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Supplementary information

Donor-acceptor polymer complex formation in solution confirmed by spectroscopy and atomic-scale modelling

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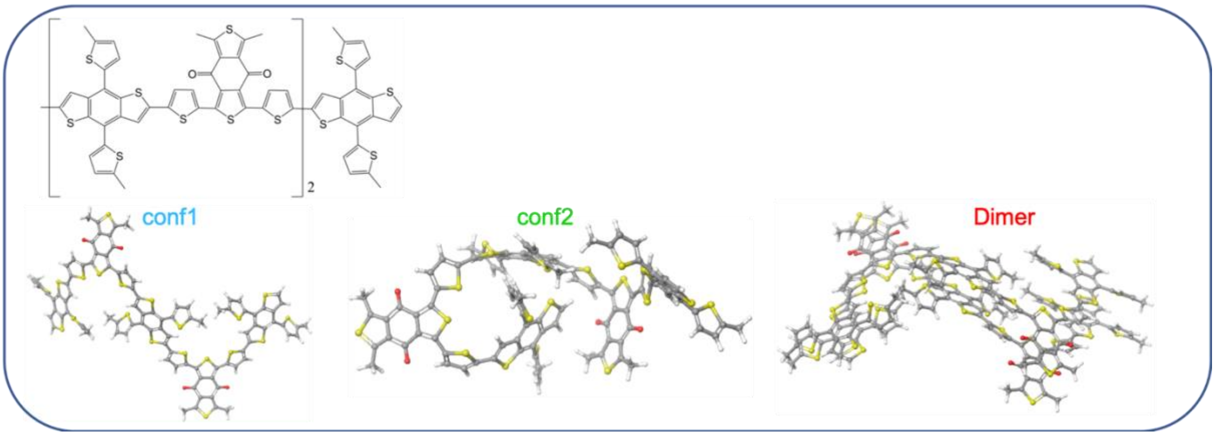

Figure SI-1: *Structure for the PBDB-T single molecule oligomer models in two different conformations and for a dimer model in π-stacked relative orientation.*

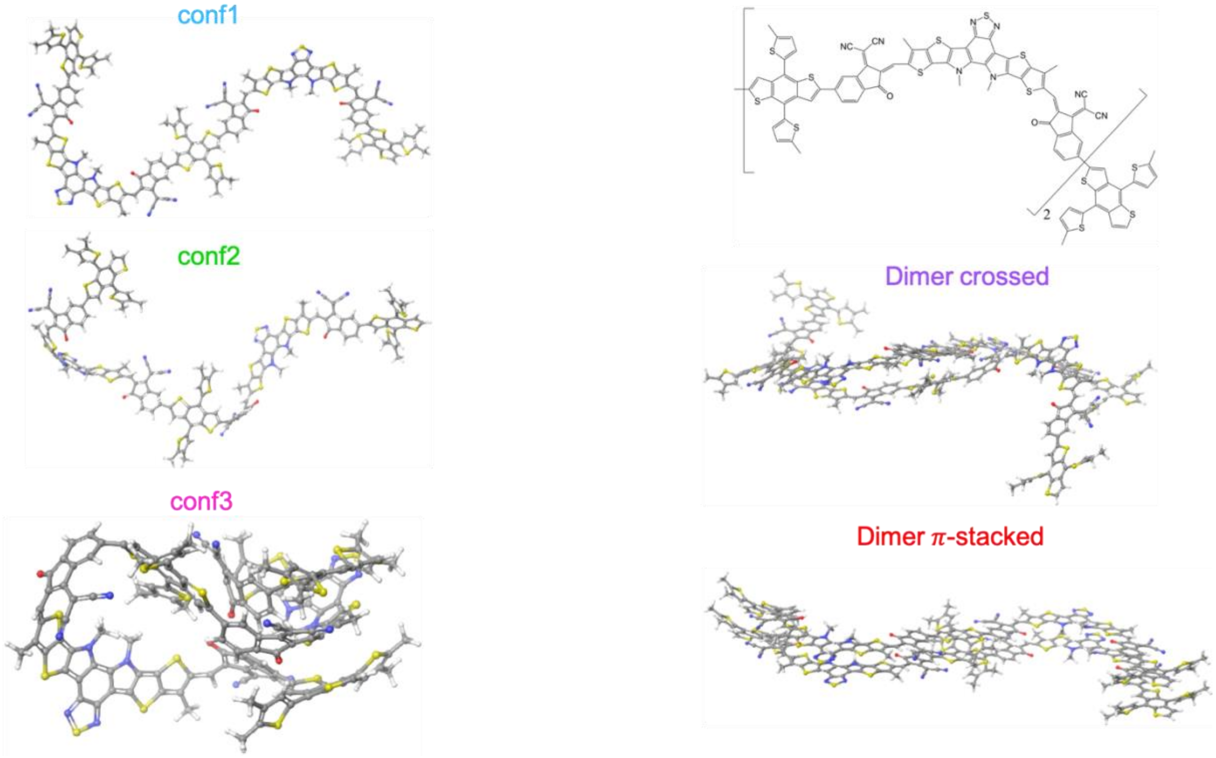

Figure SI-2: *Structure for the PF5-Y5 single molecule oligomer models in three different conformations and PF5-Y5 dimer models in two relative orientation: crossed and* π*-stacked.*

