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Flavonols - Carbon Nanostructure Hybrid Systems: A DFT Study on the

Interaction Mechanism and UV/Vis Features

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Electronic Supplementary Information

THEORETICAL METHODOLOGY

In order to fulfill the goals of this research doing a rational use of computational resources, different approximations as well as common functionals (for which moderate computational cost are expected) were used.

Isolated Flavonols. Ground states of flavonoids FO-F1 were optimized using B3LYP functional¹⁻³ in combination with 6-31G(d) basis set. B3LYP functional was used because of its ability for describing the ground state properties of a great variety of molecular systems.⁴ Flavonols F1-F3 show several intramolecular H-bonds,⁵ which should determine their behavior in pure state and after adsorption or confinement. Although non-corrected dispersion standard functionals have been useful applied to the description of isolated flavonols,⁶⁻¹² the consideration of dispersion corrections should be recommendable considering the molecular characteristics of flavonols, and thus, B3LYP-D2 method according to Grimme's approach has been considered.¹³ In addition, binding energies were also computed at B3LYP-D2/6-31G(d) theoretical level for quantifying dispersion forces. The optimized geometries were characterized as minima through frequency calculations. Based on optimized geometries, vertical transition energies to the first five excited states were computed using TD-CAM-B3LYP¹⁴ in combination with the 6-311+G(d,p) basis sets. Range separated functionals are able to correctly reproduce vertical transition energies,^{15, 16} while large Pople's basis sets with polarization and diffuse functions provided converged vertical transitions.^{17, 18} All optimizations and TD-DFT calculations were performed both in gas phase and in solvent (methanol), using the continuum polarizable conductor solvation model (CPCM).¹⁹

Our TD-DFT simulations are able reproduce the main UV/Vis features of selected flavonoids. In general, the most intense absorption band (which also shows the highest wavelength) computed in solvent is located at 298 nm / 339 nm / 346 nm / 347 nm (see Table 1) for F0 / F1 / F2 / F3, which is mainly described by an H \rightarrow L transition. As seen in section 3.3, this H \rightarrow L transition is the most affect upon the interaction with selected carbon nanostructures. Thus, TD-CAM-B3LYP¹⁴ in combination with the 6-311+G(d,p) basis sets can be considered as a good choice for studying Fn-CNs systems.

S2

Flavonols-CNs systems. A graphene sheet, the fullerene C₆₀ and a single-walled carbon nanotube (12,8) were the carbon nanostructures considered in this work. Graphene sheet (Gr) was modeled using a layer composed of 63 rings (160 carbon atoms), while the single-walled carbon nanotube (CNT) was defined as a cluster of 304 carbon atoms, whose length is able to fully adsorb on its surface or encapsulate a flavonol molecule. Both graphene-sheet and carbon nanotube structures were hydrogen terminated. The optimizations of flavonoid-CNs systems were carried out in the context of the two-layer ONIOM approach.²⁰ This approximation has allowed the optimization of systems with large number of atoms at moderate computational cost. For the considered Fn-CNs (n=0-3) systems, the flavonols (model systems) were studied at B3LYP/6-31G* theoretical level (high level), while the real system (flavonoid + carbon nanostructure) was studied at PBE/STO-3G (low level). Van der Waals interactions are the main expected contribution to the interaction between flavonoids and CNs, and thus, the Grimme's D2 dispersion corrections term was considered for the low level. The use of dispersion corrections has proven be useful for an improved description of dispersion interactions.²¹⁻²⁵ This QM/QM (B3LYP/6-31G*:PBE-D2/STO-3G) approach allows the optimization of Fn-CNs systems with a moderate computational cost.

This approach treats intermolecular interactions at the low level (PBE-D2/STO-3G). Aimed at assessing the effects of the methods on the molecular geometry, F1-C₆₀ was fully optimized at PBE-D2/6-31G* while F1-Gr, F1-CNT and F1@CNT were optimized at PBE-D2/6-31G*:PBE-D2/STO-3G (through ONIOM approach). In these ONIOM optimizations, both F1 molecule and the interacting surface of carbon nanostructure were included in the model systems and treated at the high level (Figure 1S). Significant differences on the optimized geometries were not found between both selected methods for studying the intermolecular interactions (PBE-D2/6-31G* or PBE-D2/STO-3G). Therefore, single point calculations at B3LYP-D2/6-31G* were performed over optimized geometries. Energy differences between geometries optimized at B3LYP/6-31G*:PBE-D2/STO-3G or PBE-D2/6-31G*:PBE-D2/STO-3G are roughly 1.0 kcal mol⁻¹. Hence, the optimization through ONIOM approach at B3LYP/6-31G*:PBE-D2/STO-3G level seems to be an adequate choice for optimizing Fn-CN systems with a reasonable computational cost.

