Supporting Information

Structural Relaxation in the Singlet Excited State of Star-Shaped Oligofluorenes having a Truxene or Isotruxene as a Core

Mamoru Fujitsuka,[†]* Dae Won Cho,[†,‡] Hsin-Hau Huang,[§] Jye-Shane Yang,[§]* and Tetsuro Majima[†]*

[†] The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan, [‡] Konkuk University-Fraunhofer ISE Next Generation Solar Cell Research Center (KFnSC), Konkuk University, Seoul, 143-701, Korea, and [§]Department of Chemistry, National Taiwan University, Taipei, Taiwan 10617

Details of the calculation of two-photon absorption cross section

Assuming a Gaussian beam profile, the nonlinear absorption coefficient β can be obtained by curve fitting to the observed open-aperture traces ($T(z)$) with the following equation:

$$T(z) = 1 - \frac{\beta I_0 (1 - e^{-\alpha_0 l})}{2\sqrt{2}\alpha_0 (1 + ((z - z_c)/z_0)^2)}$$

where α_0 is the linear absorption coefficient, l is the sample length, z_c is the position of the focal plane and z_0 is the diffraction length of the incident beam. After obtaining the nonlinear absorption coefficient

β, the two-photon absorption cross section $\sigma^{(2)}$ of one solute molecule (in units of 1 GM = 10^{-50} cm^4·s/photon·molecule) can be determined by using the following relationship:

$$\beta = \frac{\sigma^{(2)} N_A d \times 10^{-3}}{h\nu},$$

where N_A is the Avogadro constant, d is the concentration of the TPA compound in solution, h is the Planck constant, and ν is the frequency of the incident laser beam. So as to satisfy the condition of $\alpha_0 l \ll 1$, which allows the pure two-photon absorption $\sigma^{(2)}$ values to be determined using a simulation procedure, the two-photon absorption cross-section value of rhodamine 6G was measured as a reference compound; this control was found to exhibit a $\sigma^{(2)}$ value of 65 GM at 800 nm.