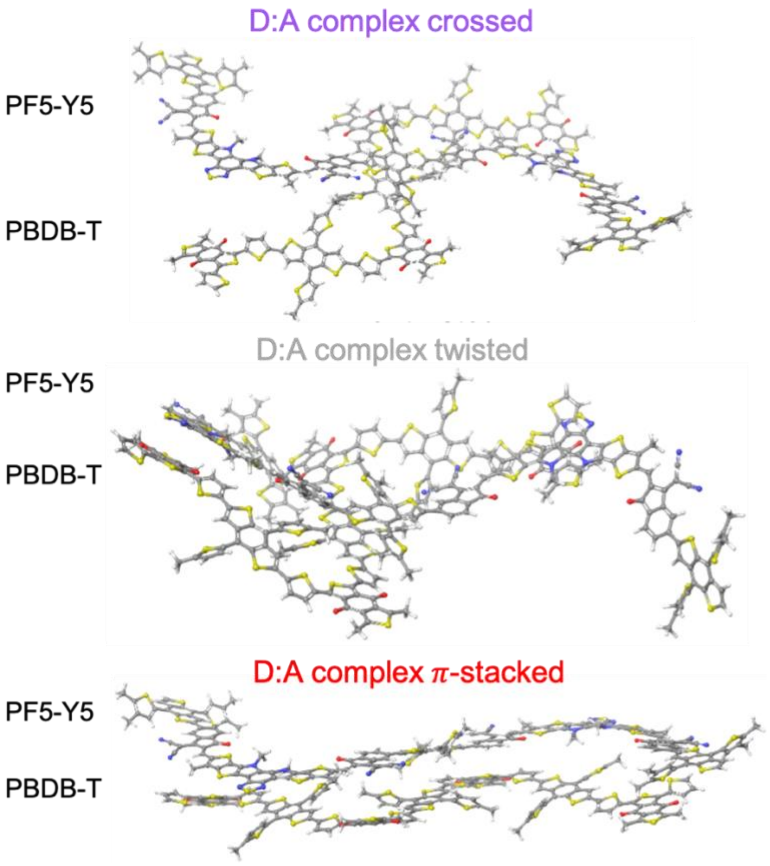

Figure SI-3: *Structure for the PBDB-T:PF5-Y5 complexes in three different relative orientations: crossed, twisted and* π*-stacked.*

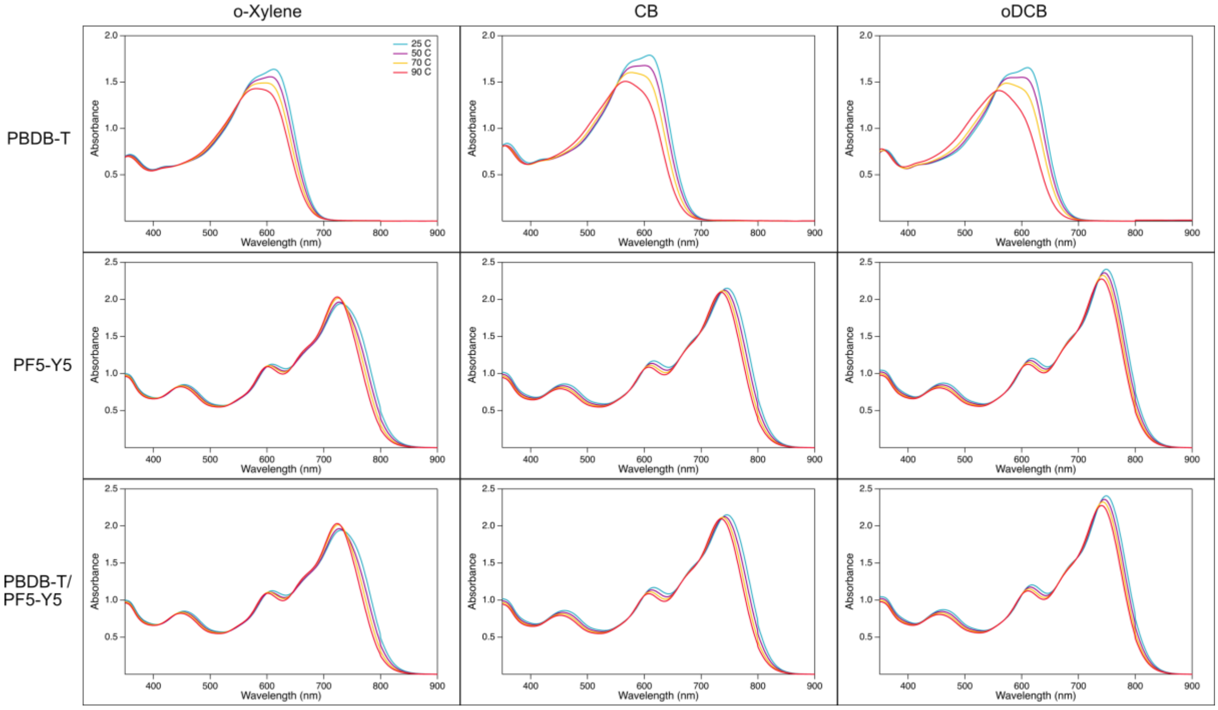

Figure SI-4: *Unnormalised absorption spectra of PBDB-T (top row), PF5-Y5 (middle row) and PBDBT:PF5-Y5 4:3 (bottom row) solutions in o-Xylene (left), CB(middle) and o-DCB(right)* concentration of 40.0 μg/ml *at 25°C, 50°C, 70°C, and 90°C.*

