Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for: Self-trapping and excited state absorption in fluorene homo-polymer and copolymers with benzothiadiazole and tri-phenylamine

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The molecules used in this report are sketched in figure S1. The molecular geometries shown are the optimised ground-state geometries. Typical dihedral angles between units are 40 degrees, (35 degrees in fluorene oligomers). We notice that F8BT and fluorene oligomers are straight molecules. However, F8PFB and F8TFB are “zigzag” molecules, due to the nitrogen atoms, which require 120 degrees angle between the three benzene rings attached to it.

We have investigated the planarisation of the molecules with exciton self-trapping upon molecular relaxation to the S_1-geometry, as this has been observed before in a variety of molecules, such as fluorene oligomers[1]. The results are displayed in figure S2. We notice that only two dihedral angles diminished, corresponding to excitation relaxation onto two to three co-polymer units.

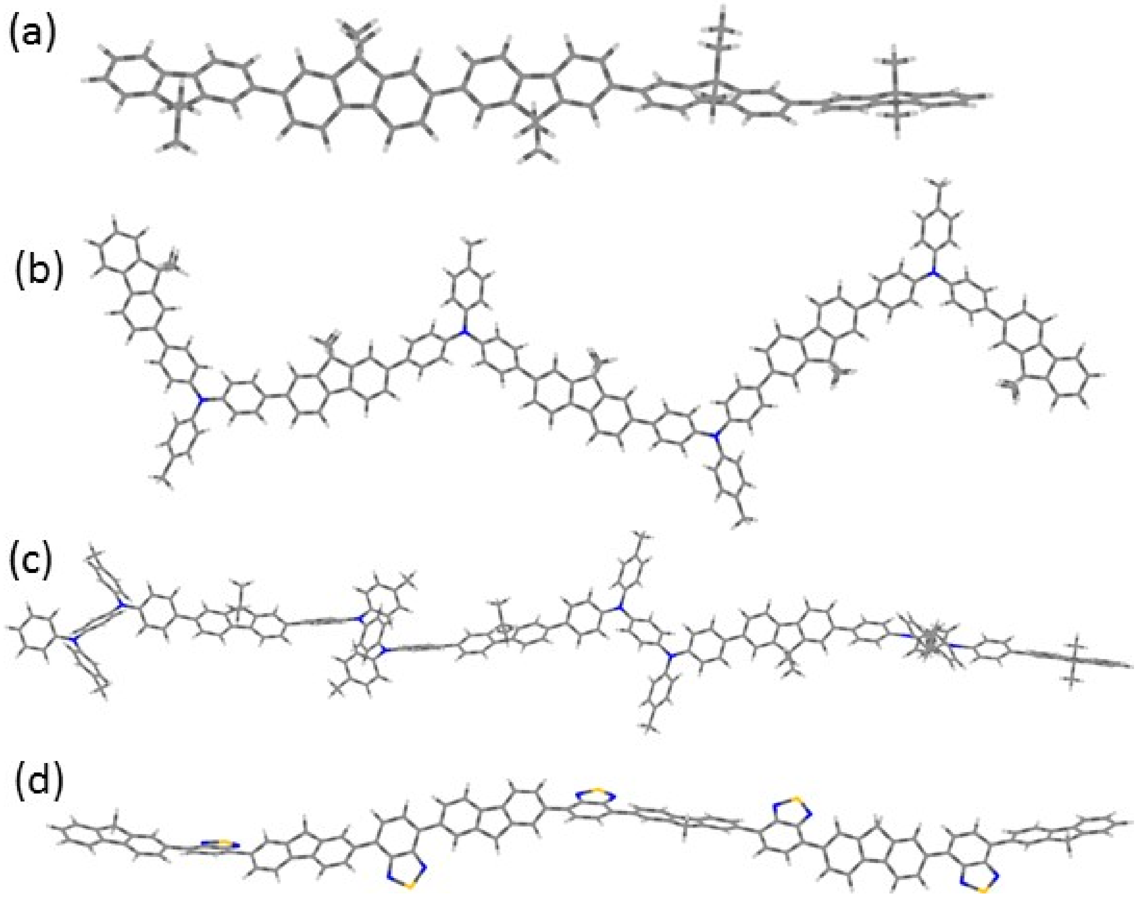

Figure S1: Sketch of the molecules used in the calculations, here in their optimised ground-state geometries: (a) Fluorene pentamer, (b) TFB with 5 fluorenes and 4 TFB units, (c) PFB with 4 fluorenes and 4 PFB units (d) F8BT with 5 fluorenes and 4 BT units.

