

Cyclopentadithiophene Derivatives: a Step Towards the Understanding on Thiophene Copolymers Excited State Deactivation Pathways

João Pina^a, Anika Eckert^b, Ulli Scherf^b, Adelino M. Galvão^c and J. Sérgio Seixas de Melo^{a*}

^a) CQC, Department of Chemistry, University of Coimbra, P3004-535 Coimbra, Portugal

^b) Bergische Universitat, Wuppertal, Macromolecular Chemistry Group (buwmakro) and Institute for Polymer Technology, Gauss-Str. 20, D-42097, Wuppertal, Germany

^c) Centro de Química Estrutural, Instituto Superior Técnico (IST), Universidade de Lisboa, Portugal

Keywords: cyclopentadithiophene • excited state dynamics • oligothiophenes • photophysics • ultrafast dynamics

Email: sseixas@ci.uc.pt

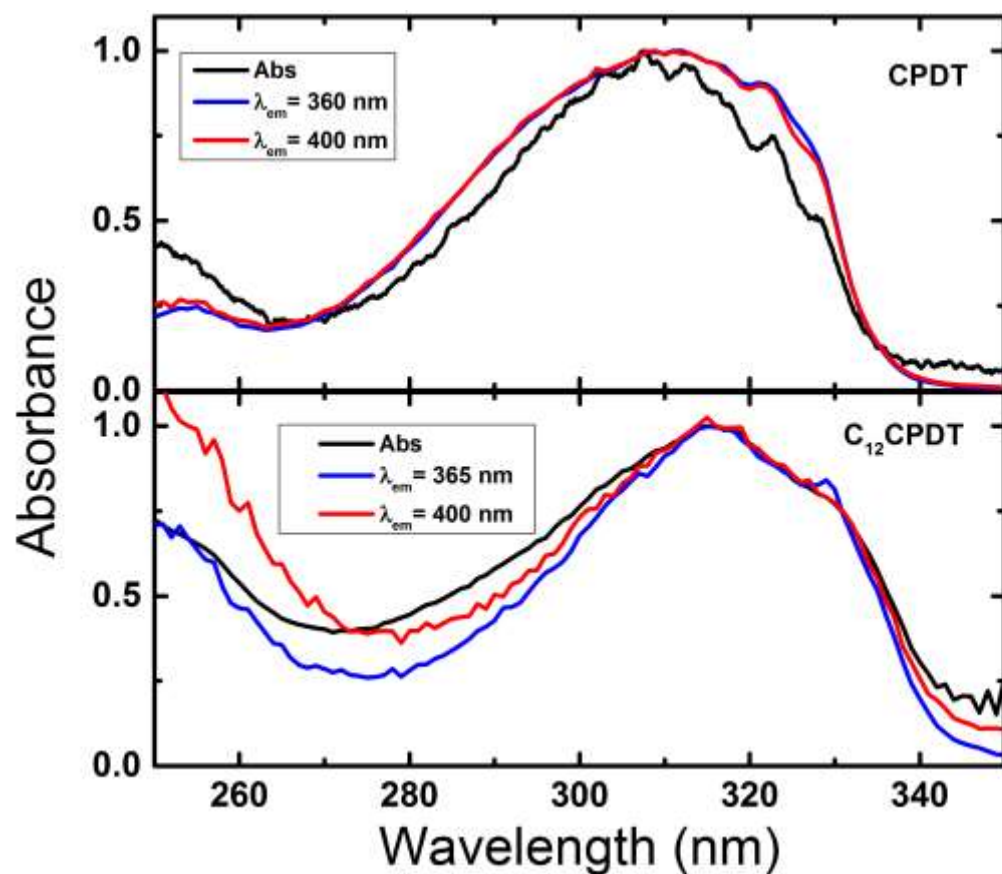


Figure S1- Comparison between the normalized absorption and fluorescence excitation spectra of CPDT and C₁₂CPDT (after purification by HPLC) collected in methylcyclohexane and methanol solutions at 293 K, respectively.