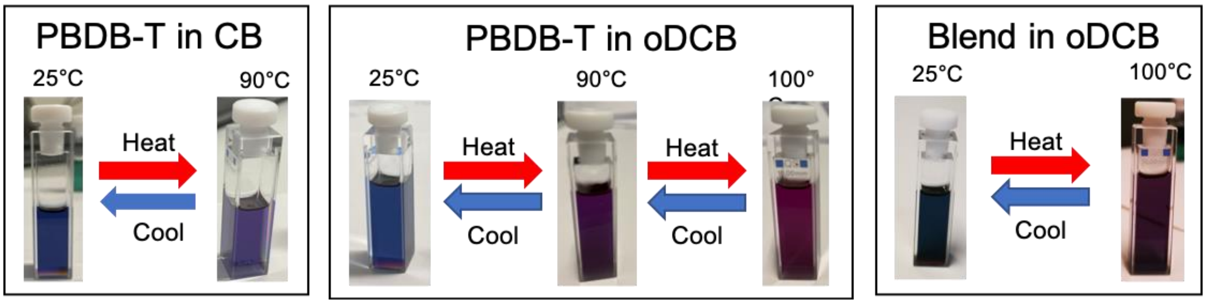

Figure SI-5*: Photographs of a selection of solutions that visualize the colour change upon heating and cooling.*

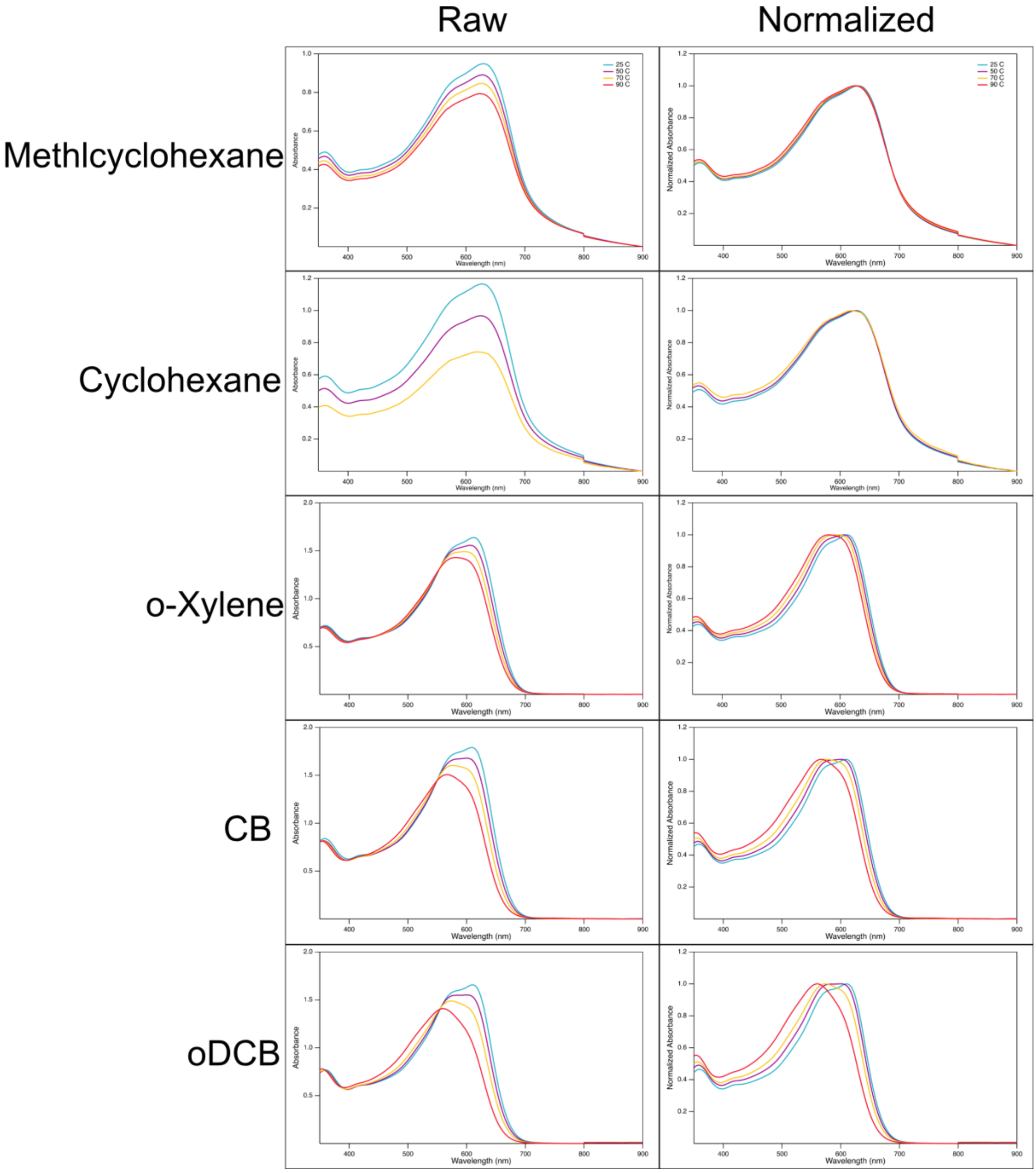

Figure SI-6: *Unnormalised (left) and normalized (right) absorption spectra of PBDB-T solutions in different solvents at 25°C, 50°C, 70°C, and 90°C.*

