Computational lab:

Excited States of Donor-Acceptor Materials

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1 Introduction

In this report, a set of organic donor-acceptor (D-A) molecules will be investigated. The molecules will be investigated through ground state optimization and electronic structure calculations. Every structure and plot from the results will not be included but selected examples will be showcased.

2 Methodology

Electron donors and acceptors are characterized by their high HOMO and low LUMO levels respectively. An advantage of organic molecules in applications such as photovoltaics and light-emitting diodes is their ability to be tuned and optimized for different electronic properties. Molecular modification can be done by combining donor and acceptor molecules to a D-A, it can also be done by attaching a substituent group. An electron donating group (EDG) can be attached to increase the electron density of the core, while an electron withdrawing group (EWG) can be attached to decrease the electron density of the core.

In this report we investigated the donor unit 2,2'-bithiophene (2T) with and without substituent groups ($-NH_2$, $-NO_2$). Two acceptor units and the D-A combinations were investigated, namely tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ). The molecules in question is presented in figure 1. For each molecule 4 tasks were conducted: 1. ground-state geometry optimization, 2. electronic structure calculation of the ground-state geometry, 3. excited-state geometry optimization, and 4. excited-state electronic structure calculations.
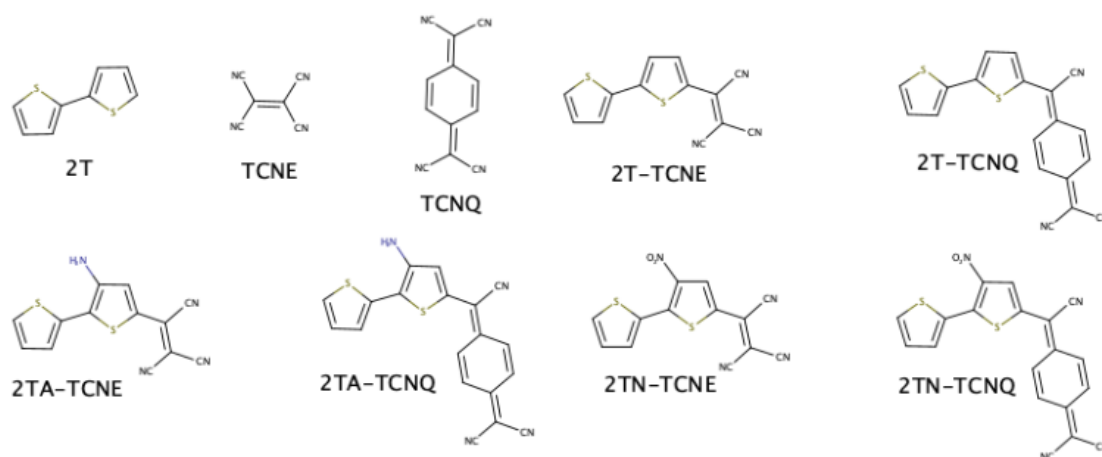

Figure 1: Structure of the investigated donor, acceptor, and donor-acceptor molecules.

3 Data analysis and Discussion

3.1 The ground-state geometry of the D-A molecules

From the data analysis of the ground-state geometry a table of the dihedral angles between the thiophenes in the donor unit and the dihedral angles between the donor and acceptor units was compiled in table 1.

Table 1: Dihedral angles for donor-acceptor planes and thiophene units in the donor for the different D-A units.

Molecule	Donor - Acceptor		Thiophenes in Donor	
	Measured atoms	Dihedral angle	Measured atoms	Dihedral angle
2T-TCNE	C6-C8-C9-C10	184.6°	C11-C12-C16-C18	173.7°
2T-TCNQ	C6-C8-C9-C10	180.6°	C10-C11-C18-C20	184.3°
2TA-TCNE	C7-C8-C9-C10	175.4°	C3-C4-C5-C6	220.3°
2TA-TCNQ	C6-C8-C9-C10	173.3°	C11-C12-C18-C20	224.5°
2TN-TCNE	C14-C13-C12-C11	204.8°	C10-C6-C4-C2	175.2°
2TN-TCNQ	C7-C8-9-C10	202.6°	C3-C4-C5-C6	154.4°

From the results it can be concluded that the substituents affect the geometric parameters. The substituent with the greatest affect on the donor-acceptor angle is the 2TN. Looking at the dihedral angle between the thiophenes, the 2TA is the substituent that cause the largest change in dihedral angle. This goes for the compounds with TCNE as the acceptor, as well as the ones having TCNQ as the acceptor. Interestingly adding a substituent group will twist the molecule for both angles resulting in a geometry which is less planar.