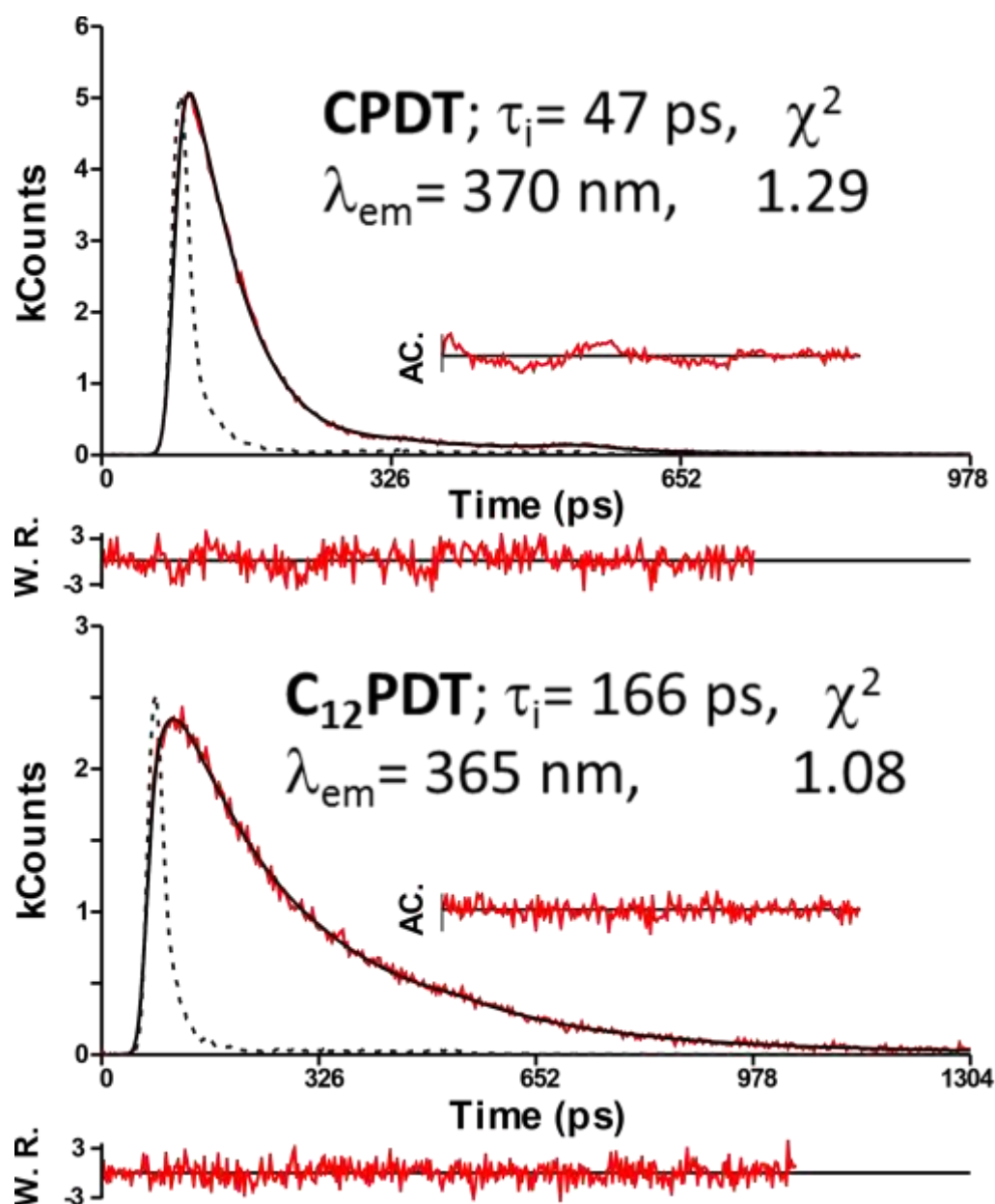


Figure S2- Fluorescence decays for the CPDT ($\lambda_{exc} = 285$ nm) and C₁₂CPDT ($\lambda_{exc} = 272$ nm) derivatives in methylcyclohexane and methanol solutions at 293 K, respectively. For a better judgment of the quality of the fits, weighted residuals (W.R.), autocorrelation functions (A.C.) and χ^2 values are also presented. The dashed line is the instrumental response function.

