

## Supporting Information

# Oligothiophene Dendrimers as New Building Blocks for Optical Applications

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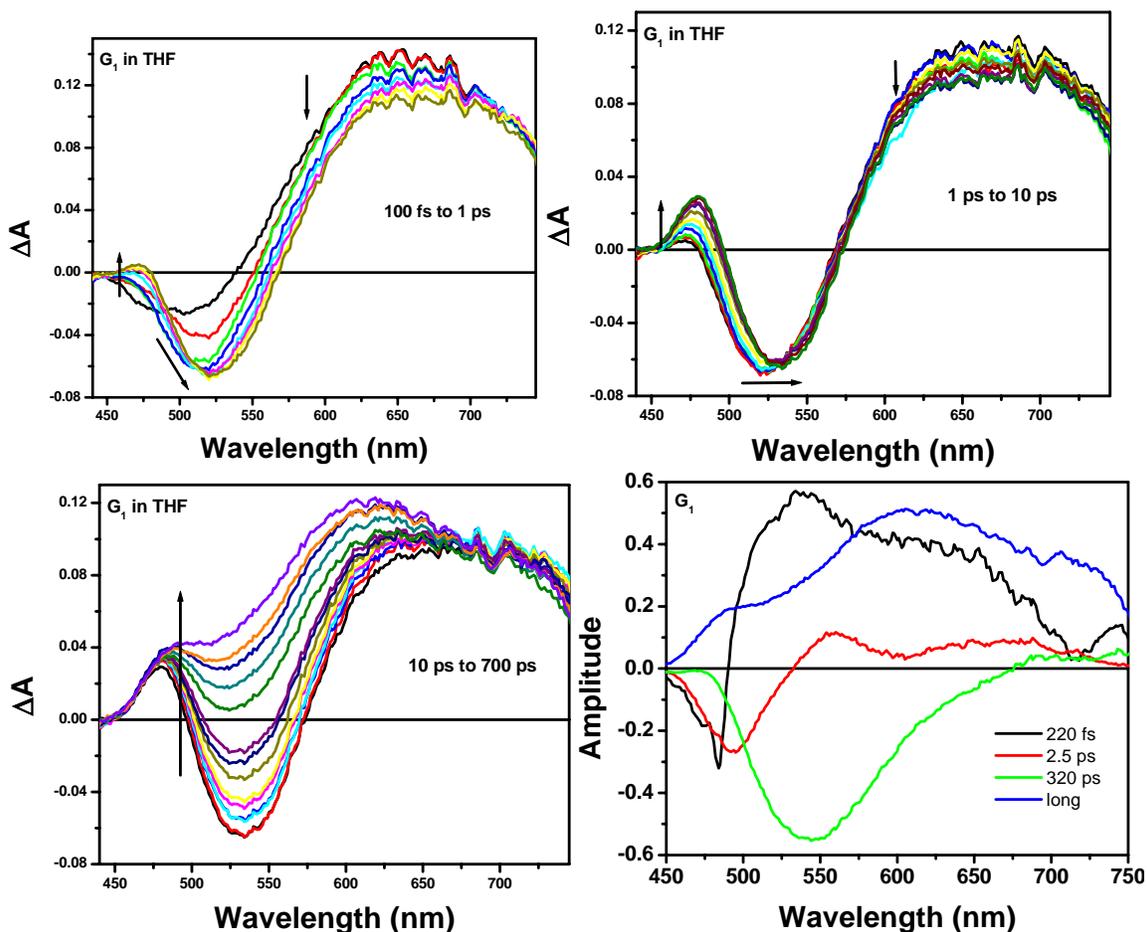
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### *Transient absorption measurements of G<sub>1</sub> and G<sub>3</sub>*

