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Charge Transfer Relaxation in Donor-Acceptor Type Conjugated Materials

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Supporting Information

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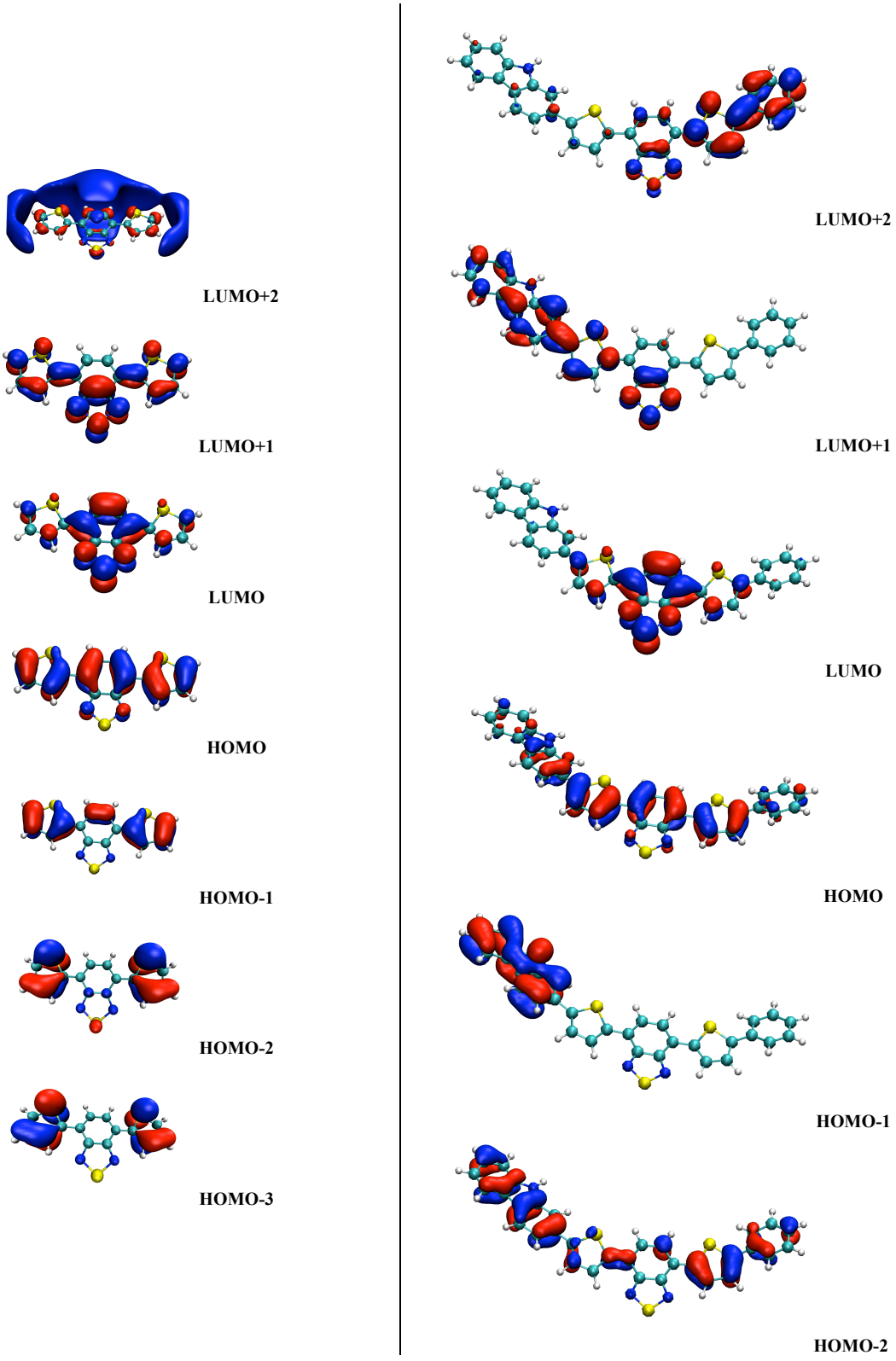
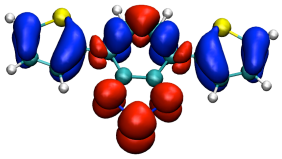
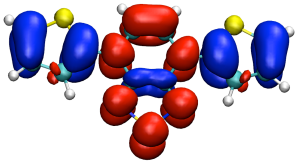


Figure S1. Molecular orbitals of dTBT (left) and CDTBT (right) calculated by TD-DFT (M062X/6-31+G*, gas phase). Geometries were previously optimized using B3LYP/6-31G**.