3.2 HOMO and LUMO orbitals and energies

In Figure 2, the HOMO and LUMO levels of the D-A 2TN-TCNE are visualised. It can be seen the HOMO orbitals are mainly localized at the donor (D) and the LUMO orbitals on the acceptor (A). This is the same pattern across the different D-A molecules. The separated D and A fragments show a change in the shape of the orbitals. But there is not a distinct localization difference between the HOMO and LUMO as seen in Figure 3. The separated D fragments have high HOMO energy levels and the A fragments have low LUMO energy levels. By combining the D and A fragments the energy levels of the D-A unit are changed to be in between the LUMO and HOMO of the separated molecules, as displayed in Table 2. The D-A molecules with TCNE as the acceptor has a larger energy gap compared to the D-A molecules with TCNQ as the acceptor. TCNE on its own has an energy gap which is almost twice as large as TCNQ. The D-A molecules with the unsubstituted 2T as the donor have very similar HOMO levels, even though TCNE on it own has a much lower HOMO than TCNQ.
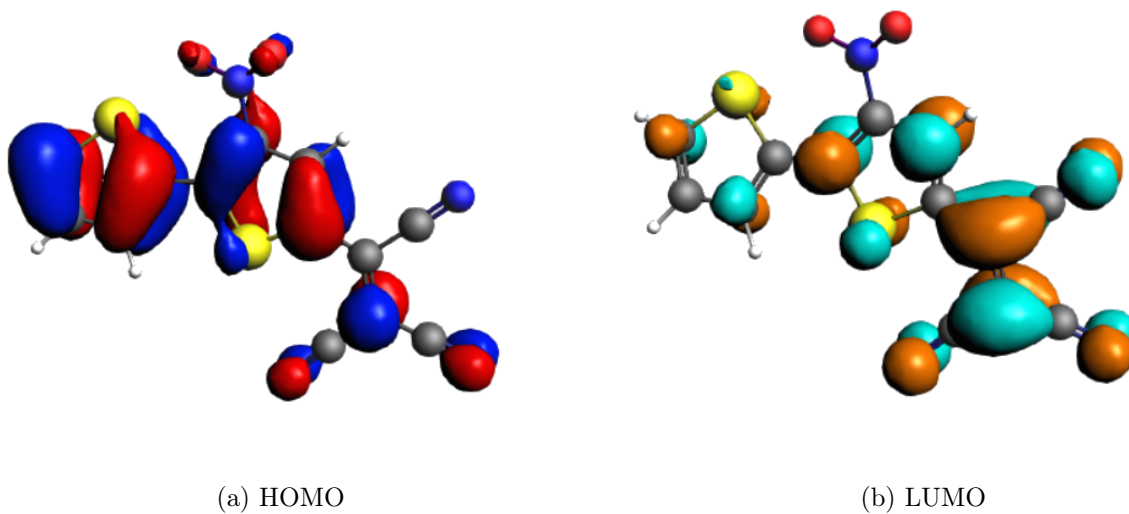
(a) HOMO