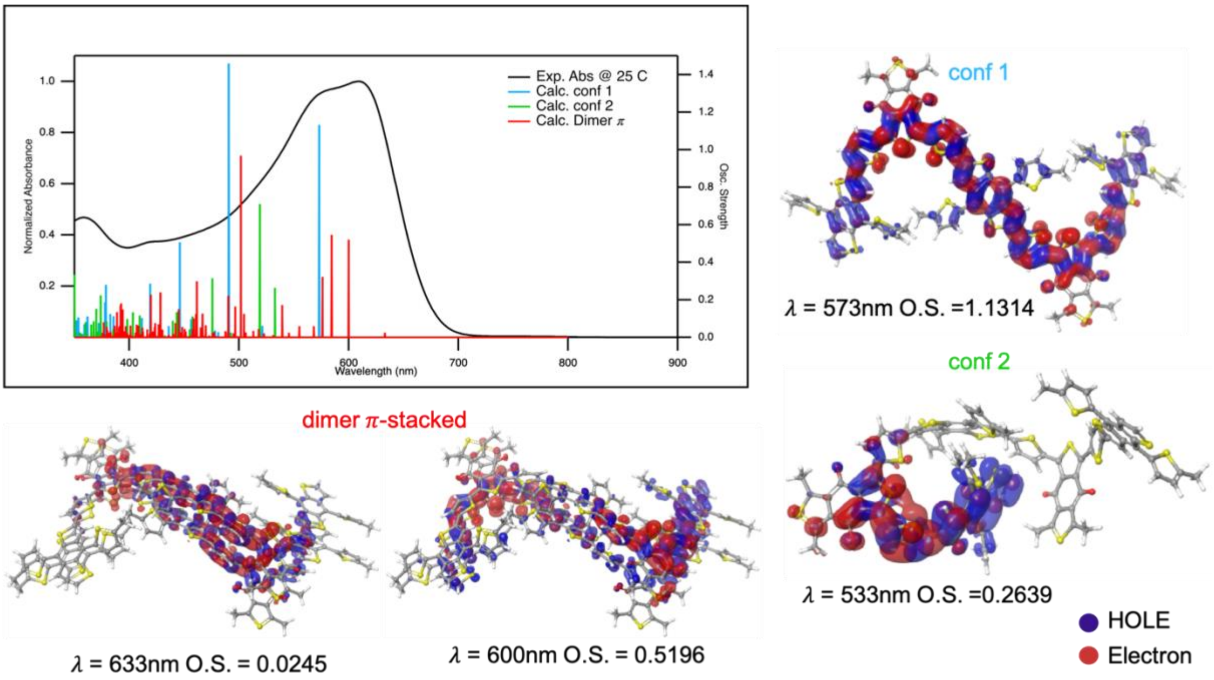

Figure SI-7: *Comparison between the experimental absorption spectrum of PBDB-T in CB at 25 °C and the calculated electronic transitions (vertical lines) for PBDB-T in two different single chain conformations and for the π-stacked dimer. For the first singlet electronic transitions (S_1) the spatial distribution of the Natural Transition Orbitals (NTO, plotted using isovalue=0.02) is displayed. Results are obtained from TD-DFT calculations performed at M06-D3/6-31G* theory level, using Jaguar 11.*

