.15 | 13 | 1.99 | 51 | - | - |
| | 525 | 0.06 | -41 | 0.15 | 7 | 1.99 | 52 | - | - |
| | 535 | 0.07 | -42 | 0.17 | 6 | 1.99 | 52 | - | - |
| | 545 | 0.08 | -43 | 0.45 | 7 | 1.99 | 50 | - | - |
| | 552 | 0.08 | -42 | 0.45 | 12 | 2.00 | 46 | - | - |
| | 570 | 0.09 | -41 | 0.45 | 20 | 2.00 | 39 | - | - |
| | 590 | 0.09 | -38 | 0.45 | 23 | 1.99 | 39 | - | - |
| | 620 | 0.09 | -39 | 0.45 | 24 | 1.99 | 37 | - | - |
| | 650 | 0.10 | -36 | 0.45 | 24 | 1.99 | 40 | - | - |
| 1-Hexanol | 450 | 0.11 | 91 | 0.68 | 5 | 2.48 | 4 | - | - |
| | 460 | 0.13 | 85 | 0.57 | 6 | 2.19 | 9 | - | - |
| | 470 | 0.15 | 80 | 0.72 | 5 | 2.10 | 15 | - | - |
| | 480 | 0.06 | -19 | 0.18 | 60 | 1.98 | 21 | - | - |
| | 490 | 0.06 | -31 | 0.21 | 42 | 2.00 | 27 | - | - |
| | 500 | 0.06 | -31 | 0.25 | 33 | 2.03 | 36 | - | - |
| | 511 | 0.08 | -33 | 0.24 | 22 | 2.03 | 45 | - | - |

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| solvent | $\lambda_{em}$ (nm) | $\tau_1$ (ns) | $a_1$ (%) | $\tau_2$ (ns) | $a_2$ (%) | $\tau_3$ (ns) | $a_3$ (%) | $\tau_4$ (ns) | $a_4$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1-Hexanol | 520 | 0.08 | -37 | 0.23 | 13 | 2.03 | 50 | - | - |
| | 530 | 0.08 | -41 | 0.79 | 6 | 2.06 | 53 | - | - |
| | 540 | 0.10 | -41 | 0.80 | 7 | 2.05 | 52 | - | - |
| | 552 | 0.10 | -42 | 0.80 | 13 | 2.06 | 45 | - | - |
| | 570 | 0.10 | -41 | 0.80 | 18 | 2.05 | 41 | - | - |
| | 590 | 0.10 | -40 | 0.80 | 21 | 2.05 | 39 | - | - |
| | 620 | 0.09 | -39 | 0.79 | 21 | 2.05 | 40 | - | - |
| | 650 | 0.10 | -34 | 0.79 | 22 | 2.05 | 44 | - | - |
| 1-Decanol | 400 | 0.08 | 92 | 0.27 | 8 | - | - | - | - |
| | 420 | 0.11 | 93 | 0.53 | 7 | - | - | - | - |
| | 440 | 0.14 | 89 | 0.57 | 9 | 2.23 | 2 | - | - |
| | 450 | 0.16 | 84 | 0.61 | 12 | 2.06 | 4 | - | - |
| | 460 | 0.20 | 77 | 0.68 | 15 | 2.08 | 8 | - | - |
| | 470 | 0.07 | -18 | 0.18 | 53 | 0.56 | 18 | 1.99 | 11 |
| | 480 | 0.07 | -29 | 0.20 | 39 | 0.63 | 18 | 2.06 | 14 |
| | 490 | 0.06 | -31 | 0.39 | 42 | 1.99 | 27 | - | - |
| | 498 | 0.06 | -35 | 0.43 | 31 | 2.02 | 34 | - | - |
| | 510 | 0.06 | -36 | 0.51 | 16 | 2.07 | 48 | - | - |
| | 520 | 0.09 | -37 | 0.46 | 7 | 2.06 | 56 | - | - |
| | 530 | 0.11 | -39 | 0.40 | 2 | 2.02 | 59 | - | - |
| | 540 | 0.12 | -39 | 1.10 | 11 | 2.04 | 50 | - | - |
| | 552 | 0.14 | -38 | 1.11 | 23 | 2.07 | 39 | - | - |
| | 570 | 0.15 | -36 | 1.09 | 30 | 2.05 | 34 | - | - |
| | 590 | 0.13 | -36 | 1.12 | 33 | 2.05 | 31 | - | - |
| | 620 | 0.11 | -35 | 1.13 | 36 | 2.07 | 29 | - | - |
| | 650 | 0.08 | -38 | 0.98 | 30 | 2.01 | 32 | - | - |

