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We present a computational investigation on the effect of halogen substitution on the electronic, optical, and transport properties of the nucleobase guanine. We performed all-electrons Density Functional Theory and Time-Dependent Density Functional Theory calculations with a localized Gaussian basis-set and the hybrid exchange-correlation functional B3LYP. Results obtained with the above level of theory are in good agreement with the available experimental data for the unsubstituted molecule. We report and discuss the effect of functional substitution on several physico-chemical properties such as: electron affinities, ionization energies, fundamental energy-gap, optical absorption, exciton binding energy and molecular reorganization energies for holes and electrons.

Introduction

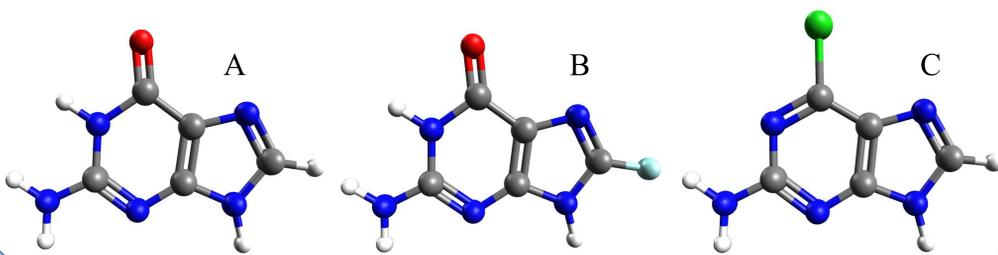
DNA and RNA contain genetic information of all living systems and have a crucial role in the development and functioning of all living organisms. Helical nanowires of DNA and RNA molecules have been regarded for long time as molecules with the sole purpose to store genetic information.

On the other hand nowadays, they are also considered as promising candidates for molecular devices toward a further miniaturization of electronic technology. [1,2]

The study of electronic and optical properties of nucleobases has attracted therefore increasing attention.

Precise control of the electronic properties, at the molecular level, is of great importance in order to improve the device performances. This can be achieved by modifying the (bio)molecules with specific atomic substitutions. [3]

The present work is devoted to the computational analysis of the electronic, optical and transport properties of Guanine (**Gua**, Fig. **A**), 8 Fluoro guanine (**8F-Gua**, Fig. **B**) and 6 Chloro Guanine (**6Cl-Gua**, Fig. **C**) (e. g. www.chemicalbook.com) and to the comparison with the available experimental data and other theoretical results.



Computational Details: We performed all-electrons calculations using the hybrid exchange-correlation functional B3LYP in conjunction with a Gaussian localized orbital basis set to expand the molecular orbitals. All the calculations are performed within DFT and TDDFT for ground and excited state properties respectively as implemented in the NWChem code (www.nwchem-sw.org).

Δ SCF Calculations: We computed, via total energy differences, the adiabatic first ionization energy and electron affinity. At the optimized geometry of the neutral molecules we evaluated the vertical ionization energy (IE_V) and electron affinity (EA_V). This enabled the calculation of the quasi-particle corrected HOMO-LUMO gap, which is defined in the Δ SCF scheme as:

$$QP_{GAP} = IE_V - EA_V = (E_{Cat}^{(N)} - E_N) - (E_N - E_{An}^{(N)})$$

where E_N is the total energy of neutral molecules, $E_{Cat}^{(N)}$ and $E_{An}^{(N)}$ are the cation and anion total energies calculated at the neutral optimized geometry.

Molecular Reorganization Energies: An important parameter affecting charge mobility in molecular semiconductors is the molecular reorganization energy λ . This quantity can be computed as the sum of two contributions: [3]

$$\lambda = \lambda_1 + \lambda_2 = (E_c^{(n)} - E_c) + (E_n^{(c)} - E_n)$$

where E_c and E_n are the total energies of the neutral and charged (± 1) molecules at their optimized geometries. $E_n^{(c)}$ is the total energy of neutral system at the charged optimized geometry and $E_c^{(n)}$ is the total energy of the charged molecule at the neutral geometry.

Electronic, Optical and Transport Properties I:

	Gua	8F-Gua	6Cl-Gua	Gua (GW) ^a	Gua (G_0W_0) ^a	Gua (Exp.) ^a
IE_V [eV]	7.85	8.00	8.12	7.81 ^a	7.76 ^a	8.0 – 8.3 ^a
IE_A [eV]	6.62	7.72	7.93	--	--	7.77 – 7.85 ^c
EA_V [eV]	-0.41	-0.32	-0.30	-1.58 ^a	-1.77 ^a	--
EA_A [eV]	-0.38	-0.26	0.07	--	--	--
QP_{Gap} [eV]	8.26	8.32	8.42	9.39 ^{a,b}	9.53 ^{a,b}	--
E_{opt} [eV]	4.89	4.81	4.34	--	--	4.4 – 4.5 ^d
E_{bind} [eV]	3.37	3.51	4.08	--	--	--
λ_h [eV]	0.48	0.56	0.40	--	--	--
λ_e [eV]	0.07	0.10	1.44	--	--	--

Comparison between observables calculated for **Gua** and halogen substitutes (also experiments for pure **Gua** have been reported).

Adiabatic and vertical ionization energies (IE_A , IE_V), adiabatic and vertical electron affinities (EA_A , EA_V), fundamental gaps (QP_{Gap}), first optically active transition (E_{opt}), exciton binding energy (E_{bind}), and molecular reorganization energies for holes and electrons (λ_h , λ_e).

Upon halogen substitutions we observe an increase of the ionization energies (from 2÷3.5 % for the vertical quantities to 17÷20 % for the adiabatic ones) and a rise of the electron affinities (up to 32 %).