(b) LUMO

Figure 2: HOMO and LUMO orbitals of 2TN-TCNE after ground-state optimization.
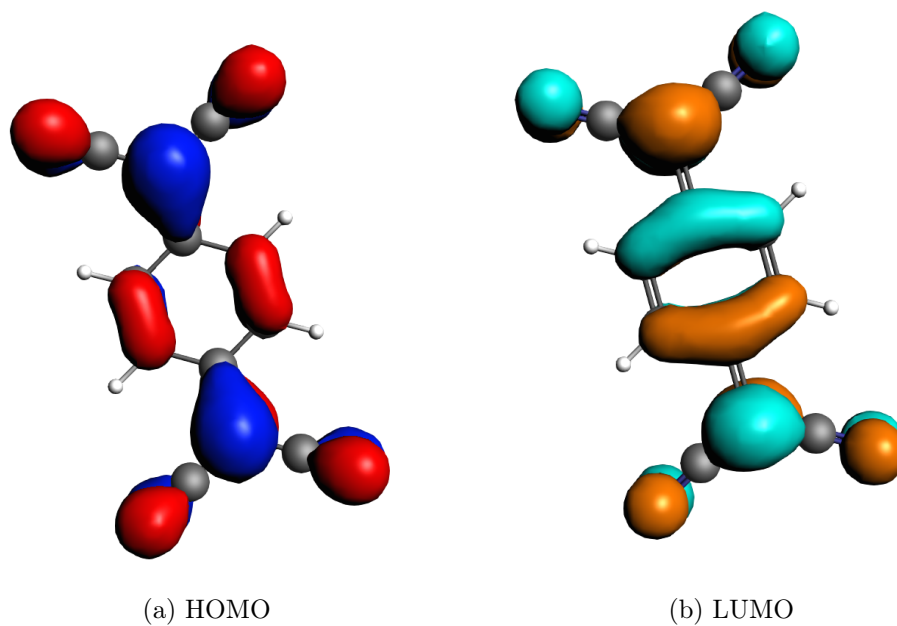

(a) HOMO

(b) LUMO

Figure 3: HOMO and LUMO orbitals of TCNQ after ground-state optimization.

By adding different substituents on the D-A molecule we can appreciate a shift in the HOMO - LUMO levels. Namely by adding an EDG the energy levels will be shifted to lower energies (downwards in the molecular orbital diagram), whereas by adding an EWG the energy levels will instead be shifted to higher energies (upwards). As the TCNE has a lower LUMO than TCNQ, the energy gap will be slightly larger for the D-A units were TCNE is used as the acceptor. Seeing as the importance for the acceptor in a D-A unit is the LUMO level and not the HOMO level, the large difference in HOMO levels between the two acceptors will not have a significant effect when comparing the energy gap of the combined D-A molecule.

Table 2: Energy levels for the HOMO and LUMO orbitals and the energy gap for the investigated molecules.

Molecule	HOMO (eV)	LUMO (eV)	Energy gap (eV)
2T	-5.445	-2.548	2.897
TCNE	-9.033	-6.343	2.690
TCNQ	-7.506	-6.083	1.423
2T-TCNE	-6.514	-4.868	1.646
2T-TCNQ	-6.554	-5.039	1.515
2TA-TCNE	-6.088	-4.756	1.332
2TA-TCNQ	-5.915	-5.007	0.908
2TN-TCNE	-6.960	-5.274	1.686
2TN-TCNQ	-6.542	-5.427	1.115

3.3   Electronically excited states

The absorption spectra of the separated D and A molecules 2T, TCNE and TCNQ are plotted in Figure 4. As visible light appear at wavelengths between 400-800 nm, the graph shows that the absorption spectra of 2T and TCNE are completely outside it. TCNQ are partly within the visible light spectra, but only absorb the shorter wavelengths.
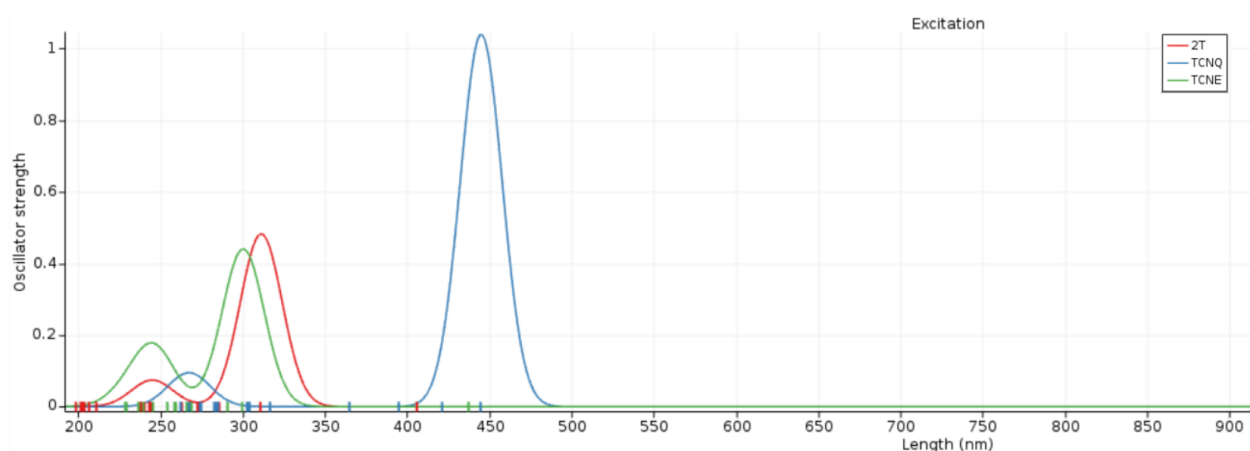