**Table ST2:** Fitting parameters for fluorescence time-profiles of DMA3MeF at different emission wavelengths in the three n-alcohols ($\lambda_{ex}$ = 375 nm)

| solvent | $\lambda_{em}$ (nm) | $\tau_1$ (ns) | $a_1$ (%) | $\tau_2$ (ns) | $a_2$ (%) | $\tau_3$ (ns) | $a_3$ (%) | $\tau_4$ (ns) | $a_4$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1-Butanol | 400 | 0.07 | 97 | 0.36 | 2 | 2.35 | 1 | - | - |
| | 410 | 0.08 | 97 | 0.36 | 2 | 2.34 | 1 | - | - |
| | 420 | 0.08 | 97 | 0.36 | 2 | 2.45 | 1 | - | - |
| | 430 | 0.09 | 96 | 0.35 | 2 | 2.52 | 2 | - | - |
| | 450 | 0.12 | 92 | 0.92 | 1 | 2.67 | 7 | - | - |
| | 470 | <0.06 | -30 | 0.14 | 57 | 2.63 | 13 | - | - |
| | 485 | <0.06 | -45 | 0.17 | 35 | 2.66 | 20 | - | - |
| | 503 | <0.06 | -46 | 0.25 | 18 | 2.69 | 36 | - | - |
| | 515 | 0.07 | -50 | 0.45 | 8 | 2.73 | 43 | - | - |
| | 530 | 0.09 | -52 | 1.39 | 6 | 2.79 | 43 | - | - |
| | 560 | 0.14 | -50 | 2.08 | 11 | 2.79 | 39 | - | - |
| | 590 | 0.16 | -50 | 2.63 | 50 | - | - | - | - |
| | 620 | 0.18 | -50 | 2.62 | 50 | - | - | - | - |
| 1-Hexanol | 400 | 0.08 | 96 | 0.38 | 3 | 2.65 | 1 | - | - |
| | 410 | 0.09 | 95 | 0.38 | 4 | 2.68 | 1 | - | - |
| | 420 | 0.11 | 96 | 0.45 | 3 | 2.68 | 1 | - | - |
| | 430 | 0.12 | 93 | 0.45 | 5 | 2.64 | 2 | - | - |
| | 450 | <0.06 | -55 | 0.15 | 39 | 0.48 | 3 | 2.52 | 3 |
| | 465 | <0.06 | -57 | 0.19 | 35 | 0.76 | 3 | 2.65 | 5 |
| | 480 | <0.06 | -55 | 0.25 | 31 | 1.40 | 3 | 2.72 | 11 |
| | 500 | 0.07 | -47 | 0.30 | 19 | 1.70 | 11 | 2.82 | 23 |
| | 515 | 0.08 | -50 | 1.52 | 14 | 2.78 | 36 | - | - |
| | 530 | 0.14 | -45 | 1.98 | 21 | 2.83 | 34 | - | - |
| | 560 | 0.22 | -46 | 2.12 | 22 | 2.78 | 32 | - | - |
| | 590 | 0.25 | -50 | 2.53 | 50 | - | - | - | - |
| | 620 | 0.29 | -50 | 2.53 | 50 | - | - | - | - |

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| solvent | $\lambda_{em}$ (nm) | $\tau_1$ (ns) | $a_1$ (%) | $\tau_2$ (ns) | $a_2$ (%) | $\tau_3$ (ns) | $a_3$ (%) | $\tau_4$ (ns) | $a_4$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1-Decanol | 400 | 0.13 | 86 | 0.41 | 13 | 2.39 | 1 | - | - |
| | 410 | 0.17 | 85 | 0.50 | 14 | 2.54 | 1 | - | - |
| | 425 | <0.06 | -50 | 0.19 | 37 | 0.52 | 12 | 2.34 | 1 |
| | 440 | <0.06 | -50 | 0.23 | 32 | 0.60 | 16 | 2.68 | 2 |
| | 455 | <0.06 | -36 | 0.36 | 39 | 0.84 | 19 | 2.89 | 6 |
| | 470 | 0.06 | -40 | 0.58 | 37 | 1.34 | 12 | 3.13 | 11 |
| | 489 | <0.06 | -24 | 0.16 | -24 | 1.01 | 26 | 3.02 | 26 |
| | 510 | 0.07 | -26 | 0.31 | -25 | 1.94 | 20 | 3.22 | 29 |
| | 530 | 0.09 | -21 | 0.54 | -31 | 2.57 | 26 | 3.20 | 22 |
| | 560 | 0.14 | -9 | 0.72 | -38 | 2.87 | 53 | - | - |
| | 590 | 0.11 | -5 | 0.80 | -43 | 2.85 | 52 | - | - |
| | 620 | 0.06 | -5 | 0.86 | -44 | 2.85 | 51 | - | - |