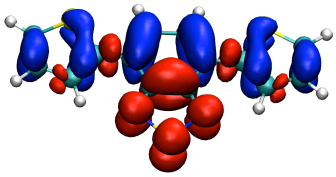
S_0 → S_1 2.8146 eV f=0.4434
HOMO → LUMO 0.70160



S_0 → S_2 4.2164 eV f=0.0351
HOMO-4 → LUMO 0.17433
HOMO-2 → LUMO -0.14419
HOMO-1 → LUMO 0.65451

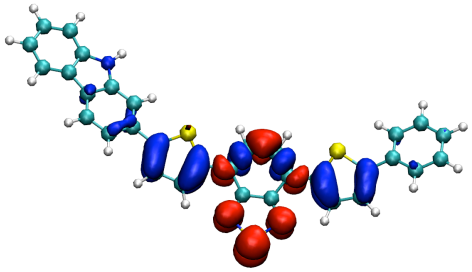


S_0 → S_3 4.3570 eV f=0.3822
HOMO-3→ LUMO -0.24556
HOMO-1 → LUMO+2 -0.11164
HOMO → LUMO+1 0.64055

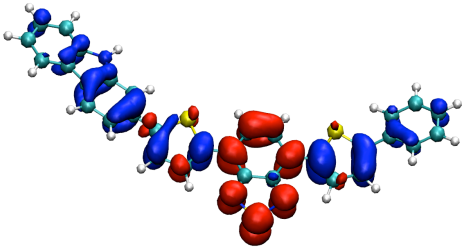


S_0 → S_4 4.3596 eV f=0.0372
S_0 → S_5 4.5390 eV f=0.1053
S_0 → S_6 4.5804 eV f=0.0980

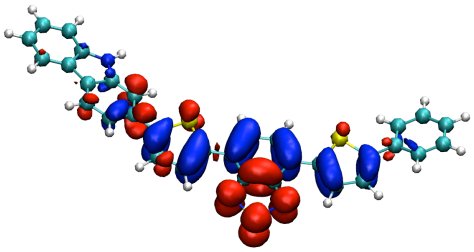
S_0 → S_1 2.5159 eV f=1.0178
HOMO → LUMO 0.68801