Figure 4: Adsorption spectra for the donor and the two acceptors

For the donor-acceptor molecules, whose absorption spectres have been plotted in Figure 5 and 6, the absorption range becomes wider. Using TCNQ as the acceptor unit allows for a wider absorption spectra with excited states between 250 nm and 750 nm compared to TCNE which spans the range of 250 nm to 600 nm. This is reasonable as it follows the calculated excited states from the individual spectra of TCNE as it absorbs fewer and shorter wavelengths. As for the substituents, the 2TA is the donor unit causing the widest absorption spectra.
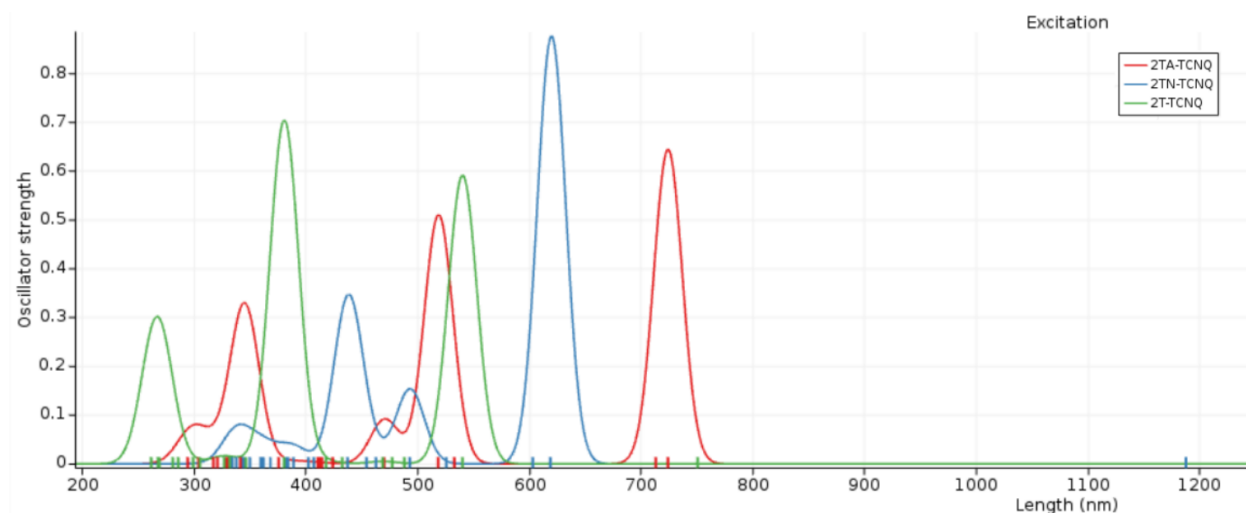