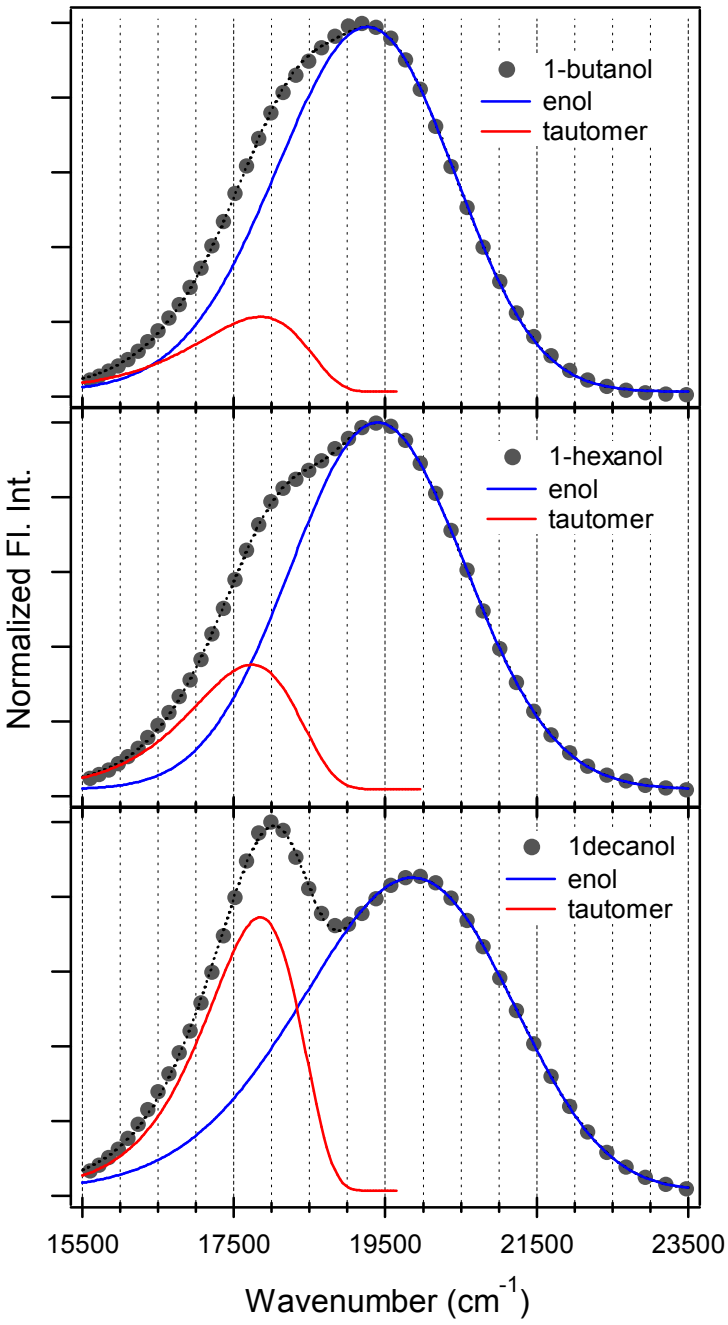


**Fig. SF1:**Normalized fluorescence emission spectra of DMA3HF in different n-alcohols ($\lambda_{ex}$ = 375 nm), plotted as a function of emission energy. The component E* (enol) and T* (tautomer) peaks resolved by lognormal deconvolution are also shown.

