

Electronic and optical properties of nanometer-sized chromophores in bacterial cellulose

Amit Kumar¹, Roberto Cardia^{2,3} and Giancarlo Cappellini^{2,3*}

¹Department of Mechanical Chemical and Material Engineering, University of Cagliari, Italy

²Department of Physics, University of Cagliari, Italy

³CNR-IOM, UOS Cagliari, Italy

*corresponding author: giancarlo.cappellini@dsf.unica.it



We present a **computational** investigation on the **electronic and optical** properties of the **principal chromophores** found in **bacterial cellulose** (BC). We focus on the three key structures that were isolated from aged BC: (A) 2,5-Dihydroxy-[1,4]benzoquinone, (B) 5,8-Dihydroxy-[1,4]naphthoquinone (C) 2,5-Dihydroxyacetophenone, while (D) p-benzoquinone was used as a reference structure. For all the isolated molecules, we performed all-electrons **Density Functional Theory** (DFT) and **Time Dependent DFT** (TDDFT) calculations with a localized Gaussian basis-set and the hybrid exchange-correlation functionals **B3LYP** and **PBE0**. We computed and analyzed their electronic and optical properties and compare with available experimental data.

Introduction: Bacterial cellulose

Bacterial cellulose (BC) is a biomaterial of great importance, with a wide range of applications, in medicine, pharmaceutical industry, biotechnological devices and in the food and paper industry. The importance of chromophores derived from BC has been suggested in cultural heritage applications [1-3].

Molecule	No. of atoms	Linear dimension (nm)	Volume (Å ³)	No. of rotatable bonds	Polar surface area (Å ²)	logP
A	10	0.6	110.6	0	74.6	-1.41
B	14	0.7	154.6	0	74.6	1.13
C	11	0.6	135.6	1	57.5	1.27
D	8	0.6	94.6	0	34.1	0.56

Table 1 Molecular properties.