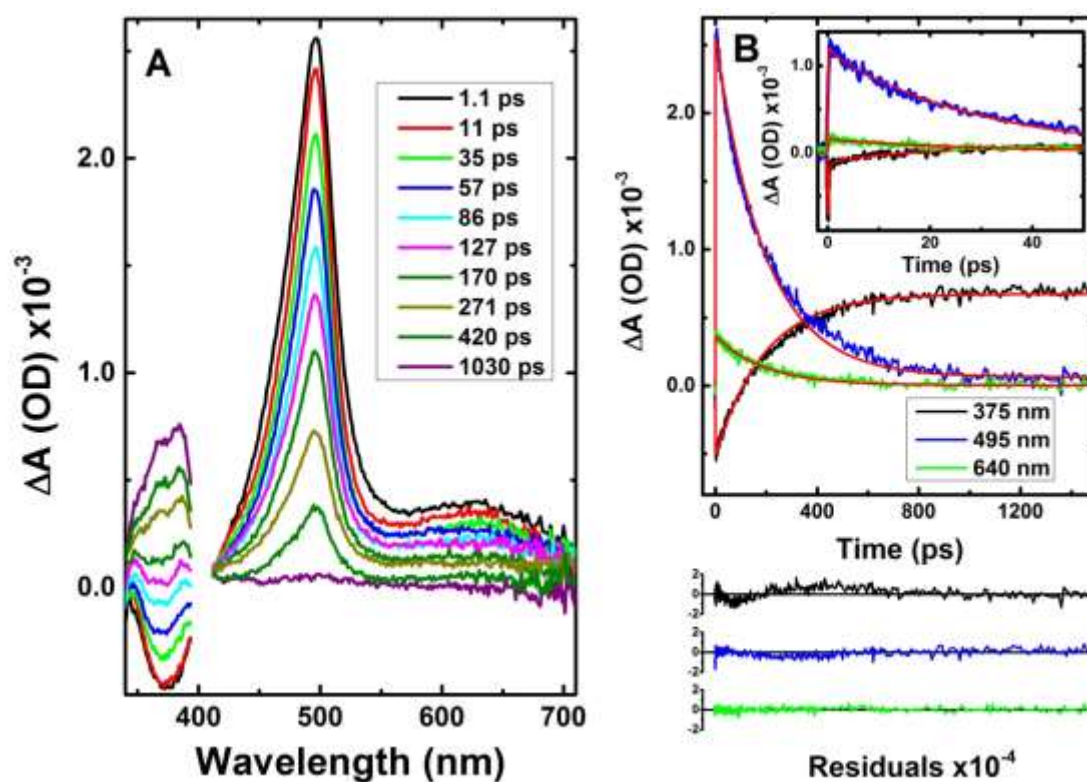


Figure S3- A) Time-resolved transient absorption data for C₁₂CPDT obtained with $\lambda_{\text{exc}} = 310$ nm in aerated dioxane solution at room temperature; together with (B) the representative kinetic traces with fits from the global analysis of the transient absorption data. For a better judgment of the quality of the fits the residuals are also presented.

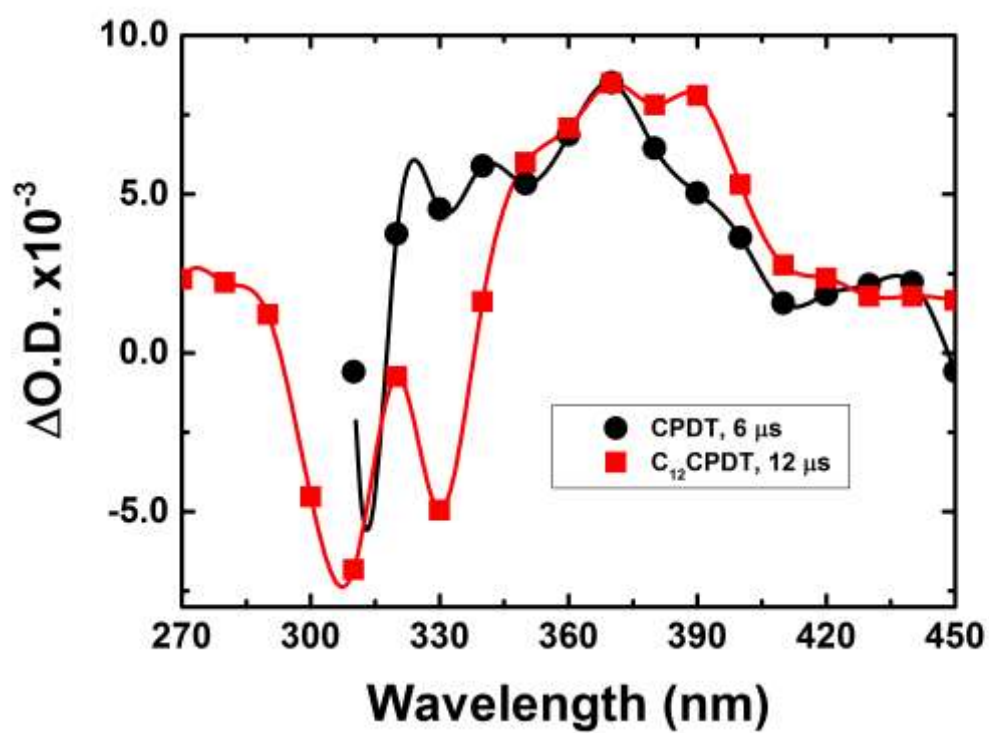


Figure S4- Normalized transient singlet-triplet difference absorption spectra for the cyclopentadithiophene derivatives in methylcyclohexane solution at T= 293 K.