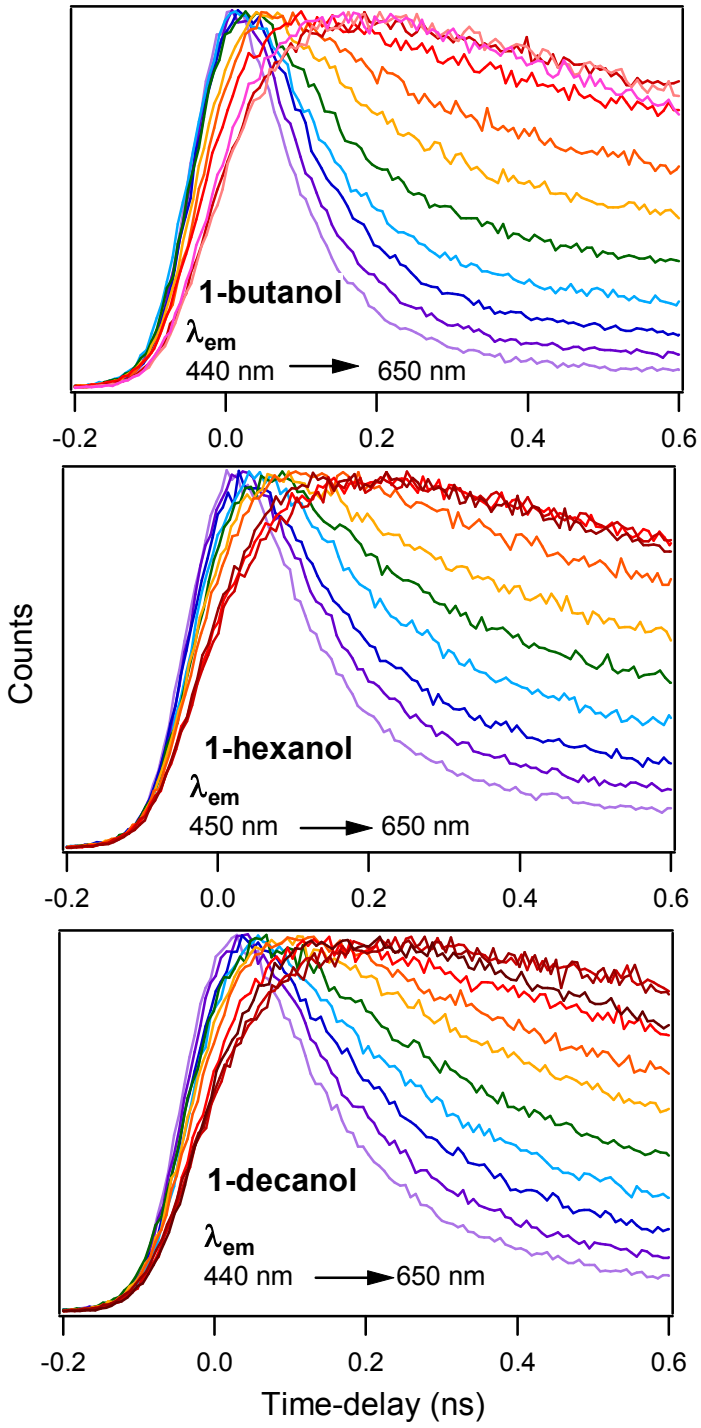


**Fig. SF2:**Fluorescence time-profiles of DMA3HF in 1-butanol, 1-hexanol & 1-decanol at short time-delays with $\lambda_{ex}$ = 375 nm.