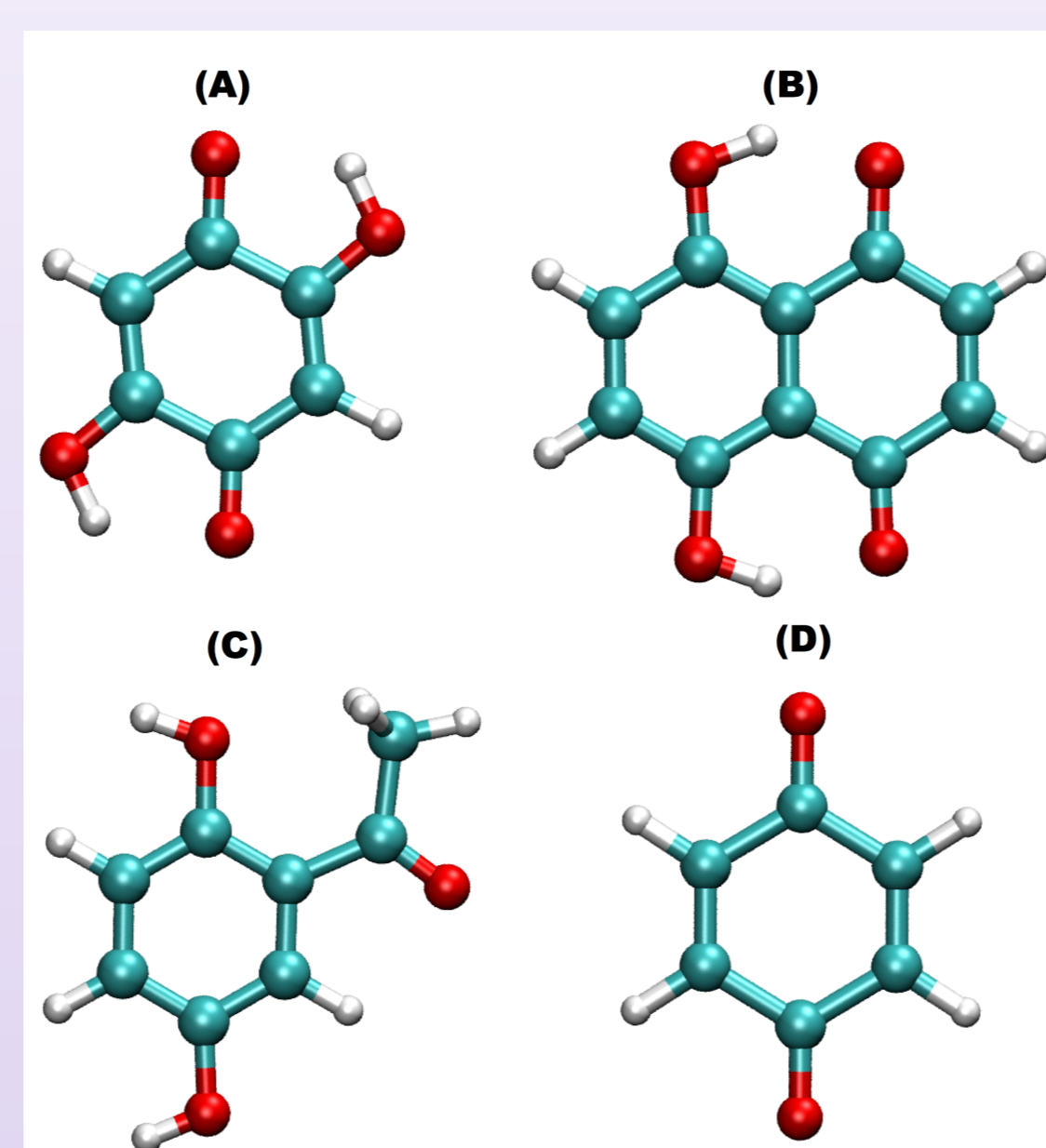


Fig. 1 Molecules under investigation. Molecules represented using ball-and-stick model with oxygen atoms in red, carbon in blue and hydrogen in white.

logP: measure of hydrophobicity [4]
No. of rotatable bonds: flexibility

Computational Methodology

- All-electrons calculations were performed using alternatively hybrid exchange-correlation functionals **B3LYP** and **PBE0**.
- Gaussian localized orbital basis set **6-31G*** for molecules (A), (B) & (D). While **6-311G*** for molecule (C).
- DFT and TDDFT calculations have been done for ground and excited states respectively as implemented in the **NWChem** software(www.nwchem-sw.org).

ΔSCF Calculations: On the optimized geometry of the neutral molecules the vertical ionization energy (IE_V) and electron affinity (EA_V). The quasi-particle was calculated as 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} and E_{an} are the cation and anion total energies calculated at the neutral optimized geometry [5-6].

Solvent effects: Geometry optimized neutral molecules were placed in a **water box** and subjected to 50 ns of **classical molecular dynamics** (MD) simulations, using **NAMD** software [7]. **Stability** during MD was monitored by evaluating **root mean square deviation** (RMSD) fluctuations. Structure of the molecules with a lowest RMSD value was then subjected to TDFT calculations.

Results

1. Electronic and Optical properties

	IE_V (eV)		EA_V (eV)		QP_{Gap} (eV)		E_{opt} (eV)		E_{bind} (eV)	
	B3LYP	PBE0	B3LYP	PBE0	B3LYP	PBE0	B3LYP	PBE0	B3LYP	PBE0
A	10.15	10.3	1.31	1.36	8.84	8.94	4.32	4.5	4.5	4.44
B	9.33	9.47	1.59	1.70	7.74	7.77	2.48	2.56	5.26	5.21
C	8.05	8.05	0.32	0.34	7.73	7.71	3.93	4.05	3.80	3.66
D	9.66	9.77	1.33	1.39	8.33	8.38	4.98	5.12	3.35	3.26