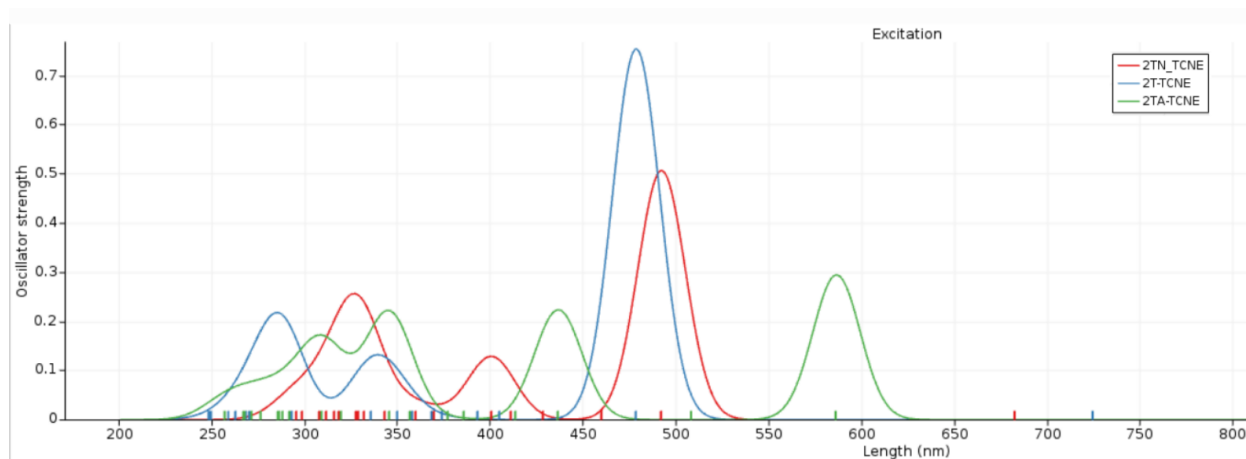Figure 5: Absorption spectra using TCNQ as acceptor

Figure 6: Absorption spectra using TCNE as acceptor

When we compare the HOMO/LUMO energy levels to the absorption spectra, we notice the D-A molecules using TCNQ as the acceptor have a lower LUMO level compared to the TCNE D-A molecules and the first excited states are also lower in energy than the TCNE molecules.

When investigating the lowest lying excited singlet and triplet states it was noted the transition was dominated by the HOMO to LUMO transition. for S0-S1 and S0-T1 when plotting the orbitals corresponding to the excitation in a D-A molecule we see characteristics of a charge-transfer as shown in Figure 7, this is the same character we observed in Figure 2 where the charge is transferred from the donor to acceptor part of the molecule, this creates a large change in the dipole moment. For the separated D and A molecules we observe characteristics of a local excitation as the shape of the orbitals is changed but the charge is not transferred from one part of the molecule to another shown in Figure 8. This is the same character we see in Figure 3.
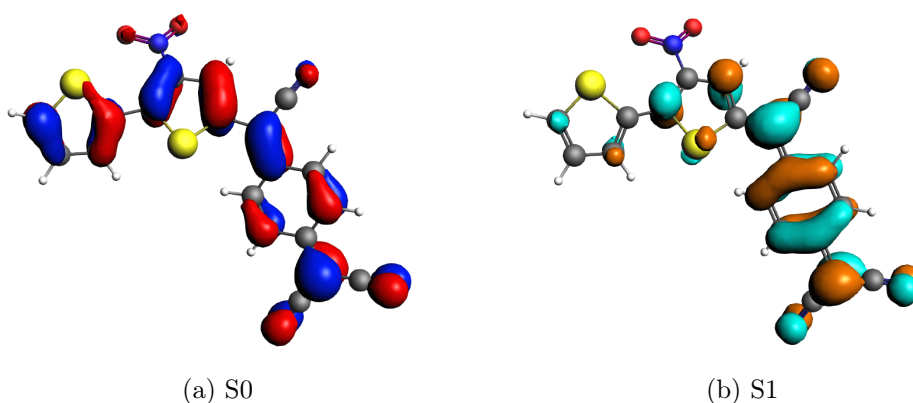

(a) S0   (b) S1

Figure 7: S0 and S1 orbitals of 2TN-TCNQ.