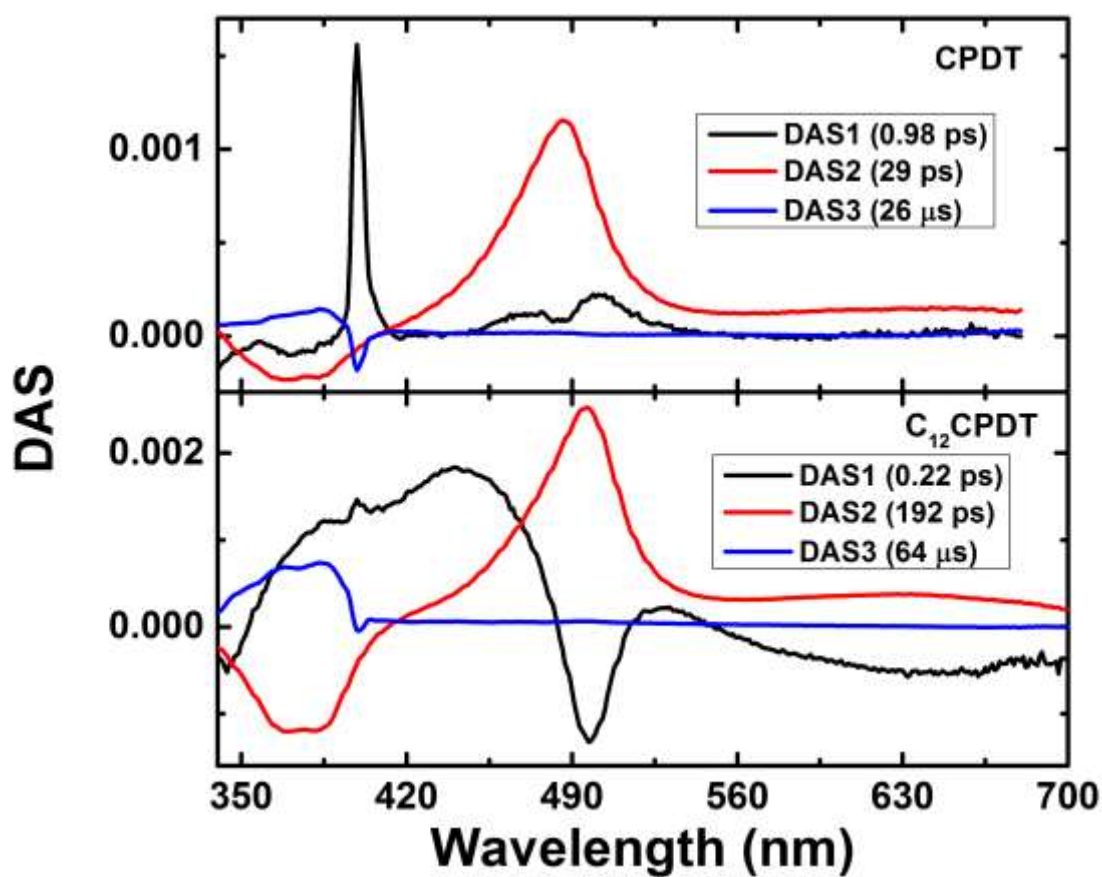


Figure S5- Decay associated spectra (DAS) obtained from the global analysis of the cyclopentadithiophene derivatives fs-transient absorption data collected with $\lambda_{\text{exc}} = 310$ nm in aerated dioxane solutions at 293 K.