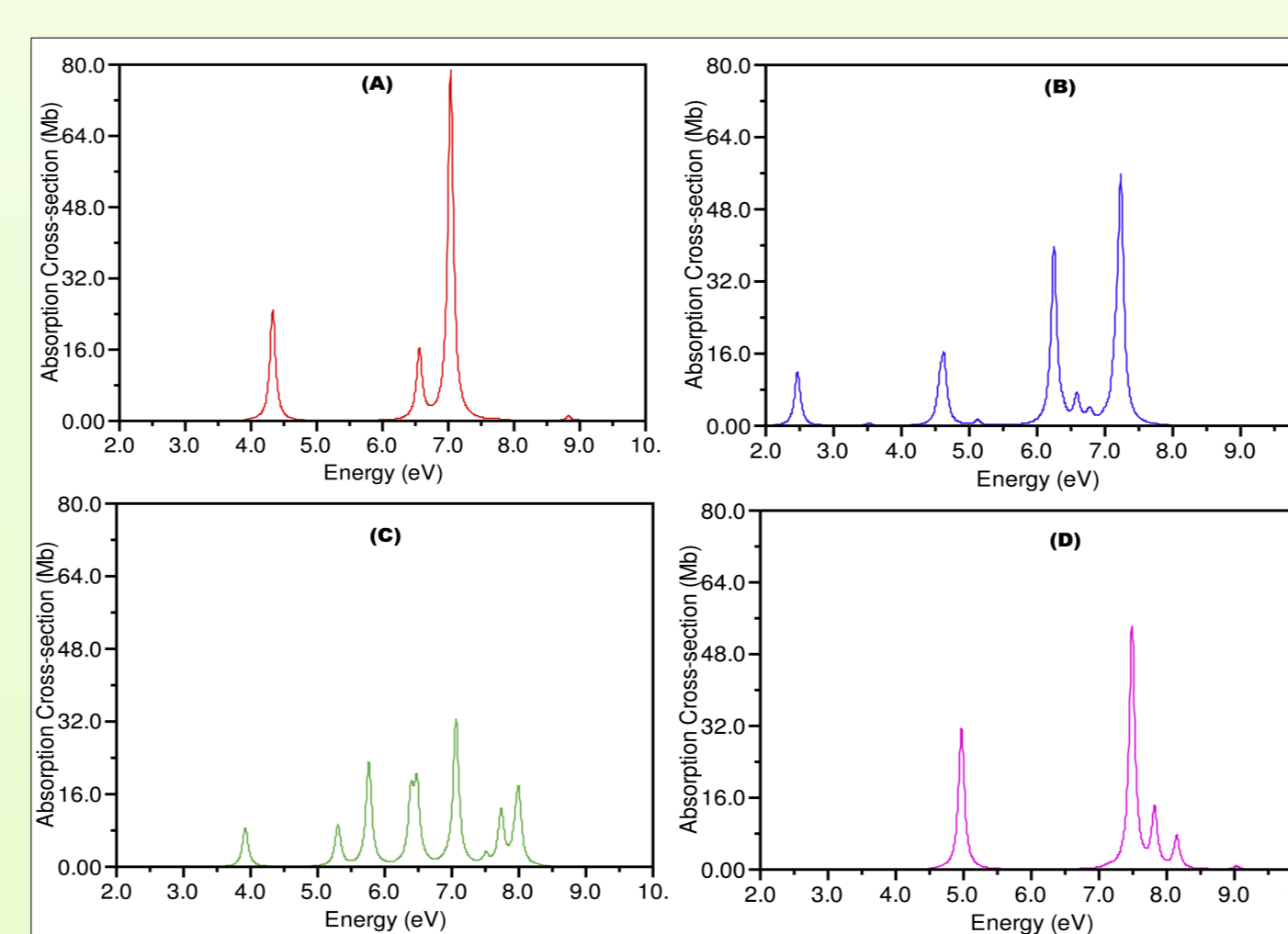
Molecule D experimental data from: <http://webbook.nist.gov> IE_V (9.67 – 10.01) eV EA_V (1.33 – 1.85) eV

Table 2. Comparison between observables calculated using two functionals. (i) B3LYP and (ii) PBE0 (in brown). Vertical ionization energies (IE_V), and vertical electron affinities (EA_V), fundamental gaps (QP_{Gap}), first optically active transition (E_{opt}) and exciton binding energy (E_{bind})

Observables IE_V , EA_V , QP_{Gap} and E_{opt} generally tend towards higher values, while a lower value for E_{bind} for PBE0 functional with respect to B3LYP in all the molecules appears.