S3

Single points calculations were performed at B3LYP-D2/6-31G* level over all optimized structures, and molecular properties (such as binding energies, charge population or density of states) were also computed at this level and used for the discussion of the interaction mechanism reported in the following sections. Intermolecular interactions were characterized through both a topological analysis of the electron density, according to Bader's²⁶ theory (Atoms in Molecules, AIM), and the analysis of the reduced density gradient (RDG) at low densities.²⁷

We are aware that theoretical methodology here employed could be not enough accurate to estimate the binding energy of selected systems. As matter of fact, it is well known that the basis set superposition error (BSSE) has a significantly effect on the estimated binding energies. However, the lack of experimental data about interaction energies as well as the size of studied systems (especially Fn-CNT and Fn@CNT) prevent us to carry out comparison between experimental data and computed binding energies. For the sake of the computational cost, basis sets larger than 6-31G*, BSSE corrections as well as more accurate computational protocols were avoided. Thus, binding energies here computed should be used as a first approximation and only qualitative trends should be considered.

The first five excited states (by means of TD-DFT approach) of optimized Fn-CNs systems were computed using ONIOM electronic embedding model,²⁸ Flavonol molecules was treated at the high level (TD-CAM-B3LYP/6-311+G(d,p)) whereas the carbon nanostructures were treated at the low level (PBE-D2/6-31G*). The embedding model allows that the wave function of the model system can be polarized due to the electrostatic interactions between high and low level.²⁸ Similar protocols based on ONIOM approach along to an electronic embedding mode have demonstrated their suitability for reproducing the structural and electronic features of dyes in complex environments.^{18, 21, 22}

Software. The Gaussian 09 (Revision D.01) package has been used for all the calculations.²⁹ AIM and RDG analysis were carried out using MultiWFN code,³⁰ while simulated UV/Vis spectra were obtained using GaussSum code.³¹

S4

AIM Analysis

According to AIM theory,²⁶ there are four kinds of critical points: atomic critical points, bond critical points, ring critical points and cage critical points (ATC, BCP, RCP and CCP, respectively), but giving the characteristics of the studied systems (dispersion interactions are the main contribution to the binding energies) and to improve and clarify the data analysis, we have focused on the total electronic density sum over all BCPs, RCP and CCP ($\sum \rho_{(BCP)}, \sum \rho_{(RCP)}$ and $\sum \rho_{(CCP)}$) related with intermolecular interactions. The calculated AIM parameters are gathered in Figure 6S showing that $\sum \rho_{(RCP)}$ and $\sum \rho_{(CCP)}$ follow similar trend. Palusiak *et al.*³² have shown that ring critical point features (mainly the electronic density, ρ) should reflect some characteristic properties of the ring (or quasi-ring), e.g. π -electronic delocalization. On the basis of these results, we could expect some relationship between $\sum \rho_{(RCP)}$ and $\sum \rho_{(CCP)}$ values and electronic delocalization in the intermolecular region. On the basis of these results, we could expect some relationship between $\sum \rho_{(RCP)}$ and $\sum \rho_{(CCP)}$ values and electronic delocalization in the intermolecular region. In general, binding energy tendency reported in Fig. 6S can be rationalized based on the electronic density of BCPs, RCPs and CCPs related with flavonoid – graphene interactions. For F0-Gr systems π -stacking between the backbone and the graphene sheet is the main driving force in the adsorption process. The presence of OH groups leads to larger interaction energies because the hydroxyl groups increase the number of intermolecular interactions (confirmed by an increase of $\sum \rho_{(BCP)}$), while intramolecular hydrogen bonds in flavonols also allow major electronic delocalization of the flavonols that eases π -stacking interactions with the graphene surface (in agreement with major $\sum \rho_{(RCP)}$ and $\sum \rho_{(CCP)}$ values). For example, binding energy difference between F2-Gr and F3-Gr is mainly due to the intermolecular hydrogen bond between OH group at position 5' and the graphene surface. In fact, τ_7 = -22.01 degrees for F3-Gr optimized structure.