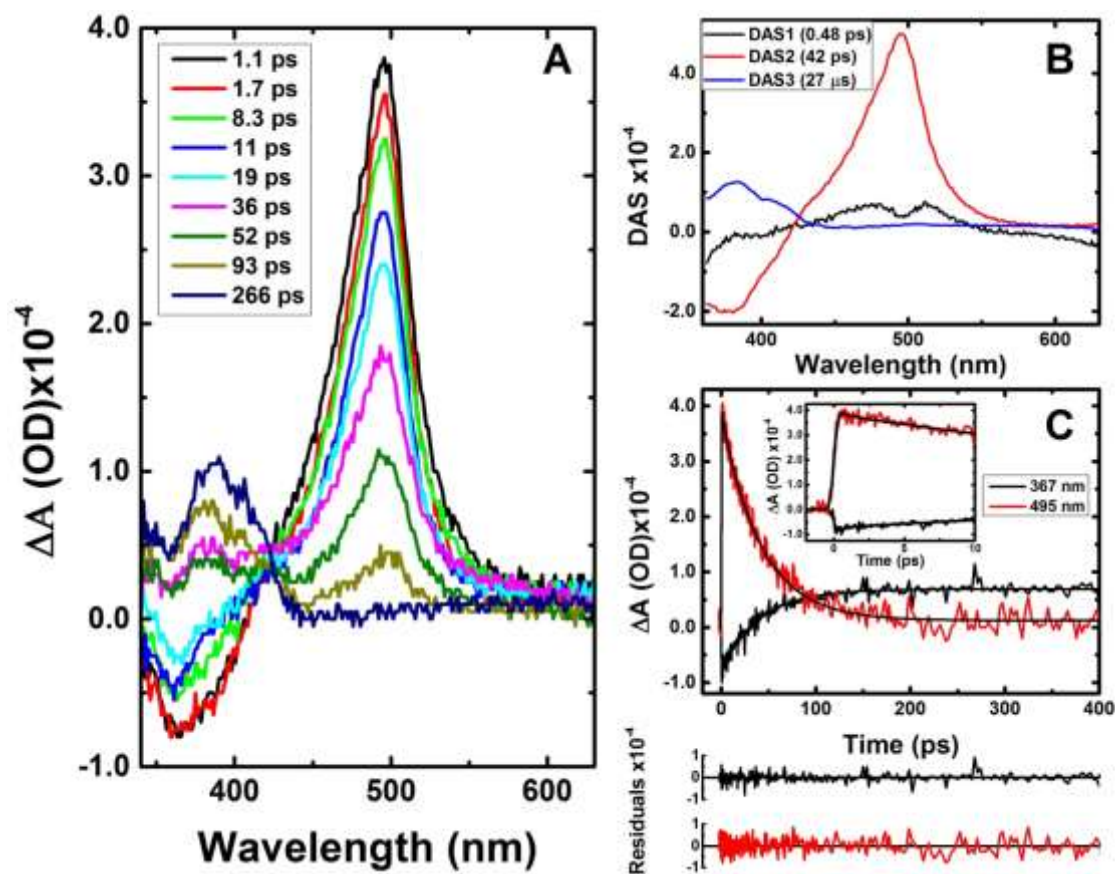


Figure S6- A) Time-resolved transient absorption data for $\alpha 2$ obtained with $\lambda_{\text{exc}} = 325$ nm in aerated hexadecane solution at room temperature; together with (B) decay associated spectra (DAS) obtained from the global analysis of the transient absorption and (C) the representative kinetic traces with fits from the global analysis of the transient absorption data. For a better judgment of the quality of the fits the residuals are also presented.