S_0 → S_2 3.5502 eV f=0.1873
HOMO-8 → LUMO -0.10020
HOMO-3 → LUMO 0.15910
HOMO-2 → LUMO 0.63603
HOMO → LUMO+1 -0.16182

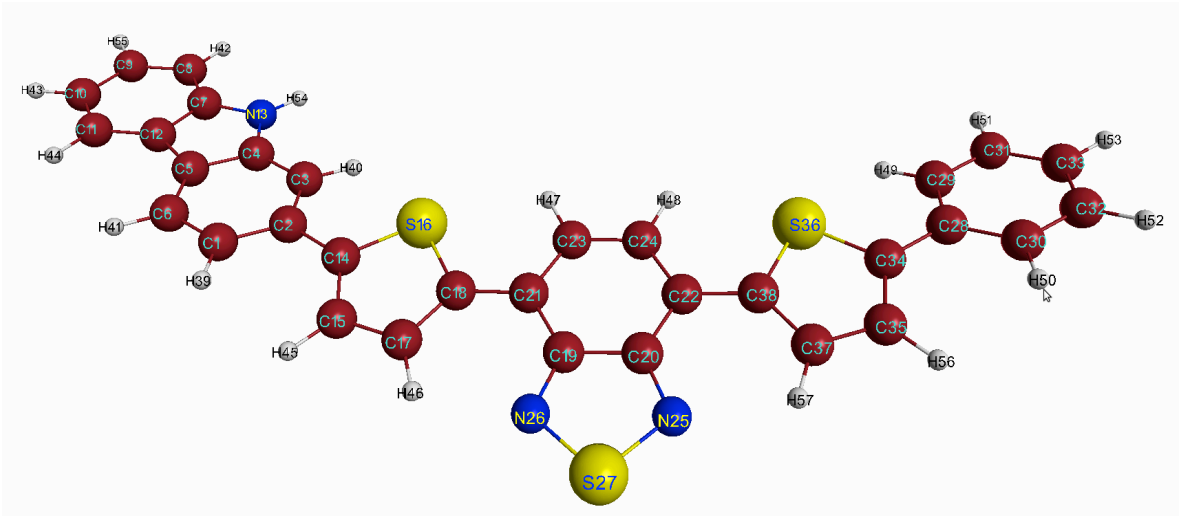


S_0 → S_3 3.7816 eV f=0.8788
HOMO-3 → LUMO 0.13393
HOMO-2 → LUMO 0.11809
HOMO-2 → LUMO+2 -0.16665
HOMO → LUMO+1 0.60140
HOMO → LUMO+2 -0.19309



S_0 → S_4 3.8684 eV f=0.0086
S_0 → S_5 4.0762 eV f=0.2077

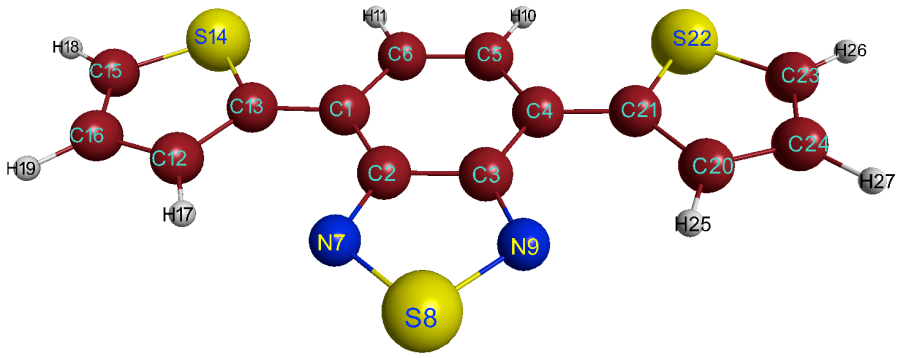
Figure S2. TD-DFT absorption transitions obtained for dTBT (left) and CDTBT (right) in the gas phase at the M062X/6-31+G* level of theory. Excitation energies, oscillator strengths and decomposition into single-particle transitions with corresponding weight are given for each excited state. For the first three transitions, the difference between the excited and ground state electron density calculated for vertical absorption are also shown.



Degree of freedom	Ground state geometry	Excited state geometry
C21-C22	2.946	2.913
C18-C38	5.866	5.760
C22-C24	1.377	1.423
C23-C24	1.421	1.375
C21-C23	1.377	1.424
C19-C21	1.441	1.439
C20-C19	1.451	1.449
C20-C22	1.441	1.438
C20-C22-C24	115.126°	116.741°
C35-C34-C28-C30	-29.056°	-20.291°
C15-C14-C2-C1	29.586°	16.664°
C19-C21-C18-C17	-15.161°	-0.536°
C20-C22-C38-C37	14.849°	0.773°
C6-C5-C12-C11	0.023°	0.038°

Root mean square deviation (RMSD) = 0.22 Å (calculated for fitted geometries)

Figure S3. Numbering scheme and representative bond lengths (in Angstrom) and angles (in degrees) for the ground state geometry and relaxed S_1 excited state geometry of CDTBT in the gas phase.



Degree of freedom	Ground state geometry	Emitting state geometry
C1-C4	2.951	2.900
C4-C5	1.376	1.428
C3-C4	1.441	1.436
C5-C6	1.421	1.373
C3-N9	1.331	1.332
C4-C21	1.463	1.427
C20-C21	1.376	1.397
N9-S8	1.621	1.663
C3-C4-C5	114.890°	114.226°
C2-C1-C13-C12	0°	0°
C3-C4-C21-C20	0°	0°

Root mean square deviation (RMSD) = 0.05 Å (calculated for fitted geometries)

Figure S4. Numbering scheme and representative bond lengths (in Angstrom) and angles (in degrees) for the ground state geometry and relaxed S_1 excited state geometry of dTBT in the gas phase.

