

Fullerene-complexes for photovoltaic devices: CNDOL approaches for describing electronic properties

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Donor-acceptor organic heterojunctions are promising materials for the development of photovoltaic devices. Thiophene oligomers are the basis of the most efficient organic heterojunctions and fullerene is considered a very efficient electron acceptor.¹

We applied the approximate quantum chemical Hamiltonian (CNDOL)² to investigate the electronic properties of dyes complexed with fullerene (C₆₀) in the gas phase. All ground-state geometries were optimized with density functional theory using the ω B97X-D³ functional and 6-31G(d) basis set.

Table 1. Calculated CNDOL spectral values of thiophene oligomers and their fullerene complexes.

Thiophene-oligomer	E (eV)	E ^{CE} (eV)	C ₆₀ /thiophene-oligomer	E (eV)	E ^{CE} (eV)
N6			N6-C₆₀		
S1	3.02 ^{vs}	2.47	S1	2.90 ^f	2.79
S2	3.77 ^{vw}	2.13	S2	2.91 ^f	2.60
S3	4.45 ^s	2.12	S3	2.91 ^f	2.72
N10			N10-C₆₀		
S1	2.85 ^{vs}	1.92	S1	2.91 ^f	2.42
S2	3.22 ^{vw}	1.65	S2	2.92 ^f	2.74
S3	3.66 ^s	1.66	S3	2.92 ^f	2.68

The results indicate that the greatest calculated electron population appears localized over the S atoms in the polymer chain at the ground state, favoring a bond-length alternation as reported in other similar systems.

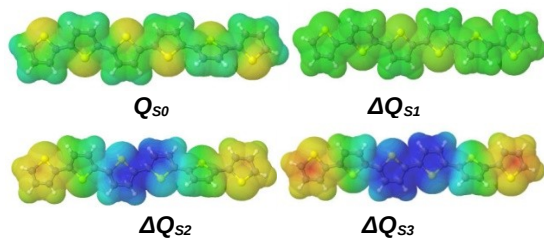


Figure 1. Electron charge maps of the CNDOL calculated lowest energy states for thiophene oligomer (N6).

In the excited states, charge separations across the molecular lengths increases from S1 to S3.

For fullerene complexes in the ground state, the electron charge appears located in the oligomer as the donor part. After the excitation, the first excited state shows a slight charge transfer character from the oligomer donor to the acceptor-playing fullerene. The excited state charges tend to delocalize over the whole complex for thiophene chains, opening the possibility of hot-exciton dissociation processes, where the charge is separated still in the initially excited states.

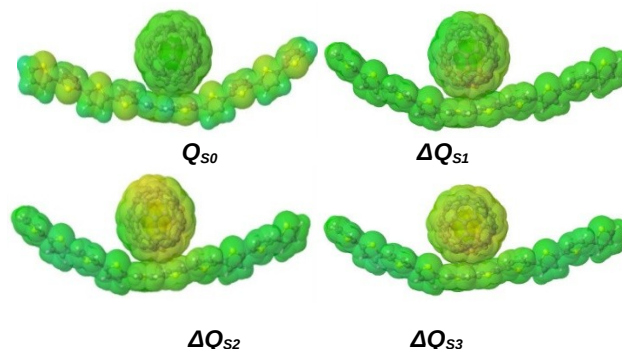


Figure 2. Electron charge maps of the CNDOL calculated lowest energy states for C₆₀/thiophene oligomer (N10-C₆₀).

The whole present modeling shows that CNDOL methods are a valuable tool for defined structure related electronic properties and for prediction the performance of donor-acceptor materials, mostly when the size of the polyatomic system. The photoexcitation of the donor followed by an electron-charge transfer to the acceptor was obtained and illustrated by means of the electron density maps of the systems.

Index Terms: fullerene, thiophene oligomer, electronic structure, excited state, organic photovoltaic.

- [1] Piotrowski, P., *et al.* "Mono- and Di-Pyrene[60]Fullerene and [70]FullereneDerivatives as Potential Componentsfor Photovoltaic Devices". *Molecules* (26), 1561, 2021.
- [2] Montero-Cabrera, L. A., *et al.* *Chem. Phys.* (127), 145102, 2007.
- [3] Chai, J. D.; Head-Gordon, M., "Systematic optimization of long-range corrected hybrid density functionals" *J. Chem. Phys.* (128) 084106-1, 2008.