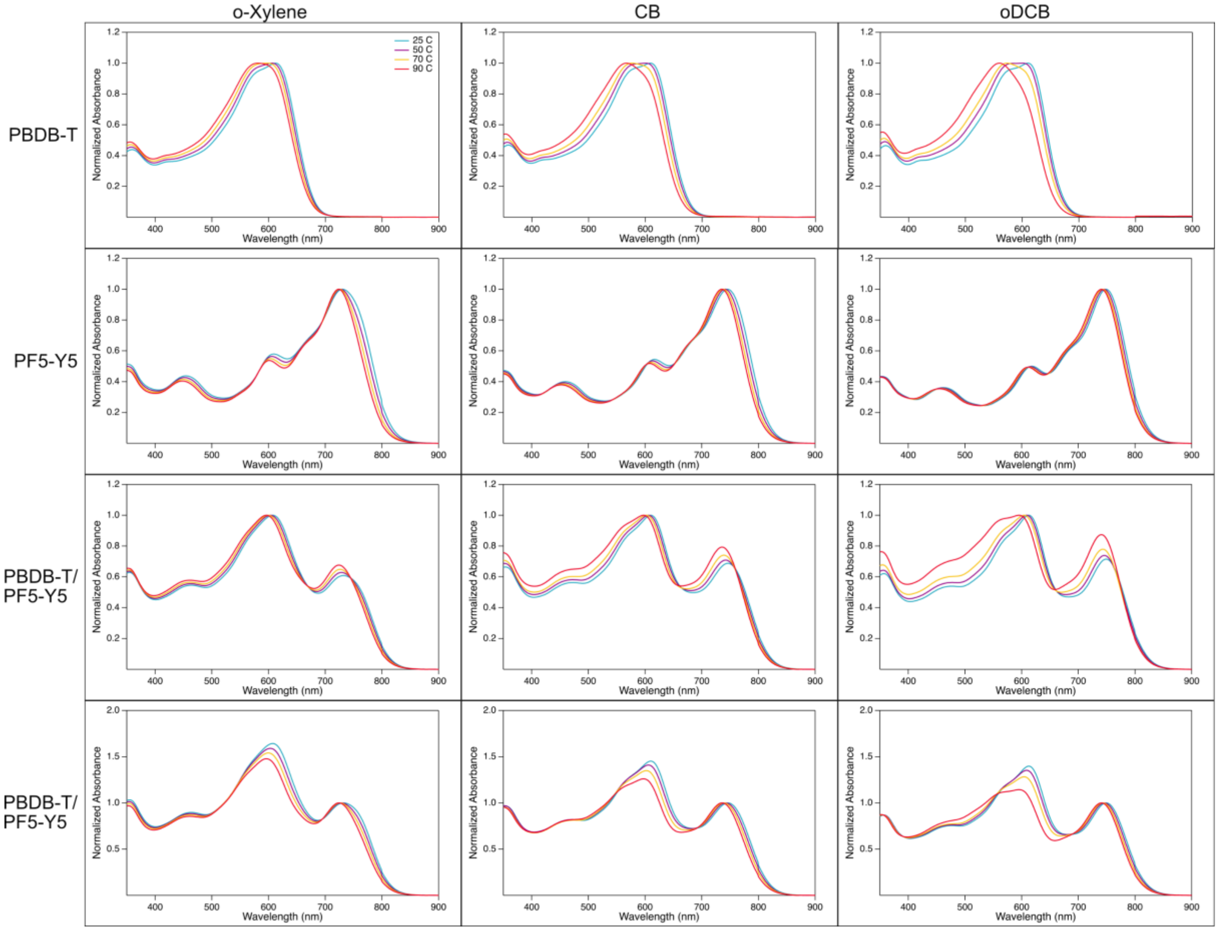

Figure SI-8: *Normalised absorption spectra of PBDB-T (top row), PF5-Y5 (middle row) and PBDBT:PF5-Y5 4:3 (two bottom rows) solutions in o-Xylene (left), CB(middle) and o-DCB(right) at 25°C, 50°C, 70°C, and 90°C. Normalisation is done to the highest intensity peak for PBDB-T and PF5-Y5 spectra. The PBDBT:PF5-Y5 spectra on the third row are normalized to the donor peak at 600 nm, while the ones on the bottom row are normalized to the acceptor peak at 750 nm.*

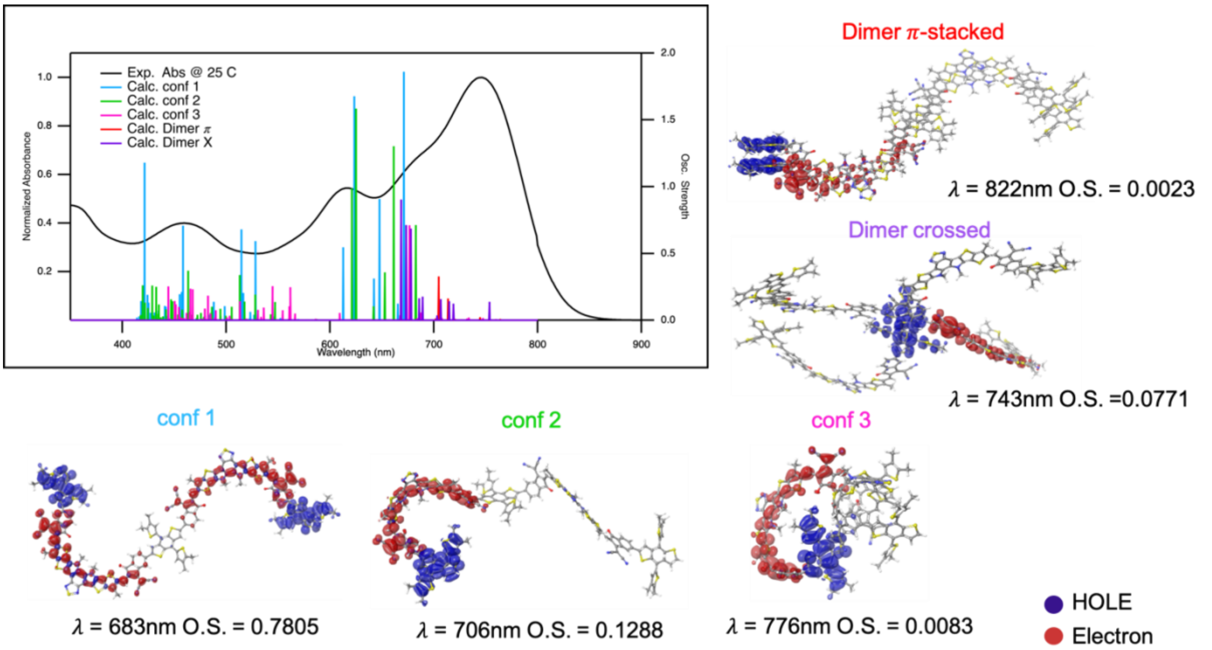

Figure SI-9: *Comparison between the experimental absorption spectrum of PF5-Y5 in CB at 25 °C and the calculated electronic transitions (vertical lines) for PF5-Y5 in its three different conformations and for two dimers (π-stacked and crossed). For the first singlet electronic transitions (S_1) the spatial distribution of the Natural Transition Orbitals (NTO, plotted using isovalue=0.02) is displayed. Results are obtained from TD-DFT calculations performed at M06-D3/6-31G* theory level, using Jaguar 11.*