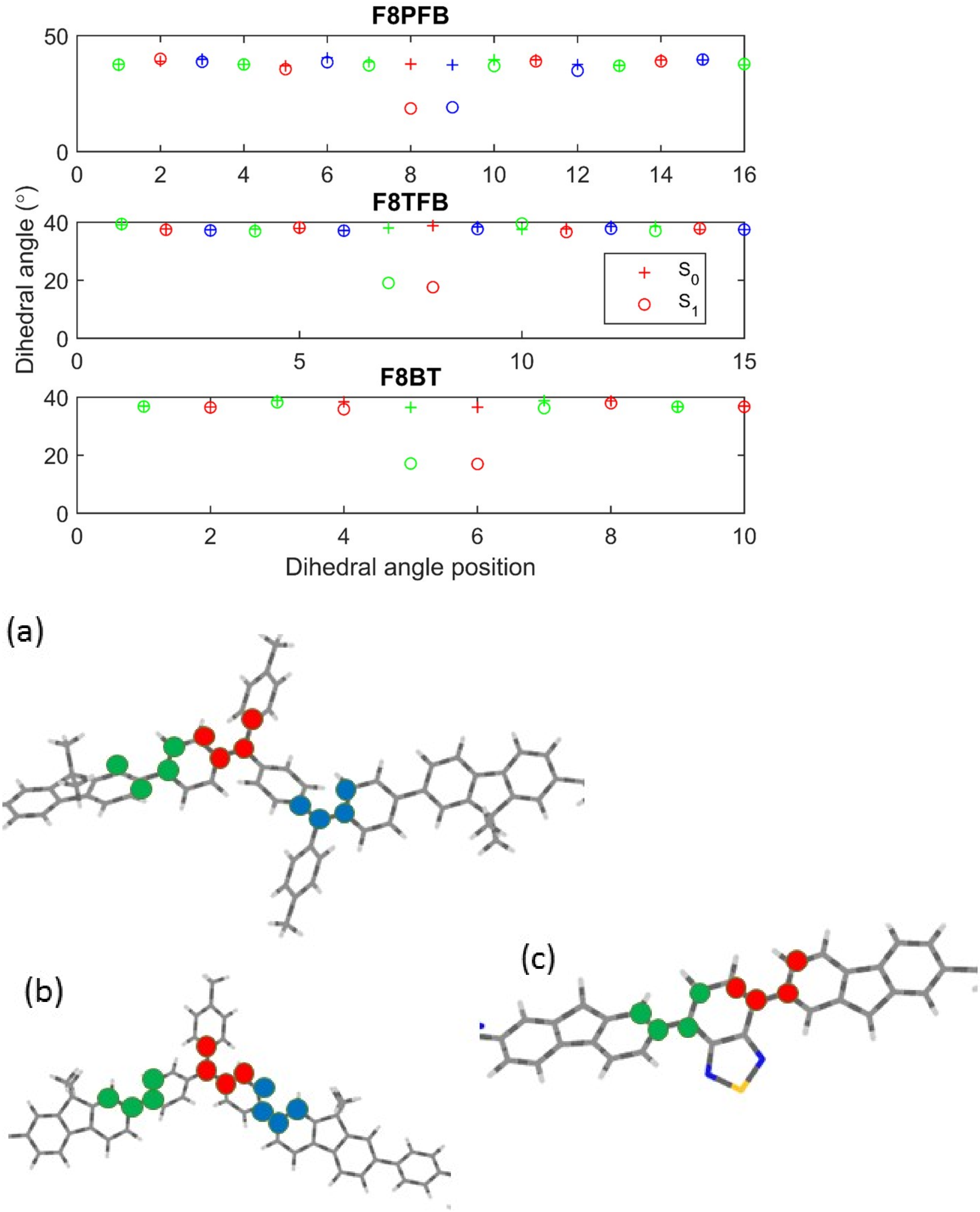

Figure S2: Dihedral angles along the chain of the oligomers we studied, calculated from arrangements of atoms like the ones highlighted in either green, red or blue, in (a) F8PFB, (b) F8TFB and (c) F8BT. Black crosses correspond to molecules in the ground-state geometries (S_0), and red circles to molecules in the excited-state geometries (S_1). We notice that in F8PFB (TFB) the molecule gets planarised in the centre between two PFB (TFB) units, whereas in F8BT, the central BT unit gets planarised with respect to its two surrounding fluorene units.

We have also investigated the effect of including solvent and adding dispersion correction for smaller oligomers than those presented our main manuscript (the fluorene pentamer (F5), an F8BT oligomer made of 3 BT and 2 fluorene units, an F8TFB molecule made of 2 TFB and 3 fluorene units and anF8PFB molecule made of 2 PFB and 3 fluorene units).

The solvent, toluene, was modelled using the polarizable continuum model (PCM) for ground-state and excited-state geometry optimisations, and then for the subsequent ESA calculations with ATDA-TDDFT. The results are presented in figure S3. Including toluene increased the main ESA peak energy by at most 70 meV (F5 in the relaxed S_1 geometry), corresponding to a change of less than 5%, and changed the oscillator strength of the main peak from 2.06 to 2.22 in the worst case (F8-TFB-F8-TFB-F8 in the relaxed S_1 geometry), or only a 7% change. We believe these changes are small enough not to materially alter any of the results we presented –note that due to the extra computational effort which would be involved, it is impractical to calculate the ESA spectra for the long oligomers presented in our main article with solvent.