2. Optical Absorption Spectra

(i) Isolated molecules



(ii) Molecules in solution

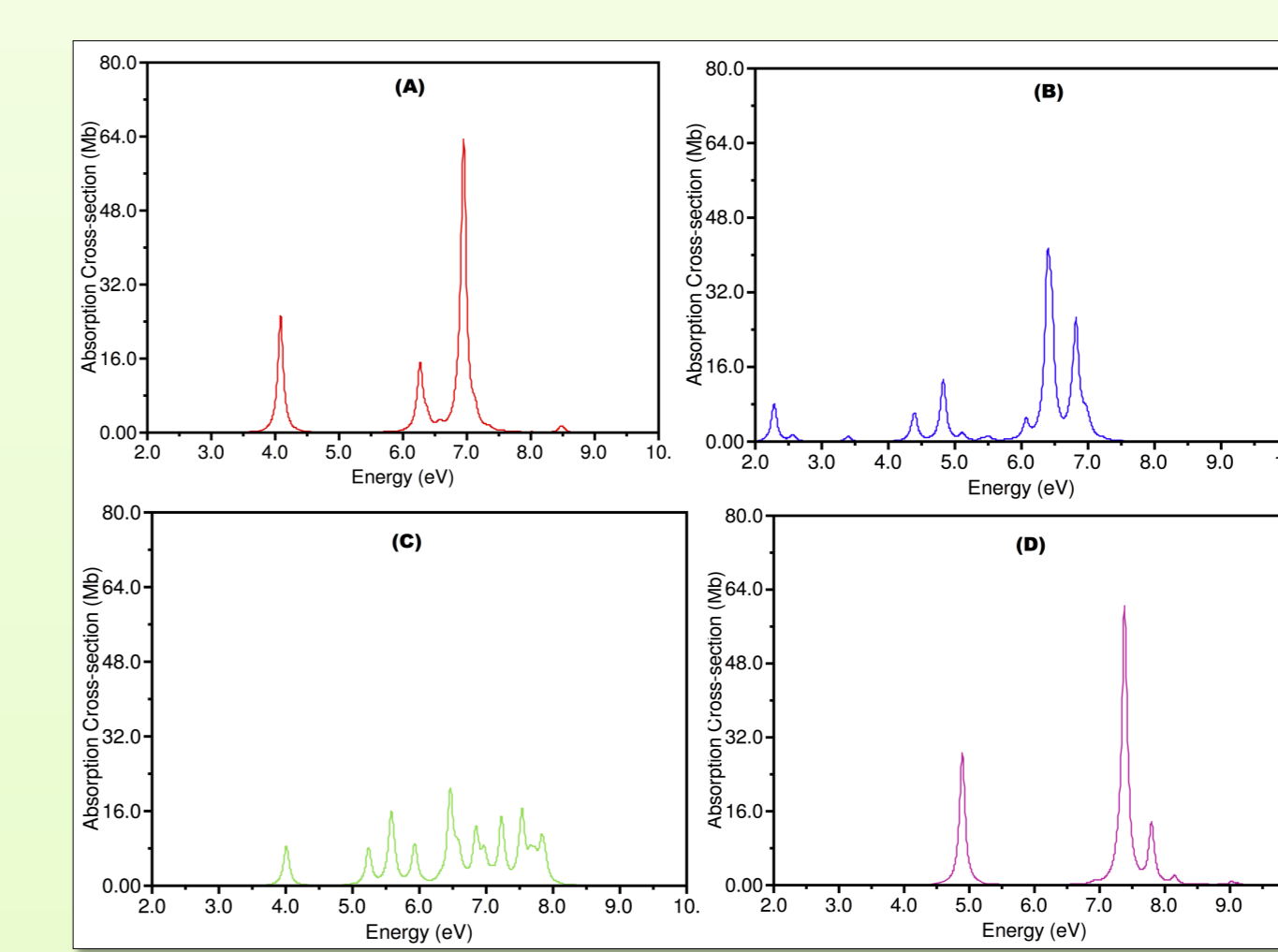


Fig. 2 Comparison of absorption spectra on structures. (i) for isolated molecules and (ii) for molecules in solution using B3LYP functional. (A) (B) (C) & (D) correspond to the four molecules respectively.