Ultrafast fluorescence profiles of TF3.
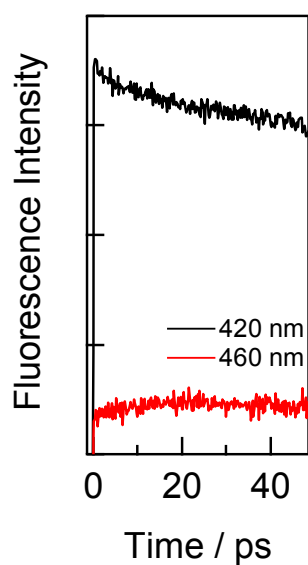

**Figure S1.** Fluorescence profiles of TF3 in toluene measured at 420 and 460 nm.

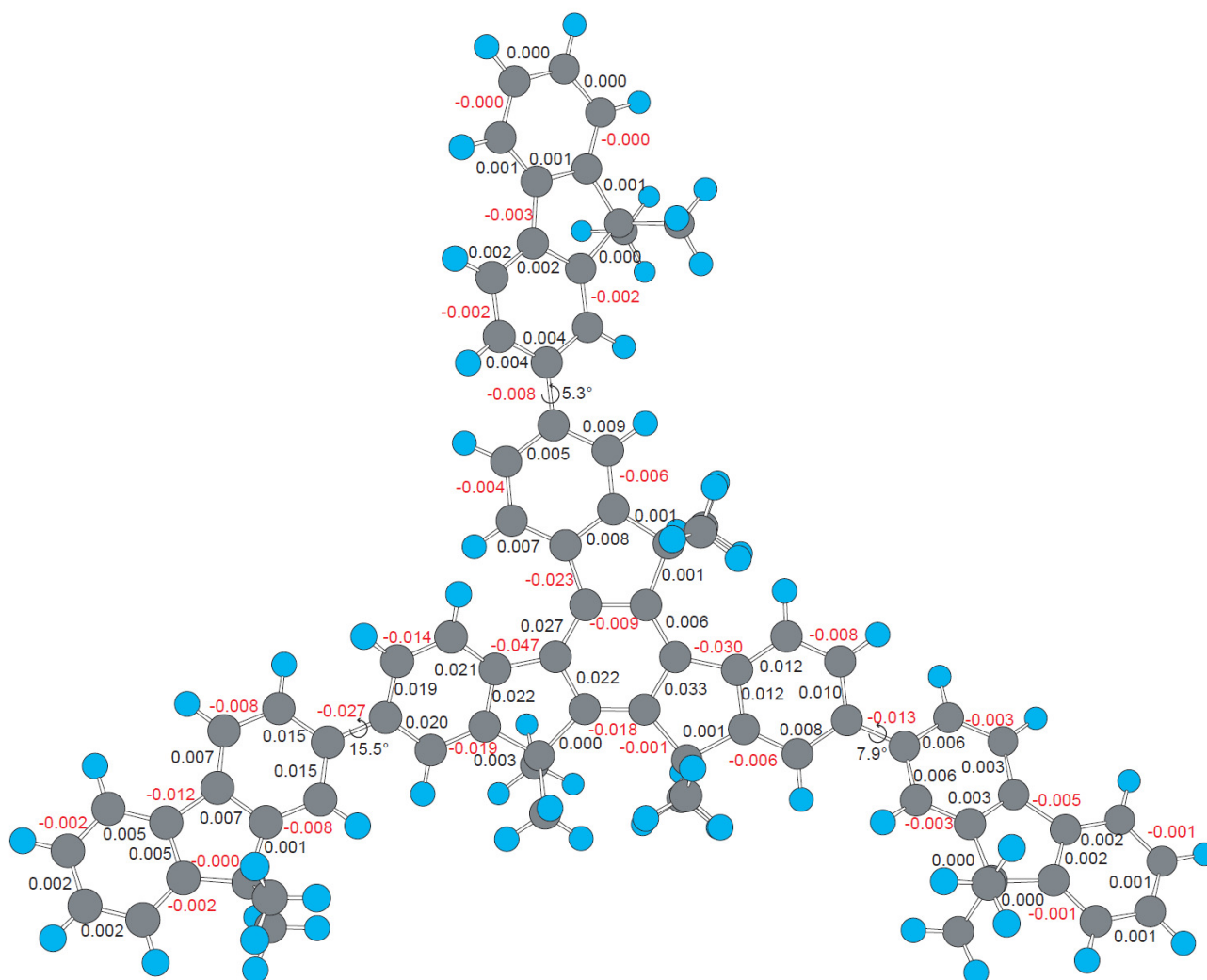**Structural change upon excitation to the singlet excited state.**
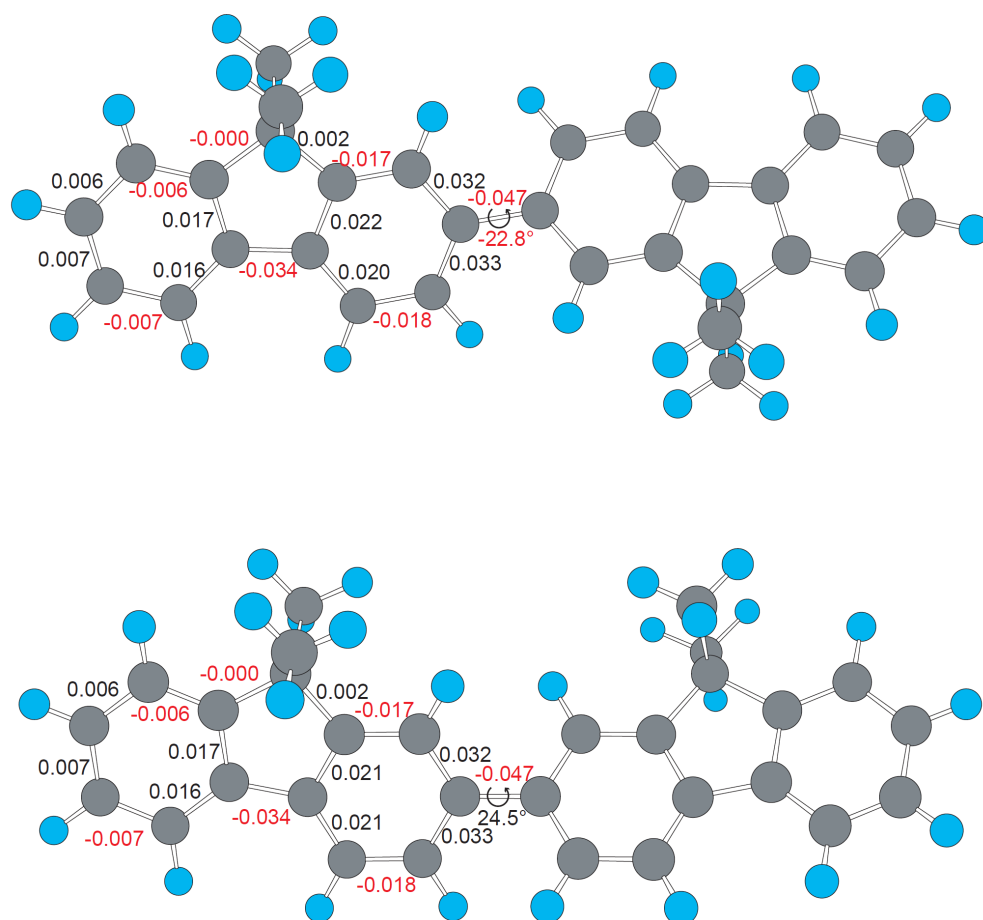
Figure S2. Structural (bond length (Å) and dihedral angle) changes of fluorene dimer upon excitation to the singlet excited state (upper: anti-form, lower: syn-form). The molecular structures in the ground and singlet excited states were calculated at B3LYP/6-31G(d) and