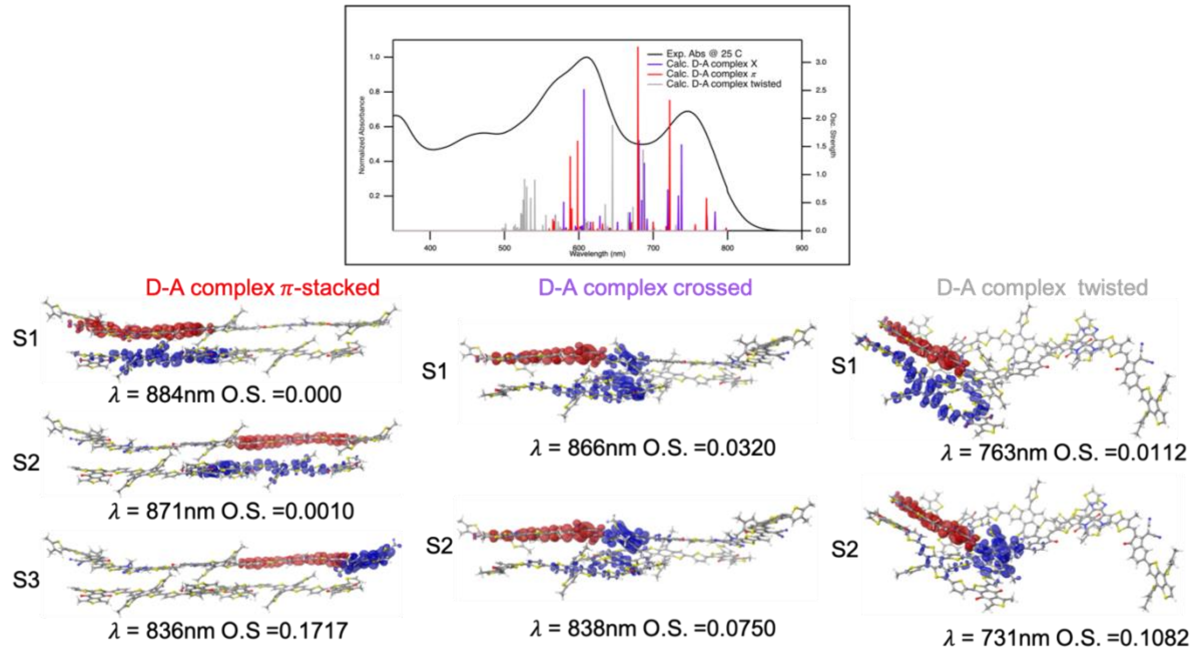

Figure SI-10: *Comparison between the experimental absorption spectrum for the PBDB-T:PF5-Y5 blend in CB at 25 °C and the calculated electronic transition (vertical lines) for the model complexes in its three different relative orientations (π-stacked and crossed and twisted). For some selected electronic transitions, labeled S_n the spatial distribution of the Natural Transition Orbitals (NTO, plotted using isovalue=0.02) is displayed. Results are obtained from TD-DFT calculations performed at M06-D3/6-31G* theory level, using Jaguar 11.*

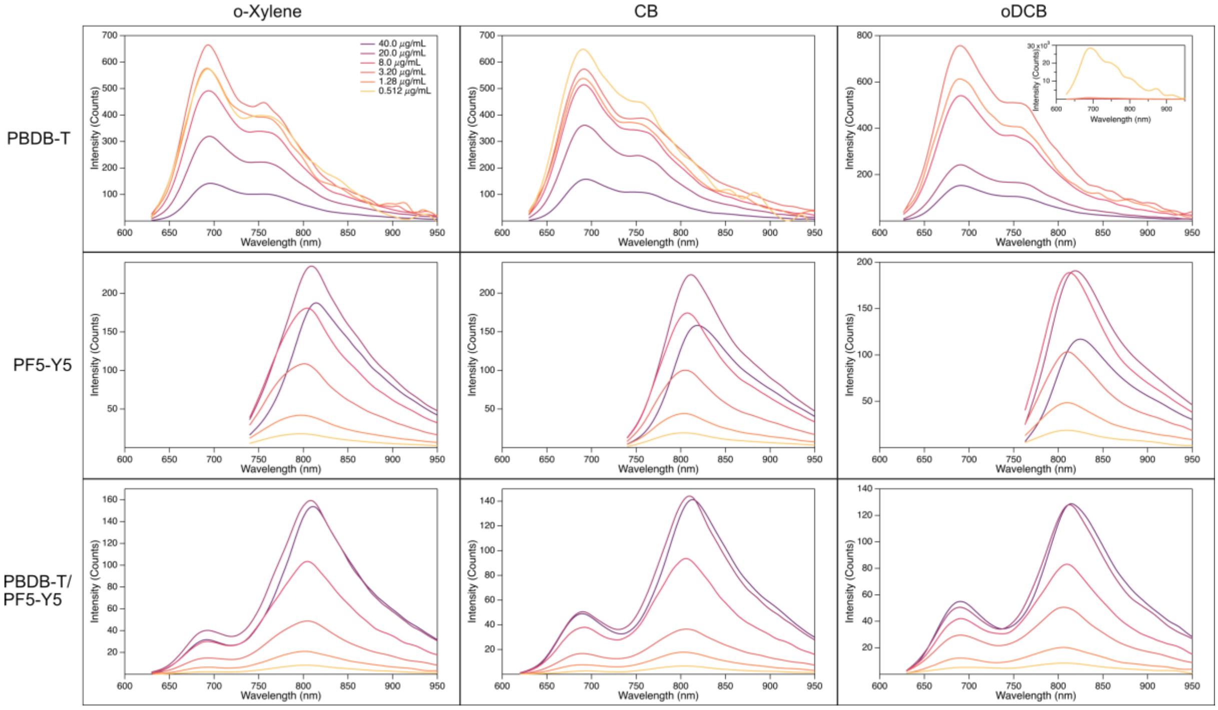

Figure SI-11: *Unnormalised concentration-dependent fluorescence spectra corrected for the absorption at the excitation wavelength of PBDB-T solutions (top row), PF5-Y5 solutions (middle row), and PBDB-T:PF5-Y5 4:3 blend solutions (bottom row) in o-Xyl (left), CB (middle) and o-DCB (right) at 25 °C. Concentrations are given in the Figure. All PBDB-T and PBDB-T:PF5-Y5 4:3 blend solutions were excited at 610 nm. PF5-Y5 solutions in o-Xyl and CB were excited at 730 nm and the PF5-Y5 solution in o-DCB at 747 nm.*