- red shift in the absorption spectra with lower value of optical gap (~0.1 eV), that corresponds to first peak and its magnitude (in Mb) with respect to calculations on the isolated molecules
- same number of peaks for molecules A and D
- one additional peak (between 4-5 eV) for molecule B
- two additional peaks (between 5-6 eV and 7-8 eV) for molecule C

3. RMSD

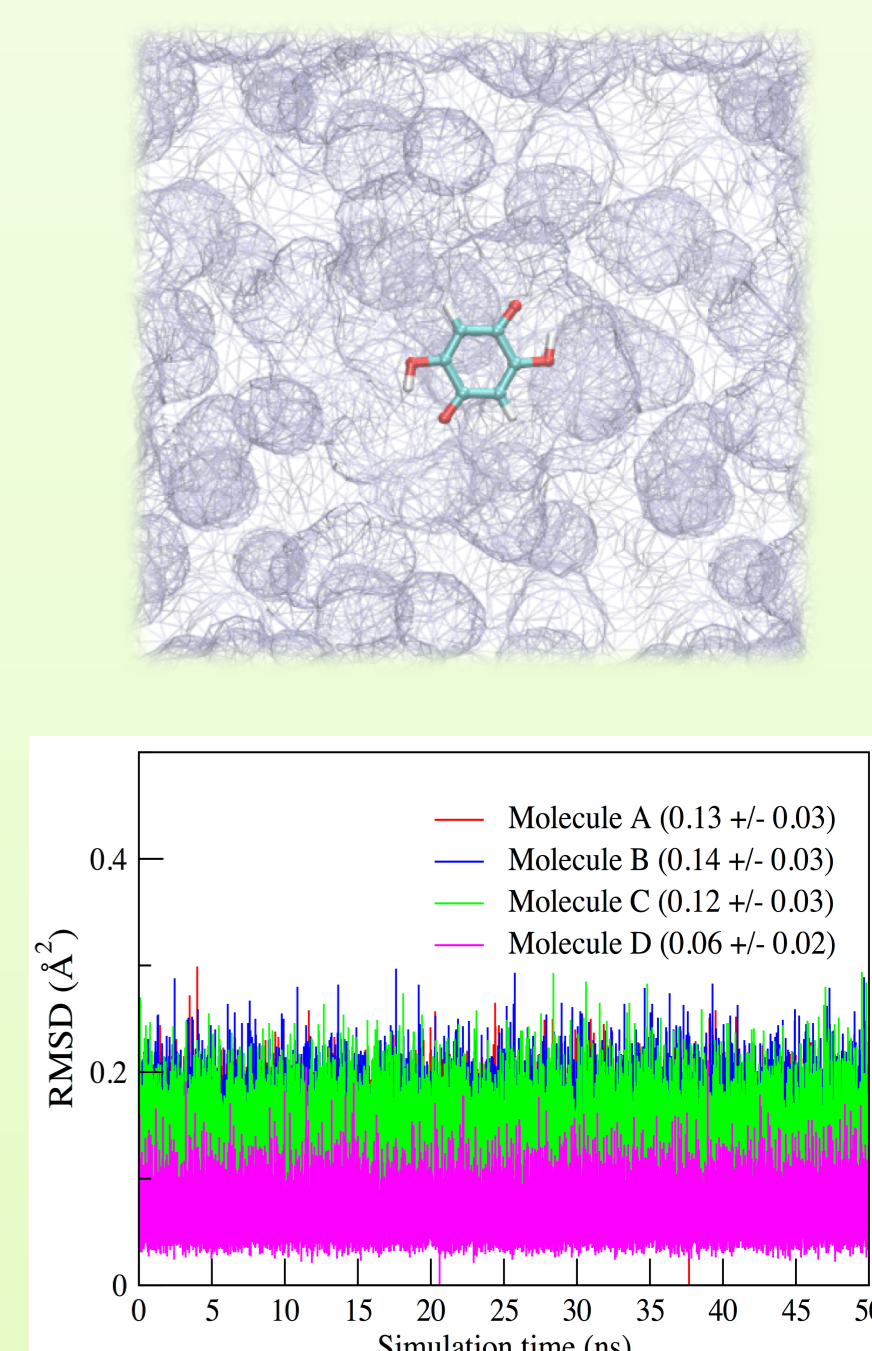


Fig. 3 (top) simulation in water. (bottom) RMSD plot during 50 ns of MD simulations.

Conclusions

- Molecule (A) displays highest values of IE_V (10.15 eV, B3LYP) and QP_{Gap} (8.84 eV, B3LYP)
- Molecule (B) displays highest values of EA_V (1.59 eV, B3LYP) and E_{bind} (5.26 eV, B3LYP)
- Molecule (C) is most flexible (one rotatable bond) and most hydrophobic (logP = 1.27)
- Solvent effect: decrease in magnitude of optical absorption spectra with red shifted peak values

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