TD-B3LYP/6-31G(d) levels, respectively. The alkyl groups were reduced to methyl groups.
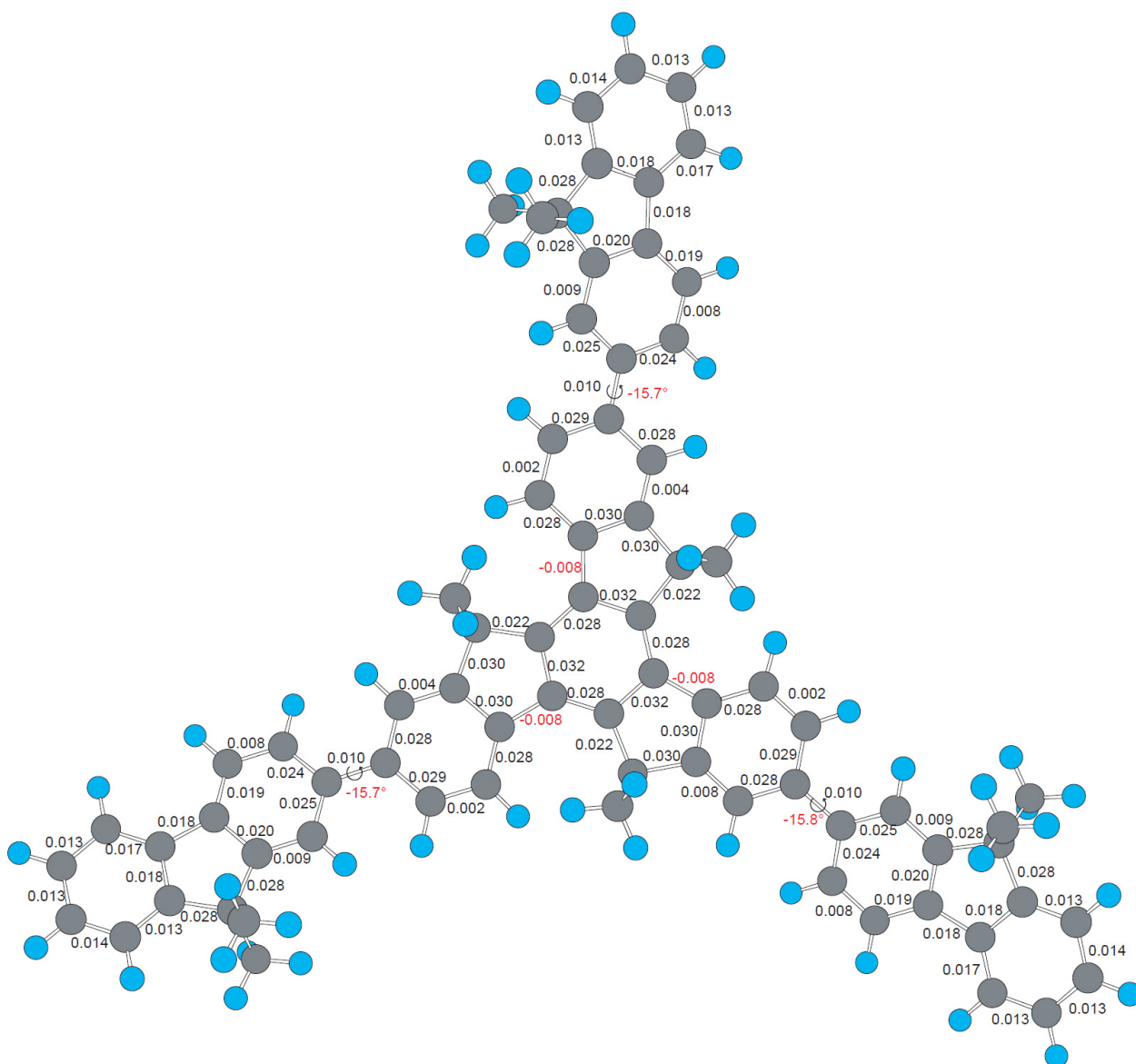
Figure S3. Structural (bond length (Å) and dihedral angle) changes of TF1 in all anti-form upon excitation to the singlet excited state. . The molecular structures in the ground and singlet excited states were calculated at B3LYP/6-31G(d) and TD-B3LYP/STO-3G levels, respectively. The alkyl groups were reduced to methyl groups.
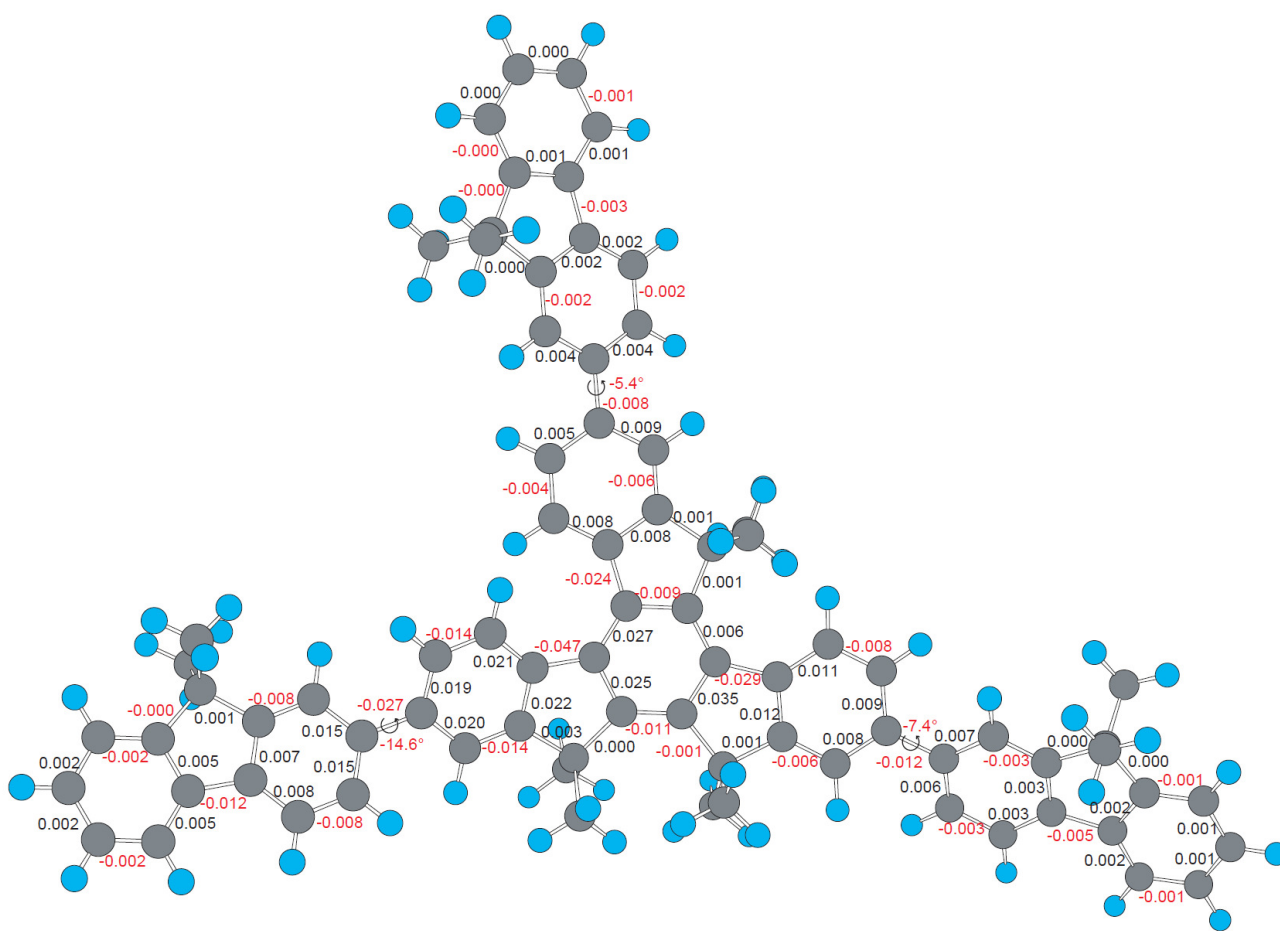
Figure S4. Structural (bond length (Å) and dihedral angle) changes of ITF1 in all anti-form upon excitation to the singlet excited state. The molecular structures in the ground and singlet excited states were calculated at B3LYP/6-31G(d) and TD-B3LYP/6-31G(d) levels, respectively. The alkyl groups were reduced to methyl groups.

Figure S5. Structural (bond length (Å) and dihedral angle) changes of ITF1 in all syn-form upon excitation to the singlet excited state. The molecular structures in the ground and singlet excited state were calculated at B3LYP/6-31G(d) and TD-B3LYP/6-31G(d) levels, respectively. The alkyl groups were reduced to methyl groups.