To check the effect of dispersion correction, we optimised both the ground-state and excited-state geometry using the dispersion correction GD3BJ. Running a TD-DFT calculations on these optimised geometries led to no difference in the results, as can be seen in figure S3. This validates our choice of neglecting dispersion correction for the calculations presented in the main manuscript.

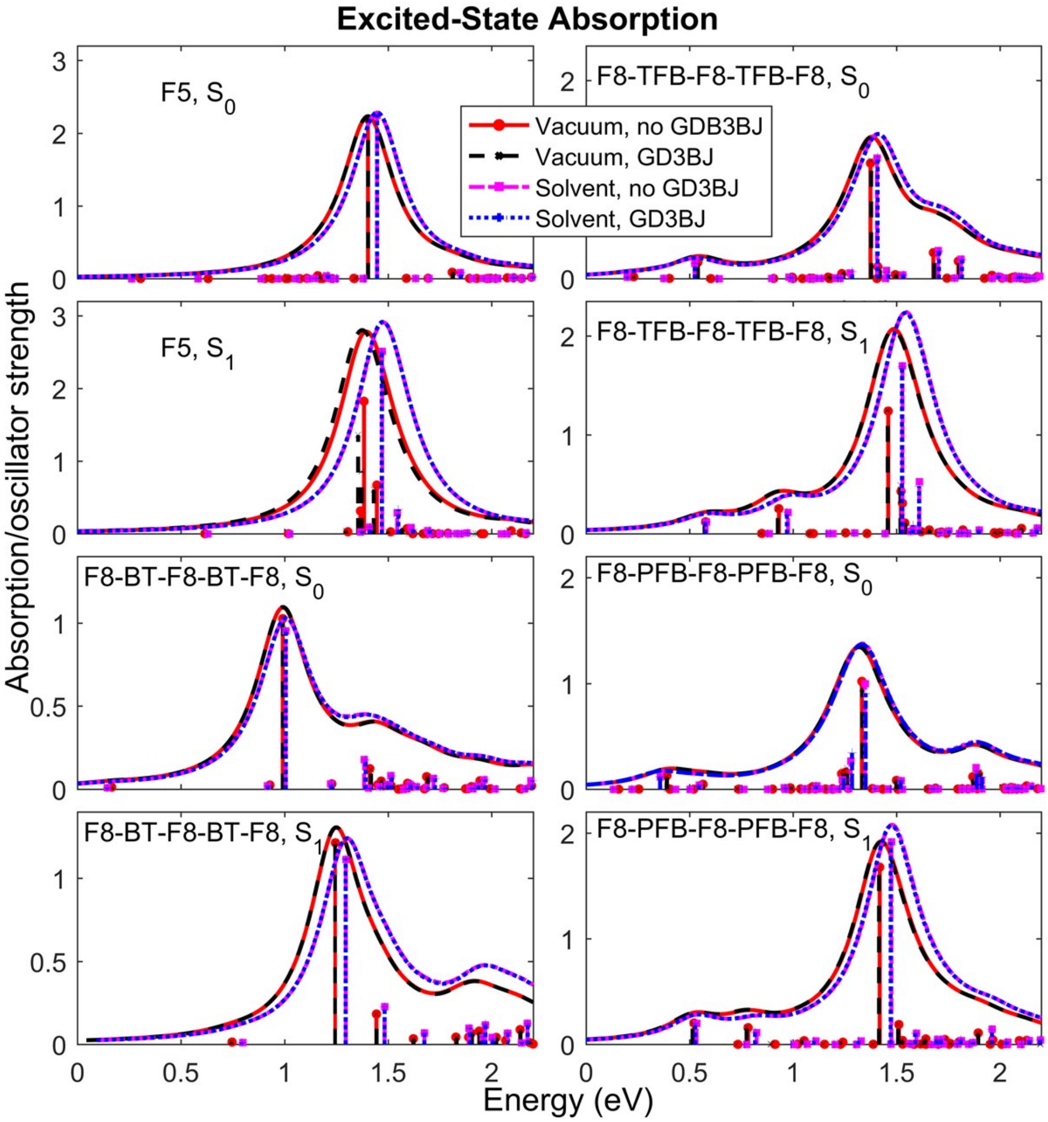

Figure S3: ESA spectra results for smaller oligomers than those presented our main manuscript. We used CAM-B3LYP 6-31G for all calculations. The red curve corresponds to the level of theory used in our main manuscript: calculations in vacuum and without dispersion correction. We added solvent (toluene) through the PCM model for the results given by the magenta and blue curves. The dispersion correction GD3BJ was used for geometry optimisations in the results presented by the black and blue lines.*

Bibliography

1. S. Schumacher, A. Ruseckas, N. A. Montgomery, P. J. Skabara, A. L. Kanibolotsky, M. J. Paterson, I. Galbraith, G. A. Turnbull and I. D. W. Samuel, *The Journal of Chemical Physics*, 2009, **131**, 154906.