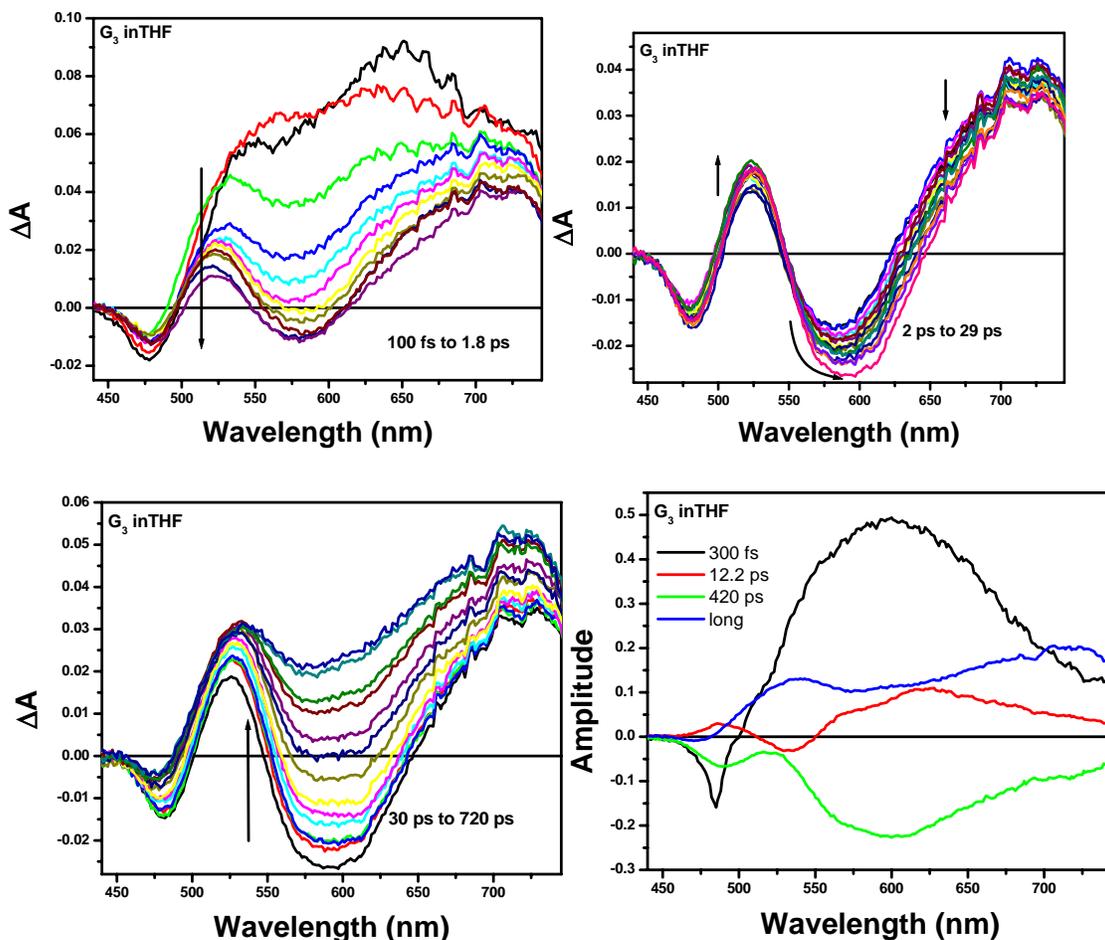
Parts A to C of Figure S1 shows the transient absorption spectra of G<sub>1</sub> in THF at various time delay ranges from 150 fs to 1 ps, 1 to 10 ps and 10 to 700 ps respectively after excitation at 425 nm from the fourth harmonic of idler beam of optical parametric amplifier. The pump photon energy is around 2.9 eV and the pump power is 250 nJ per pulse. The Initially after photo-excitation, ESA corresponding to the Franck-condon state of G<sub>1</sub> is observed which proceeded to decay to give rise to the growth of stimulated emission with a maximum at 535 nm which is ascribed to the ultrafast excitation energy transfer from the delocalized excited state to longest oligothiophene in the dendrimer. Dynamic Stoke's shift (Figure S1B) is observed from 1 ps to 10 ps which is ascribed to

the torsional energy redistribution. Stimulated emission recovery to give rise to triplet-triplet absorption is depicted in Figure S1C. Global fit analysis (Figure S1D) has yielded three main components of excited state deactivation; first one of 230 fs is ascribed to ultrafast energy transfer to longest oligothiophene present in  $G_1$  i.e  $\alpha$ -4T. Second component of 2.5 ps is attributed to the torsional energy redistribution and the final decay is the excited state recovery giving rise to triplet state with a time constant of 320 ps.