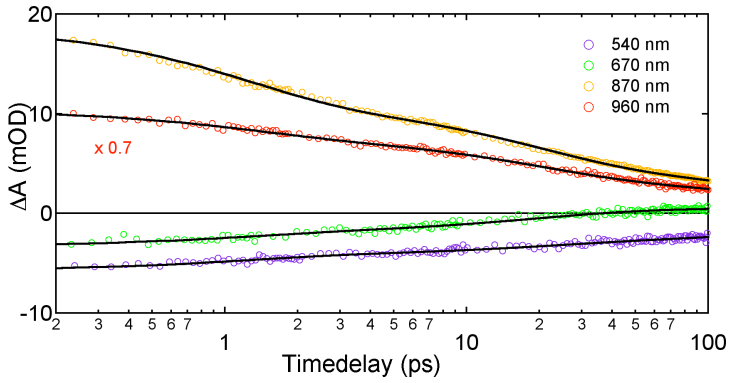


Figure S5. Transient absorption dynamics of CDTBT thin film at selected probe wavelengths, following excitation at 510 nm (solid lines represent the best multiexponental global fit).

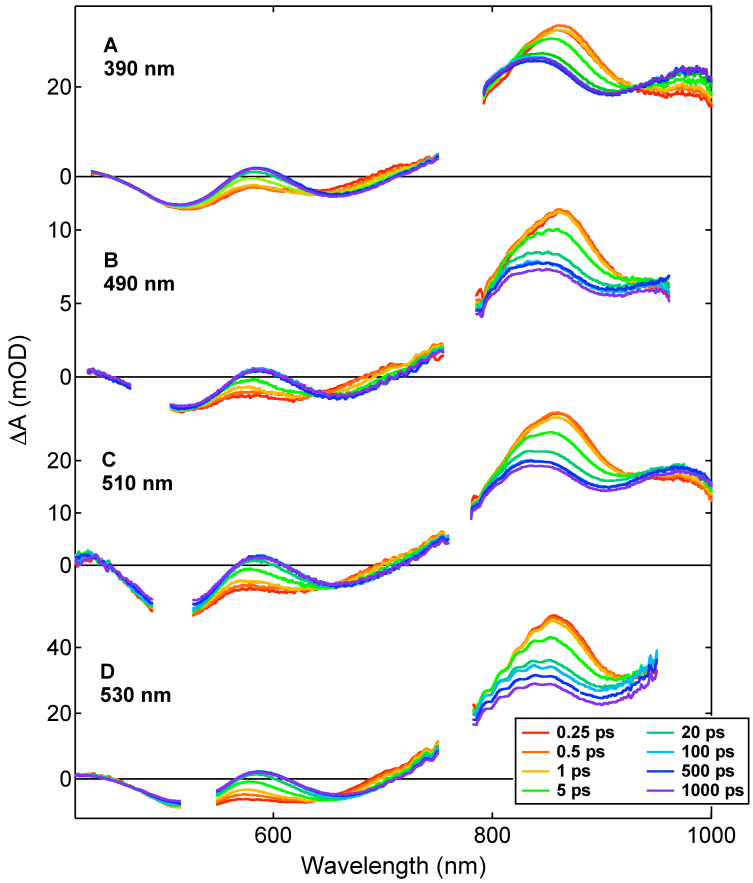


Figure S6. Transient absorption spectra of CDTBT in DCB at various time delays following excitation at 400 nm, 490 nm, 510 nm and 530 nm.