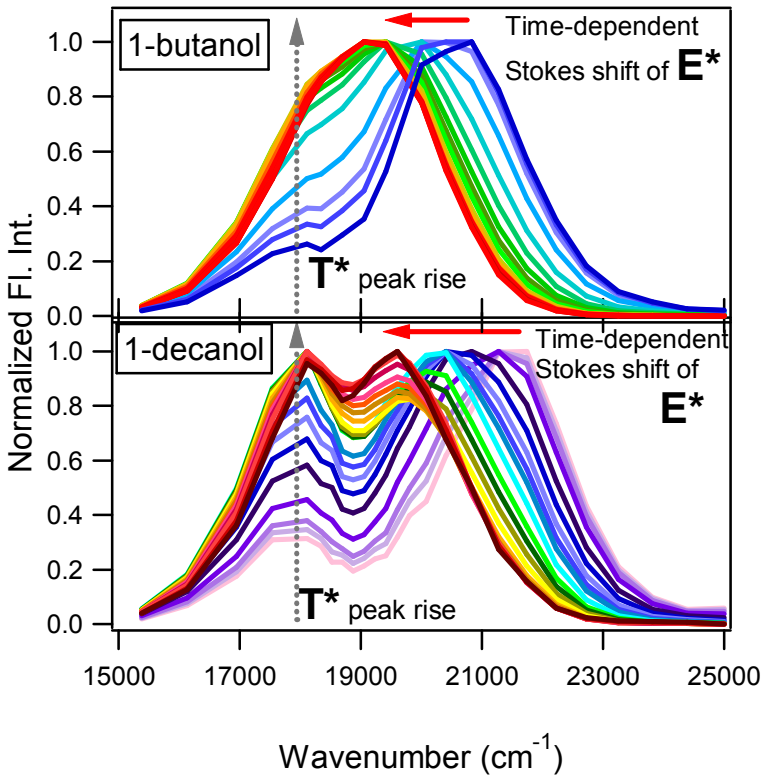


**Fig.SF3:**Normalized TRES of DMA3HF in 1-butanol and 1-decanol at various time-delays.E* emission peak undergoes time-dependent Stokes shift as indicated, while the T* peak remains static at ~18000 $cm^{-1}$, but gains in intensity with passage of time (blue curves to red curves).

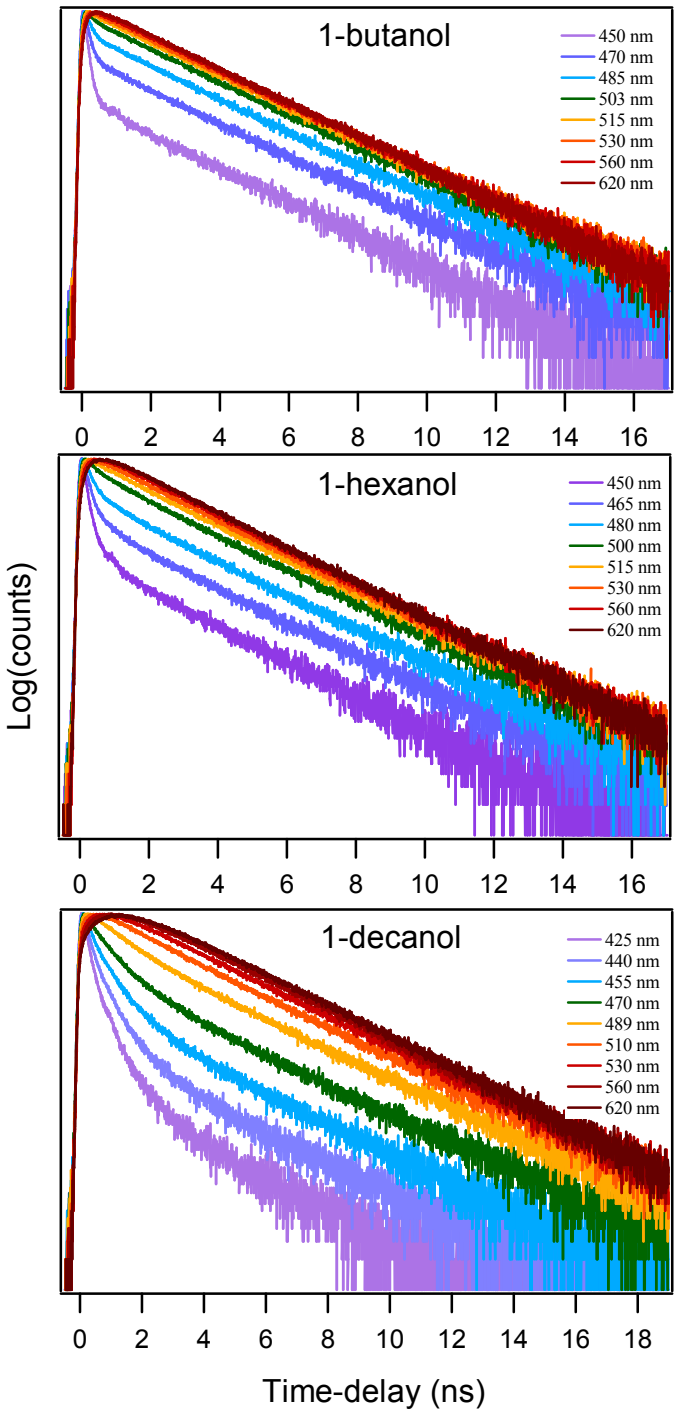


**Fig. SF4:**Fluorescence time-profiles of DMA3MeF in 1-butanol, 1-hexanol & 1-decanol at various emission wavelengths (as indicated) when excited at $\lambda_{ex}$ = 375 nm.