Regarding to F0-C₆₀ family, F0-C₆₀ yields the lowest $\sum \rho_{(BCP)}$, $\sum \rho_{(RCP)}$ and $\sum \rho_{(CCP)}$ values. In Fn-C₆₀ (n=1-3) systems, *quasi* rings due to intramolecular hydrogen bonds HB2-HB4 also contribute to the π -stacking between flavones backbone and the fullerene surface. Due to stronger intermolecular bond and π -stacking flavonols-C₆₀ systems own larger $\sum \rho_{(BCP)}$ and $\sum \rho_{(RCP)}$ (and $\sum \rho_{(CCP)}$) values, respectively. OH groups at positions 4, 3', 4' and 5' do not take part in the interaction with C₆₀, and thus, the

binding energies and AIM parameters ($\Sigma \rho$) do not show important changes between different flavonols.

Similarly to flavonols on the graphene surface, binding energy differences between flavones F0 and flavonols F1-F3 adsorbed on CNT surface is due to the presence of OH groups, which contribute to fortify intermolecular interactions (higher $\sum \rho_{(BCP)}$ values) and π -stacking interactions as well due to major electronic delocalization of the flavones backbone (higher $\sum \rho_{(RCP)}$ and $\sum \rho_{(CCP)}$ values).

For flavonoids inside the CNT, the twisted geometry improves the interaction between the carbon nanotube and both chromone and ring B motifs. Such twisted configuration of flavonols inside carbon nanotube leads to $\tau_1 = 29.0^\circ$ for flavonol F4, which brings a slight diminution of the π -stacking interactions (assessed through a small diminution of $\sum \rho_{(RCP)}$ and $\sum \rho_{(CCP)}$ values).

	Gas Phase						
	F0	F1	F2	F3			
Bond lengths / Å							
C ₂ -C _{1'}	1.473	1.467	1.464	1.463			
Intramolecular Hydrogen-bond lengths / Å							
HB1	2.402	2.317	2.332	2.337			
HB2		2.153	2.152	2.136			
HB3		1.988	1.989	1.982			
HB4		1.783	1.780	1.782			
HB5			2.167	2.201			
HB6				2.207			
Dihedral angles / Degrees							
τ ₁	18.967	-0.010	-0.002	-0.042			
τ2		-0.005	0.000	-0.002			
τ3		0.013	-0.001	-0.001			
τ ₄		0.000	0.000	0.000			
τ ₅			-0.006	-0.003			
τ ₆			-0.022	-0.012			
τ ₇				-0.008			

Table 1S. Main geometrical parameters of selected flavonoids. See Figure 1 for labeling

	F0	F1	F2	F3	F0	F1	F2	F3
	Fn-Gr Fn-C ₆₀							
Bond lengths / Å								
C ₂ -C _{1'}	1.474	1.467	1.462	1.461	1.472	1.466	1.462	1.460
Intramolecular Hydrogen-bond lengths / Å								
HB1	2.340	2.317	2.342	2.342	2.390	2.325	2.322	2.340
HB2		2.156	2.147	2.135		2.172	2.160	2.155
HB3		1.995	1.986	1.981		1.993	1.986	1.987
HB4		1.788	1.799	1.805		1.793	1.798	1.798
HB5			2.169	2.213			2.168	2.206
HB6				2.240				2.209
Dihedral angles / Degrees								
τ ₁	1.439	2.291	1.943	1.872	-16.733	-7.262	-7.243	-7.128
τ ₂		-2.465	-2.360	-2.201		0.472	0.228	0.586
τ3		1.718	1.765	1.592		0.243	0.456	0.337
τ ₄		11.816	10.876	10.298		0.558	0.536	0.658
τ ₅			-6.238	-6.085			-0.373	-1.002
τ ₆			-31.408	-16.157			-5.009	-2.512
τ ₇				-22.050				-3.864
	Fn-CNT			Fn@CNT				
			Bond lei	ngths / Å				
C ₂ -C _{1'}	1.472	1.465	1.462	1.460	1.472	1.466	1.460	1.460
		Intramole	ecular Hydro	ogen-bond le	engths / Å			
HB1	2.377	2.352	2.360	2.345	2.420	2.413	2.447	2.453
HB2		2.207	2.201	2.161		2.284	2.293	2.320
HB3		1.998	1.996	1.981		2.046	2.047	2.043
HB4		1.779	1.785	1.795		1.789	1.798	1.804
HB5			2.153	2.197			2.192	2.240
HB6				2.249				2.196
Dihedral angles / Degrees								
τ ₁	15.585	15.418	14.064	10.374	21.54	25.500	26.266	28.964
τ ₂		-1.364	-0.942	-1.140		-1.610	-0.597	-0.757
τ3		1.727	1.801	1.700		2.945	3.639	3.297
τ ₄		13.378	8.014	7.740		5.371	5.573	6.449
τ ₅			-4.551	-4.792			-9.091	-9.169
τ ₆			-35.700	-16.672			-18.973	-7.573
τ ₇				-19.357				-11.274