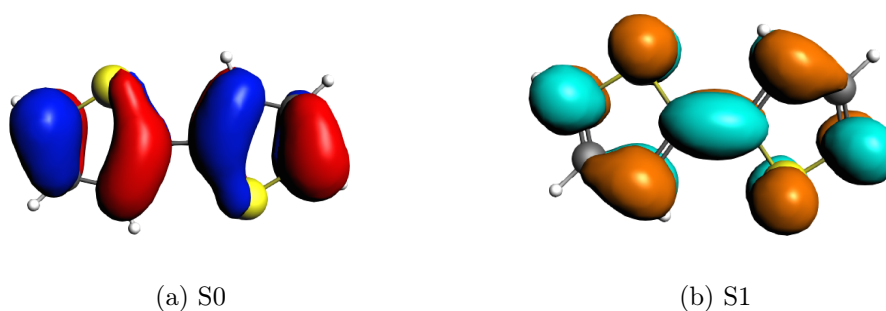
(a) S0   (b) S1

Figure 8: S0 and S1 orbitals of 2T.

For the HOMO-LUMO gap we noted adding an EDG the energy gap was smaller between the HOMO and LUMO orbitals compared to adding an EWG, it is the same pattern we see in the energy gap between the lowest lying singlet-singlet and singlet-triplet gaps across the D-A molecules.

3.4   Geometry relaxation in the excited states

After performing geometry optimization for the excited states with vibrational relaxation, we did not notes any major changes in the geometry compared to the geometry in the ground-state. This could be because the geometry optimization for the excited-state used the ground-state calculations as the starting point. Another possible explanation is that the original ground-state optimization started with an almost planar structure and got stuck in a local energy minimum thus the geometry optimization of the excited state could get stuck in the same position and energy minimum.

The relaxation has an effect on the excited states. Generally the energy of the first singlet-singlet (S1) is lower, i.e. shifted to longer wavelengths, this is true across the molecules. The magnitude of the effect is different depending on the molecule. The character of the orbital transitions were largely unchanged by the relaxation, for the lowest lying states the S0-S1 and S0-T1 is still dominated by the HOMO and LUMO orbitals. For the D-A molecules it still shows characteristics of an intramolecular charge-transfer, while for the separated D and A molecules show characteristics of a local excitation. The relaxation increased the singlet-singlet to singlet-triplet gap, lowering the energy of the first singlet-triplet more than it lowered the energy of the lowest lying singlet-singlet. The difference between the absorption and emission is illustrated in Figure 9 and 10
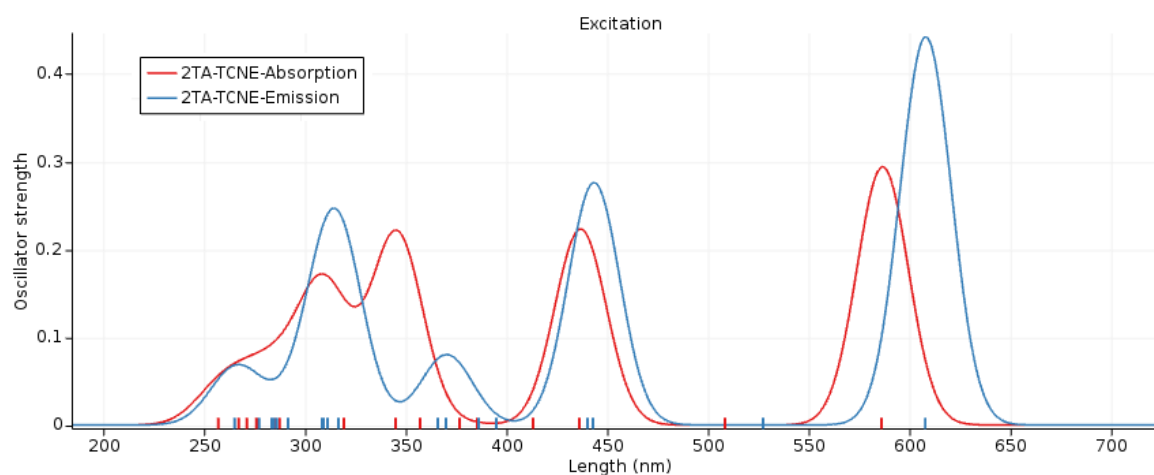