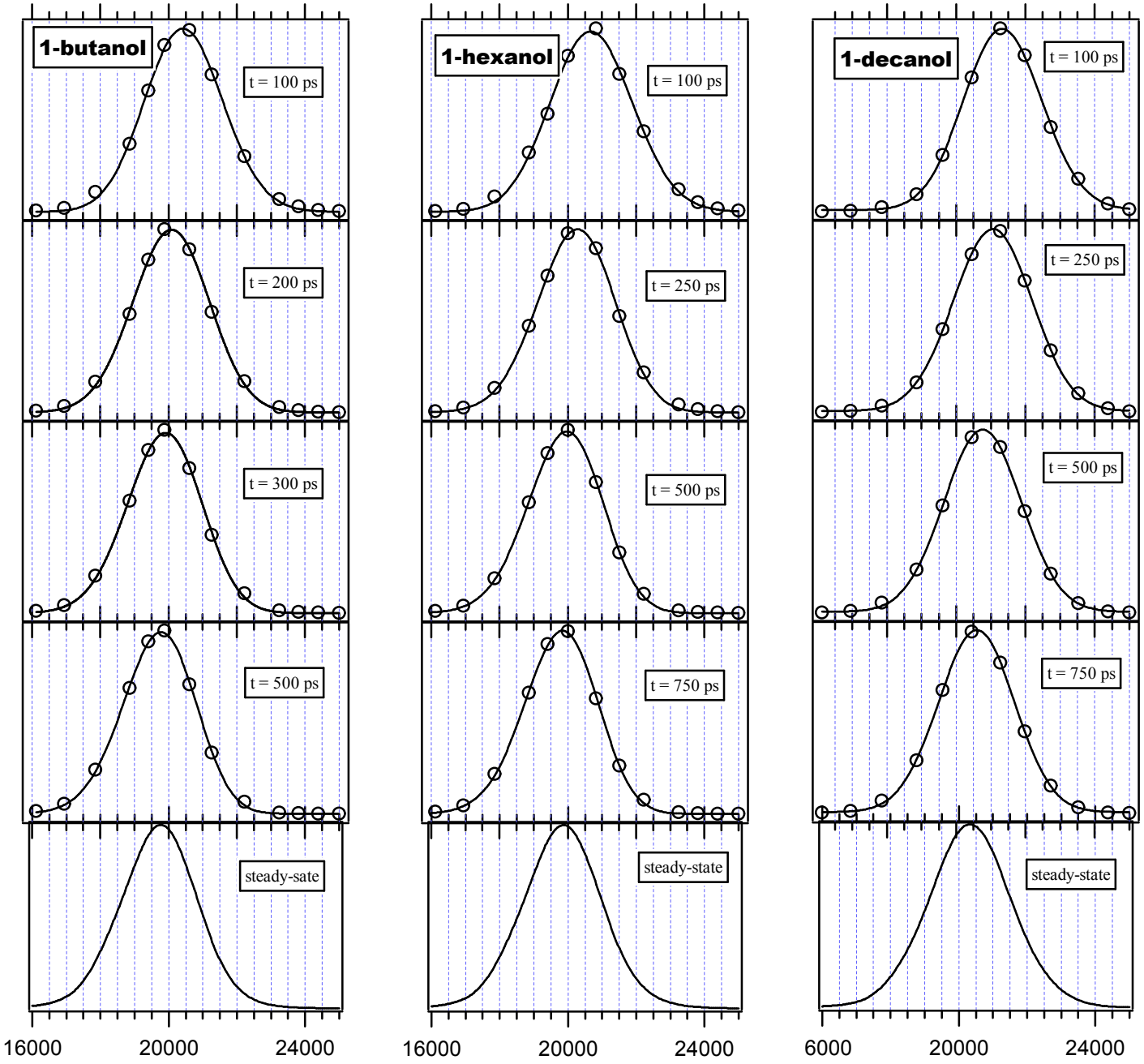


**Fig. SF5:** TRES of DMA3MeF in high n-alcohols at various time-delays as indicated. Circles represent the calculated intensities $I(\nu_{em}=\nu',t=t')$ at a given emission wavenumber $\nu_{em}$ and given time-delay t=t', while solid curves represent the double lognormal fit to these intensities.