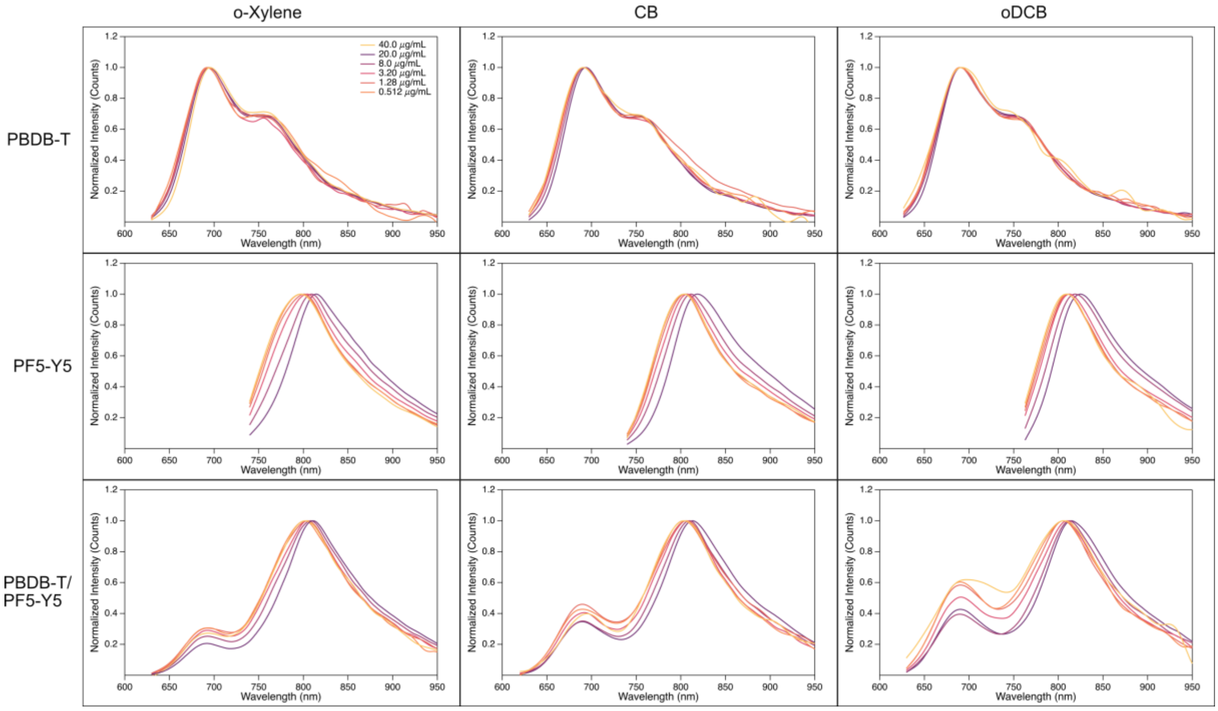

Figure SI-12: *Normalized concentration-dependent fluorescence spectra of PBDB-T solutions (top row), PF5-Y5 solutions (middle row), and PBDB-T:PF5-Y5 4:3 blend solutions (bottom row) in o-Xyl (left), CB (middle) and o-DCB (right) at 25 °C. Concentrations are given in the Figure. All PBDB-T and PBDB-T:PF5-Y5 4:3 blend solutions were excited at 610 nm. PF5-Y5 solutions in o-Xyl and CB were excited at 730 nm and the PF5-Y5 solution in o-DCB at 747 nm. Normalisation is done to the highest peak.*

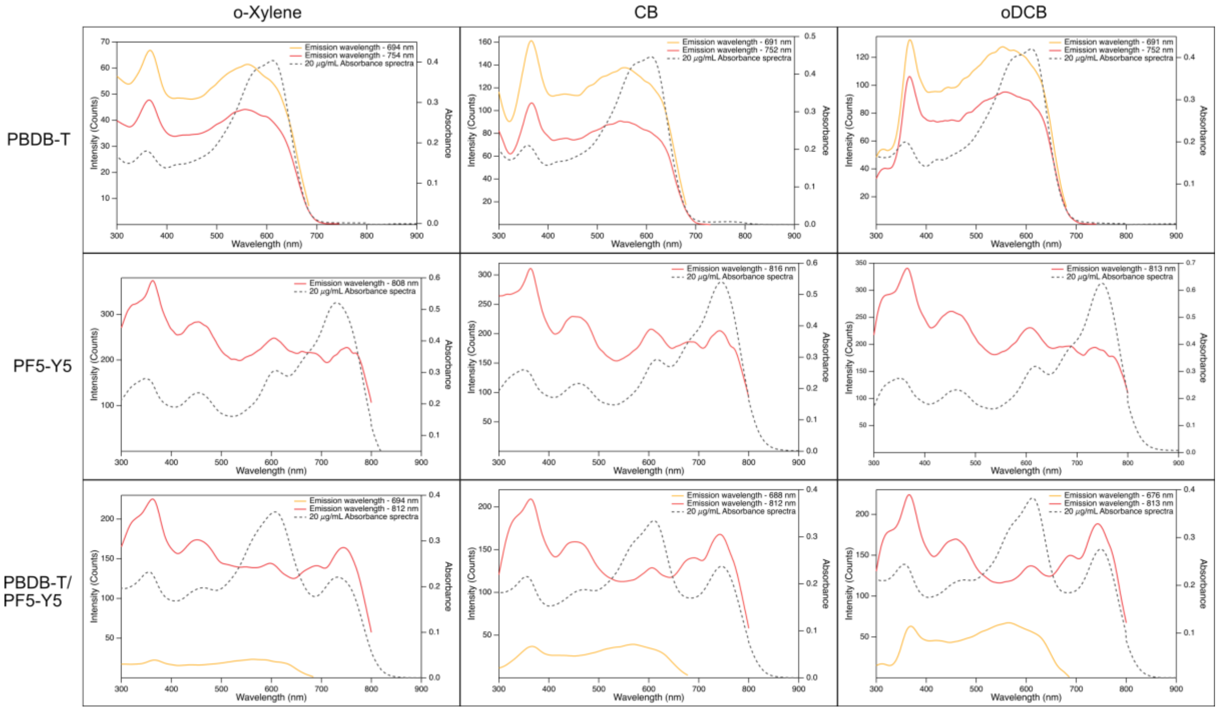

Figure SI-13: *Excitation spectra (not normalized) of a PBDB-T solutions (top row), PF5-Y5 solutions (middle row), and PBDB-T:PF5-Y5 4:3 blend solutions (bottom row) of 0.02 mg/ml in o-Xyl (left), CB (middle) and o-DCB (right) at 25 °C. The corresponding emission wavelengths for the excitation spectra are given in the figure legend. The dashed line is the corresponding absorption spectrum at 25 °C.*