The contemporary presence of these effects leads to a small increasing of the quasi-particle gaps for the functionalized compounds (+ 0,7 % for the F and + 2% for Cl) and, as a consequence, to a rise of the exciton binding energies (+ 4 % for the F and + 21% for Cl).

^a Experimental and GW calculated data taken from [4]

^b GW calculations taken from [5]

^c Experimental data taken from: [6]

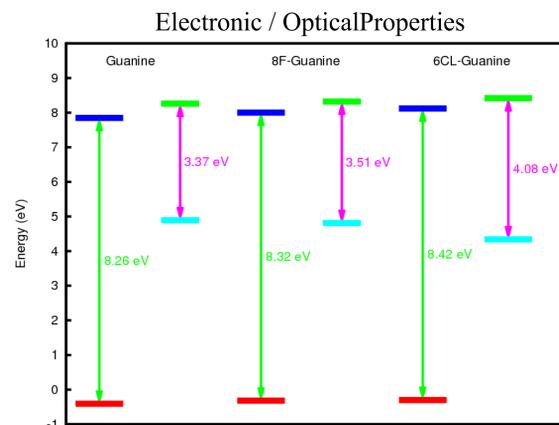
^d Experimental data taken from [7]

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Electronic, Optical and Transport Properties II:

The figure shows **ionization energies** (blue), **electron affinities** (red), **fundamental gap** (green arrows and bars), **optical gap** (light blue) and **exciton binding energies** (purple arrows) for Gua, 8F-Gua and 6Cl-Gua.

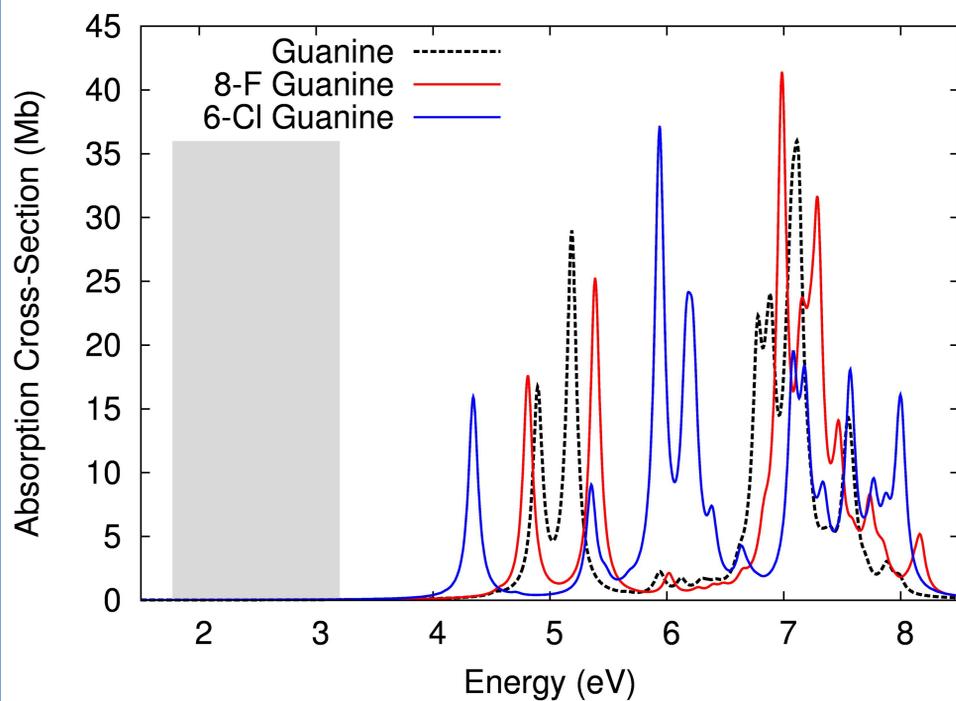


For **Gua**, fair agreement with experimental values (~ 2%) and theoretical (~ 0.5%) ones for the IE_V results. For IE_A the comparison also remains good (~ 15%). (see table also)

The electron affinity of **Gua**, on the other hand, even if correctly predicted to be negative, shows consistent deviations from the available GW results which could be ascribed to the use of the B3LYP exchange-correlation functional [8] and to the specific Gaussian basis-set employed. This explains also the underestimation of the QP_{Gap} values in comparison with the GW ones.

Optical Absorption Spectra:

Comparison between the absorption spectra of Guanine (black dashed line) 8-Fluoro-Guanine (red line), and 6-Chloro Guanine (blue line).



The optical onset is redshifted for both substitutions (F and Cl), with respect to the pure **Gua** case; in particular we found a slight shift (- 0.08 eV) in the case of F, and a larger shift (- 0.55 eV) in the case of Cl. The amplitude of the first absorption peak shows a small reduction with the Cl substitution (- 4.5 %) and a small increase for the F (+4.5 %).

Fluorine substitution maintains up to 9 eV the structure of the absorption spectrum mainly unchanged (with respect to the assembly of the main peaks) while chlorine determines a nearly complete redistribution of the absorption structures.

For **Gua** the first and the second absorption peaks result blue shifted by 0.4 and 0.2 eV respectively in comparison with the experiment [7]. The third large absorption structure results also blue shifted by 0.4 eV as compared with the experimental value [7].

The comparison with other theoretical calculations shows different level of agreement. [7,9]

Conclusions:

The halogen functionalizations determine in **Gua**:

- Lowering of the absorption onset,
- Increasing of ionization potentials and electron affinities,
- Small increase of the quasi-particle gap,
- Raise of the exciton binding energy,
- Variation of the order of ± 16 % for the hole molecular reorganization energies
- Worsening of the electron molecular reorganization energies, in particular for Cl substitution.

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