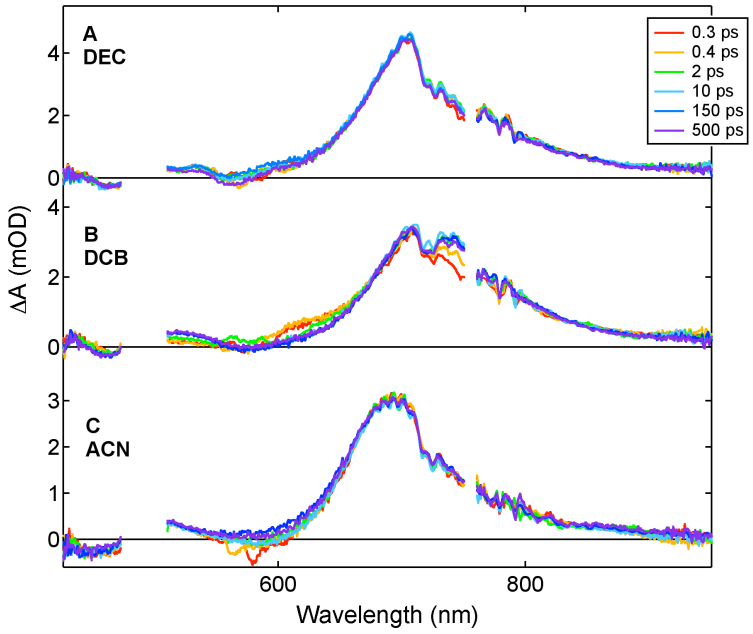


Figure S7. Transient absorption spectra of dTBT in different solvents, recorded at various time delays following excitation at 490 nm.

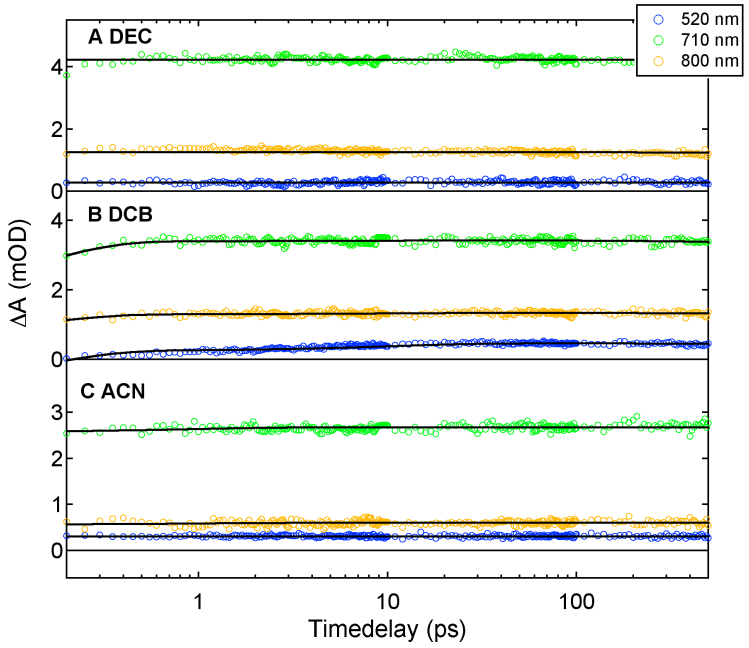


Figure S8. Transient absorption dynamics of dTBT in different solvents at selected probe wavelengths, following excitation at 490 nm (solid lines represent the best multiexponential global fit).

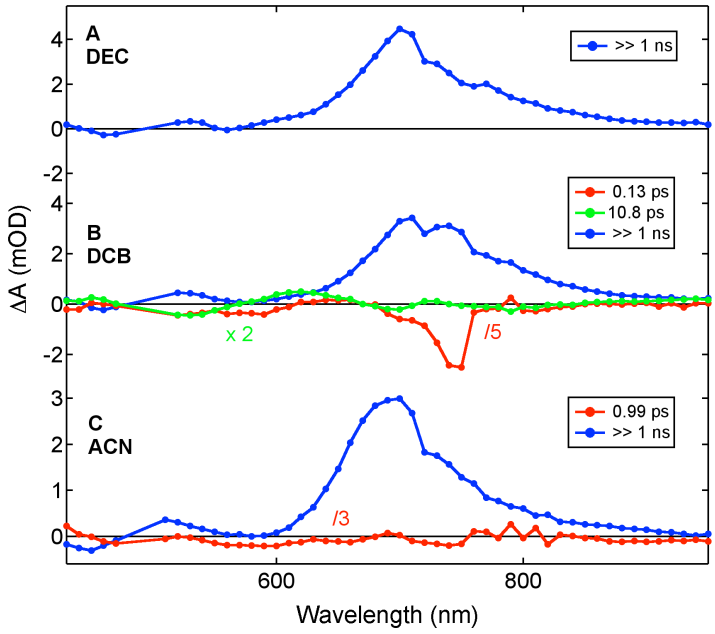


Figure S9. Amplitude spectra associated with the time constants resulting from a multiexponential global analysis of the transient absorption dynamics of dTBT in different solvents, recorded following excitation at 490 nm.