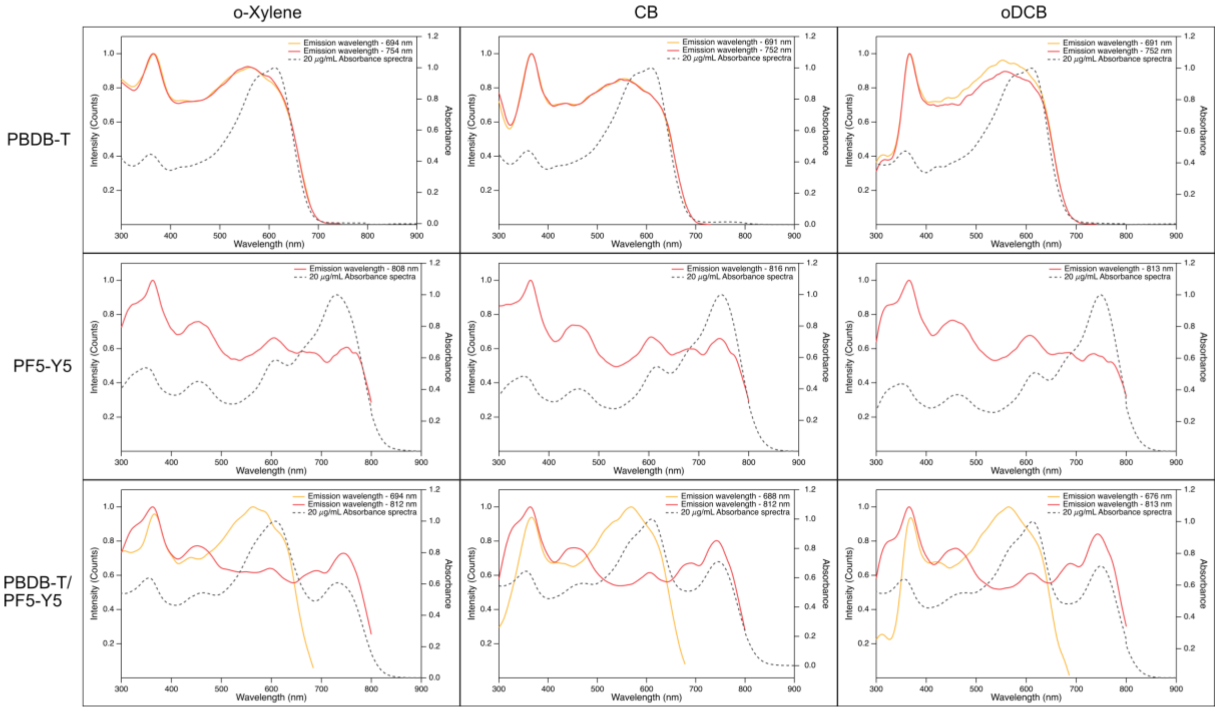

Figure SI-14: *Normalised excitation spectra (not normalized of a PBDB-T solutions (top row), PF5-Y5 solutions (middle row), and PBDB-T:PF5-Y5 4:3 blend solutions (bottom row) of 0.02 mg/ml in o-Xyl (left), CB (middle) and o-DCB (right) at 25 °C. The corresponding emission wavelengths for the excitation spectra are given in the figure legend. The normalisation is done to the highest peak for each spectrum. The dashed line is the corresponding absorption spectrum at 25 °C.*

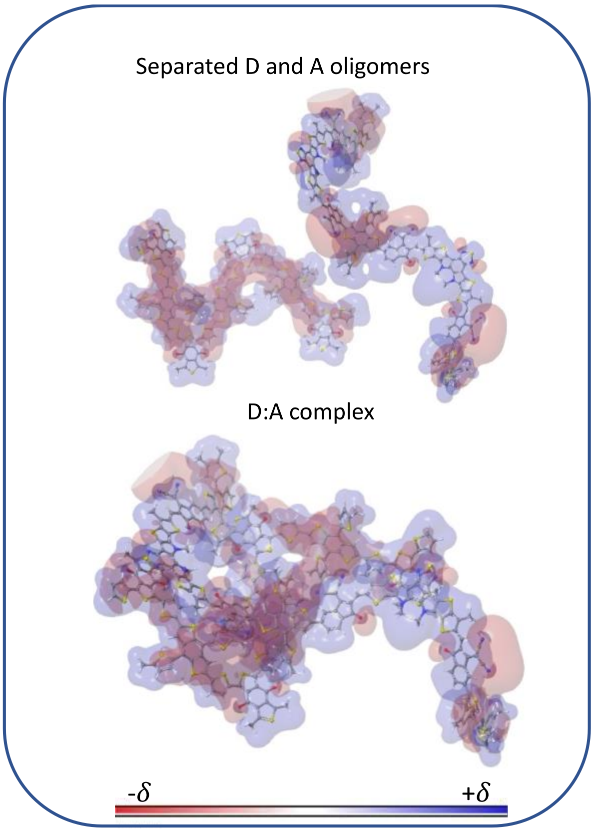

Figure SI-15: Electrostatic potential distribution on separated (~30Å) donor oligomer (left) and an acceptor oligomer (right) in proximity of one another (~3Å) showing that the BDT unit of the donor (red) and the Y5 unit of the acceptor (blue) attract each other.