Table 2S. Main geometrical parameters of flavonoids for Fn-CN systems. See Figure 1 for labeling

Table 3S. Binding Energies (*BE*), dispersion contribution to the total binding energy (*BE_{dis}*), AIM parameters related with intermolecular interactions

	BE / kcal mol ⁻¹	BE _{dis} / kcal mol ^{-1 a}	<i>∑ρ_(BCP)</i> / a.u. ^b	<i>∑ρ_(RCP)</i> / a.u. ^c	<i>∑ρ_(CCP)</i> / a.u. ^d		
Fn-Gr							
FO	33.87	47.63 (140.65)	0.0699	0.0880	0.0453		
F1	61.31	55.87 (91.12)	0.1067	0.1489	0.0612		
F2	67.70	62.11 (91.73)	0.1433	0.1752	0.0669		
F3	70.15	64.54 (92.00)	0.1432	0.1739	0.0682		
Fn-C ₆₀							
FO	13.33	20.47 (153.57)	0.0342	0.0231	0.0055		
F1	34.75	22.44 (64.56)	0.0525	0.0499	0.0150		
F2	36.93	23.24 (62.94)	0.0583	0.0459	0.0120		
F3	38.73	25.00 (64.55)	0.0581	0.0454	0.0134		
Fn-CNT							
FO	27.68	39.56 (142.92)	0.0547	0.0680	0.0275		
F1	53.66	45.68 (85.13)	0.0708	0.0823	0.0281		
F2	57.92	50.13 (86.65)	0.1010	0.0895	0.0286		
F3	59.78	52.14 (87.22)	0.1046	0.1002	0.0290		
FN@CNT							
FO	50.10	65.10 (129.96)	0.1073	0.1214	0.0356		
F1	74.89	71.42 (95.37)	0.1349	0.1395	0.0454		
F2	81.39	76.66 (94.18)	0.1444	0.1362	0.0447		
F3	84.34	79.43 (94.17)	0.1483	0.1329	0.0437		

^{*a*} Percentage of dispersion energy contribution in parentheses. $^{b/c/d} \sum \rho_{(BCP)} / \sum \rho_{(RCP)}$ stand for the sum of the electronic density (ρ) overall BCPs /RCPs /CCPs related with intermolecular interactions between the flavonoid and the carbon nanostructure.



Figure 1S. Optimized structures of F1-Gr, F1-CNT and F1@CNT systems at PBE-D2/6-31G*:PBE-D2/STO-3G theoretical level through ONIOM approach. Atoms included in the model systems are drawn as ball and sticks, while remaining atoms of carbon nanostructure are drawn in grey.



Figure 2S. Side (left) and top (centre) views for optimized structures of flavonoid-graphene (Fn-Gr, n=0-3) structures, along main structural parameters related with intermolecular interactions. Red and yellow points stand for RCP and CCP, respectively, related with intermolecular interactions. BCP were omitted for clarity. Intermolecular bond lengths are in Å.



Figure 3S. Side (left) and top (centre) views for optimized structures of flavonoid-fullerene ($Fn-C_{60}$, n=0-3) structures, along main structural parameters related with intermolecular interactions. Red and yellow points stand for RCP and CCP, respectively, related with intermolecular interactions. BCP were omitted for clarity. Intermolecular bond lengths are in Å.



Figure 4S. Side (left) and top (centre) views for optimized structures of flavonoid-graphene (Fn-CNT, n=0-3) structures. Red and yellow points stand for RCP and CCP, respectively, related with intermolecular interactions. BCP were omitted for clarity. Intermolecular bond lengths are in Å.



Figure 5S. Side (left) and top (centre) views for optimized structures of flavonoid inside carbon nanotube (Fn@CNT, n=0-3) structures. Red and yellow points stand for RCP and CCP, respectively, related with intermolecular interactions. BCP were omitted for clarity. Intermolecular bond lengths are in Å.



Figure 6S. Binding Energies for the interaction between flavonoids and carbon nanostructures (*BE*, grey bars) along to dispersion contribution to the total binding energy (BE_{dis} , green lines) and total sum of electronic density ($\Sigma \rho$) for those BCPs, RCPs and CCPs (black, red and blue, respectively) related with intermolecular interactions Data for this Figure are in Table 3S.



Fig. 75. Dihedral angles τ_1 - τ_7 of bare flavonoids and Fn-CN structures. Data for this Figure are in Tables 1S and 2S (Electronic Supplementary Information).

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