Figure 9: Absorption and emission spectra of 2TA-TCNE, showing a shift towards longer wavelengths for the S1 and S2 states.
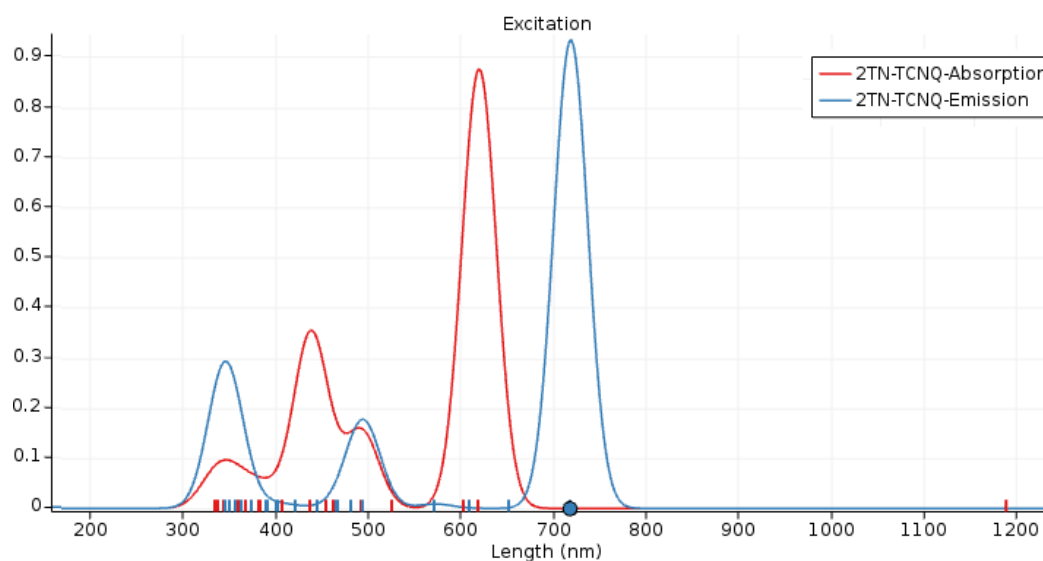
Figure 10: Absorption and emission spectra of 2TN-TCNQ showing a shift towards longer wavelengths for the S1 state.

The Stokes shift can be seen in Figure 9 and 10 as the difference between the peaks of the excited singlet states. We see a greater difference in the overlap between the absorption and emission spectra for the D-A molecules with TCNQ as the acceptor compared to D-A molecules with TCNE as the acceptor molecule. Given a larger overlap between the absorption and emission spectra for the excited state will have a higer possibility of diffusion in a material via the Förster mechanism, will lead to the assumption that D-A molecules with TCNE as acceptor will be more probable to diffusion from the Förster mechanism than the investigated TCNQ D-A molecules.

3.5   D-A materials and solar energy harvesting

In photovoltaics donor and acceptor materials get utilized in the p-n interface to split an exciton. A good donor material is categorized by a high lying HOMO and high photon absorption while a good acceptor material is categorized by a low lying LUMO. Organic D-A materials is often utilized as a donor material in organic photovoltaics because they have a narrower bandgap between HOMO and LUMO, as shown in Table 2 compared to the pure donor material, this results in better light harvesting since more photons have the required energy to get an electron to an excited state. It is also important that excitons can diffuse in the D-A material to reach the p-n interface.

When looking at the investigated molecules the HOMO-LUMO energy gap gives an indication of how well a material will be able to absorb photons. The wavelength of the excited states is another important factor since it should be in the visible light spectrum for applications in solar energy harvesting. Based on the energy gap 2TN-TCNQ and 2TA-TCNQ would make for better absorbers than 2T-TCNE for eksample.

A common metric for how well a solar cell performs is the power conversion efficiency, which compares the amount of power coming out of the cell with the power going into the cell. Since the absorbed photon is eventually converted to energy it is important to keep in mind how vibrational relaxation will result in less available energy compared to the energy of the original photon. This is related to the difference between the HOMO of the donor and LUMO of the acceptor in the cell since this will determine the open circuit voltage of the cell. So while you want donor material with a high HOMO and an acceptor with a low LUMO it is a tradeoff between kinetics and driving force of the dissociation of excitons and voltage of the cell. So a donor material with a high HOMO will result in a lower voltage and thus lower energy/power conversion but better exciton dissociation. It is thus important to select materials which will provide a sufficient driving force without compromising the output power of the cell.