**Figure S1:** (A) Transient absorption spectra of  $G_1$  in THF at different time delays from 150 fs to 1 ps depicting the intramolecular excitation energy transfer. (B) Transient absorption spectra of  $G_1$  in THF at time delays from 1 ps to 10 ps showing the dynamic Stoke's shift in stimulated emission. (C) Transient absorption spectra of  $G_1$  in THF from 10 ps to 700 ps showing the recovery of stimulated emission to give rise to triplet-triplet absorption. (D) Species associated spectra of  $G_1$  in THF after single value decomposition and global fit analysis.

Transient absorption spectra at different time delays for G3 in THF are shown in Figure S2A-C and the global fit analysis in Figure S2D. Observed excited state absorption features are explained by similar arguments presented above. All the observed features here for G<sub>1</sub> and G<sub>3</sub> are quite similar to what has been observed for G<sub>2</sub> which has been described in the main manuscript though with different ESA and stimulated emission maxima. It can also be observed here that the FC state's ESA is quite different for different dendrimers as they arise from the delocalized excited states of dendrimer which delocalization length increases with increase in dendrimer generation.

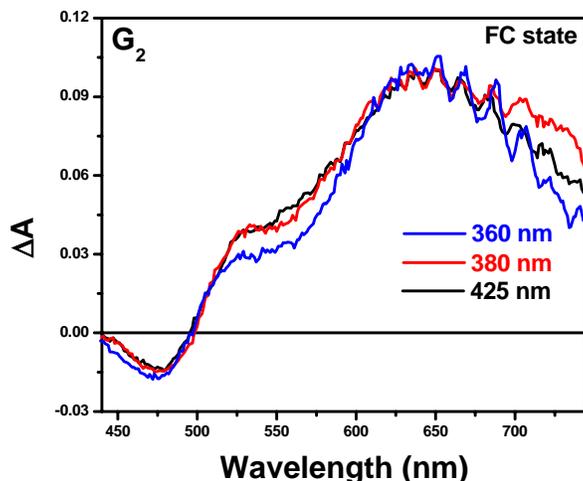


**Figure S2:** (A) Transient absorption spectra of G<sub>3</sub> in THF at different time delays from 150 fs to 1 ps depicting the intramolecular excitation energy transfer. (B) Transient absorption spectra of G<sub>3</sub> in THF at time delays from 1 ps to 10 ps showing the dynamic Stoke's shift in stimulated

emission. (C) Transient absorption spectra of  $G_3$  in THF from 10 ps to 700 ps showing the recovery of stimulated emission to give rise to triplet-triplet absorption. (D) Species associated spectra of  $G_3$  in THF after single value decomposition and global fit analysis.

### *Excitation wavelength dependence of ESA*

In an effort to understand if the absorption is delocalized or localized, measurements have been carried out after excitation at different wavelengths to the either side of the absorption spectrum so that one can monitor if there is a preferential excitation of the parts of the dendrimer. Shown in Figure S3 are the transient absorption spectra of  $G_2$  in THF immediately after photo-excitation at different wavelengths from 360 nm to all the way upto 425 nm. It can be observed from the figure that the excited state absorption spectra of FC state of the dendrimer is invariant to the excitation wavelength and arising from the delocalized excited state.



**Figure S3:** Transient absorption spectra of FC state of  $G_2$  in THF after excitation at 360 nm, 380 nm and 425 nm. Spectra are normalized to clarify the point that they do not vary with the excitation wavelength.