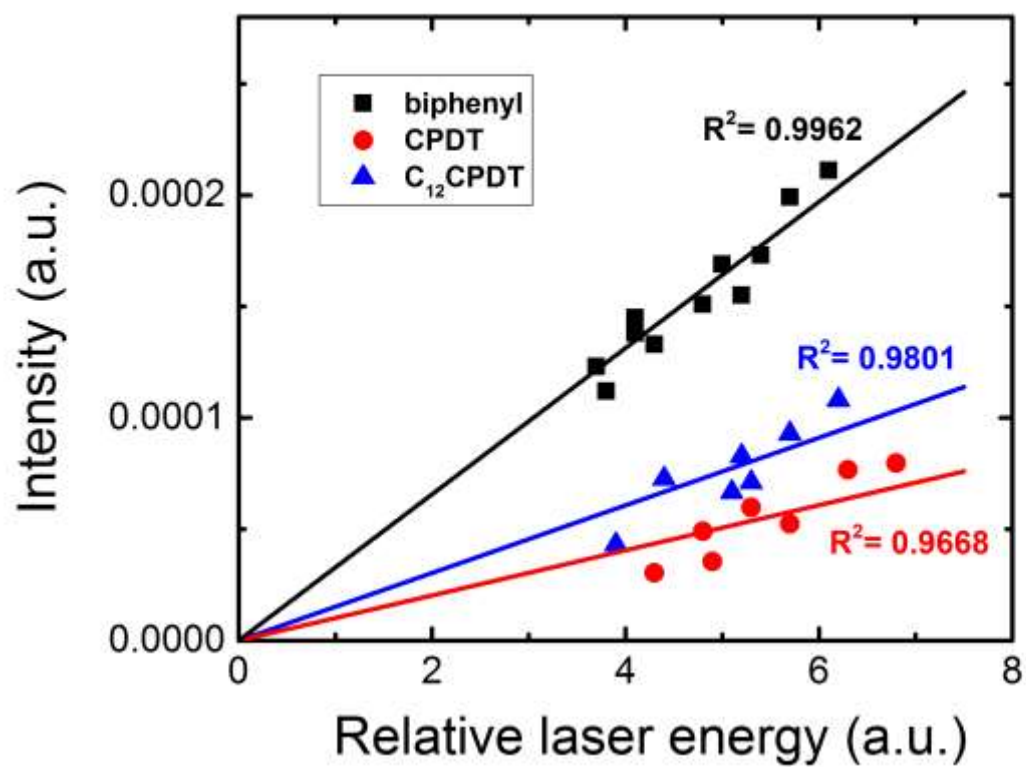


Figure S7- Plot of the sensitized singlet oxygen phosphorescence emission as a function of the laser energy ($\lambda_{\text{exc}} = 266 \text{ nm}$), collected in aerated methylcyclohexane solutions of the CPDT derivatives and the reference compound (biphenyl in cyclohexane solution) at 293 K

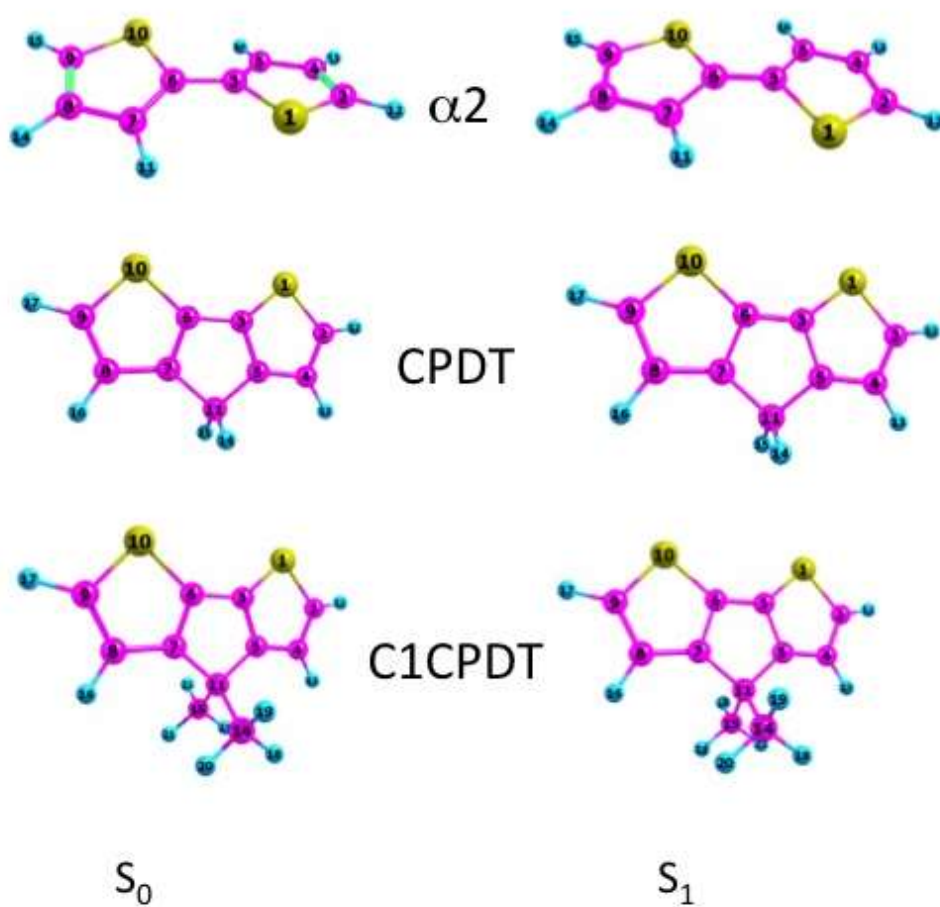


Figure S8- Structures of $\alpha 2$, CPDT and C1CPDT in the ground and excited singlet states. For the dihedral angles and bond distances see Table 3.