Note on DFT calculations

DFT calculations were carried out using the ADF suite of programs. Both geometry optimsation and property calculations were carried out using the B3LYP functional (20% Hartree-Fock exchange) and the ADF double-ζ, single polarisation function DZP basis set. This is comparable to the commonly used 6-31g* basis set. A 'small' frozen core was employed for the geometry optimizations. Calculations of the electronic spectra were carried out by TD-DFT using the EXCITATION modules implemented in the ADF program and were based on the optimized geometries, with no frozen core. The EXCITEDGO module was used to calculate geometries of the first excited states, ground-to-excited state dipole moment changes can be found by subtracting the ground state dipole moment from the excited state dipole moment. Solvent (acetonitrile) was introduced using COSMO with Klamt atomic Radii. The subkey NOCSMRSP was applied to prevent induced electronic charges (which respond on a much slower timescale than electronic excitations) from influencing COSMO surface charges, together with the ALLPOINTS key.

The files provided comprise a pdf showing the frontier orbitals calculated for each compound, csv files for the computed spectra, and the adf output files for geometry optimisations, UV-vis spectra calculations, and excited state geomery optimisations. The output files list, as relevant, cartesian coordinates, transition energies, orbital-to-orbital transitions, etc. The computed spectra have been exported with the energy axis in nanometres, with narrow lines at the computed transition energy.