

Relaxations of fluorouracil tautomers by decorations of fullerene-like SiCs: DFT studies



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ABSTRACT

Decorations of silicon carbide (SiC) fullerene-like nanoparticles by fluorouracil (FU) and its tautomers are investigated through density functional theory (DFT) calculations. Two models of fullerene-like particles including Si₁₂C₈ and Si₈C₁₂ are constructed to be counterparts of decorated hybrid structures, FU@Si₁₂C₈ and FU@Si₈C₁₂, respectively. The initial models including original FU and tautomeric structures and SiC nanoparticles are individually optimized and then combined for further optimizations in the hybrid forms. Covalent bonds are observed for FU@Si₁₂C₈ hybrids, whereas non-covalent interactions are seen for FU@Si₈C₁₂ ones. The obtained properties indicated that Si₁₂C₈ model could be considered as a better counterpart for interactions with FU structures than Si₈C₁₂ model. The results also showed significant effects of interactions on the properties of atoms close to the interacting regions in nanoparticles. Finally, the tautomeric structures show different behaviors in interactions with SiC nanoparticles, in which the SiC nanoparticles could be employed to detect the situations of tautomeric processes for FU structures.

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1. Introduction

Fluorouracil (or 5-fluorouracil, FU) has been used as an anti-cancer drug to treat various types of cancers for several years [1]. The advantages of this drug have still kept it useful for medical treatments of patients, but on the other hand, too many side effects are arisen for its users [2]. Therefore, considerable efforts have been dedicated to recognize various aspects of this drug and the method to increase its safety for patients for many years [3,4]. By the introduction of nanotechnologies, combinations of nanostructures with FU derivatives are proposed to be helpful for medical purposes [5–8]. Researchers of various fields have drastically explored other novel materials in addition to pioneering fullerenes and carbon nanotubes [9,10]. As a result, several types of nanostructures are now recognized including nanoparticles [11], nanocones [12], nanorods [13], nanorings [14], graphenes [15], and some other types. The results also indicated the possibilities of existence of non-carbon nanostructures, which could show polarities versus non-polar carbon nanostructures [16,17]. Stabilities and properties of silicon carbide (SiC) nanostructures have been investigated computationally and experimentally [18–20]. Earlier

researches demonstrated that both carbon and non-carbon nanostructures could be physically or chemically decorated by other atoms and molecules to make new hybrid systems with new properties [21–23]. Among Those, biologically related decorations of nanostructures could be expected to make more useful compounds for applications in life sciences and technologies [24]. Within this research, we investigated decorations of two representative SiC fullerene-like nanoparticles by FU species to construct SiC–FU hybrids (Fig. 1) through quantum computations. In addition to the original di-keto form, we also considered other keto-enol and di-enol tautomeric structures of FU for decorations of SiC nanoparticles. The tautomeric structures could lead to mutations in biological systems; therefore, they are important to be carefully examined for organic and bioorganic compounds [25]. Our obtained results revealed that different situations of decorated systems depend on tautomeric structures and combined SiC nanoparticles.

2. Computational details

Density functional theory (DFT) calculations are performed to employ the B3LYP exchange-correlation functional and the 6-31G* standard basis set as implemented in the Gaussian 98 program [26]. The models include the original di-keto, tautomeric keto-enol, di-enol forms of FU and two models of SiC fullerene-like

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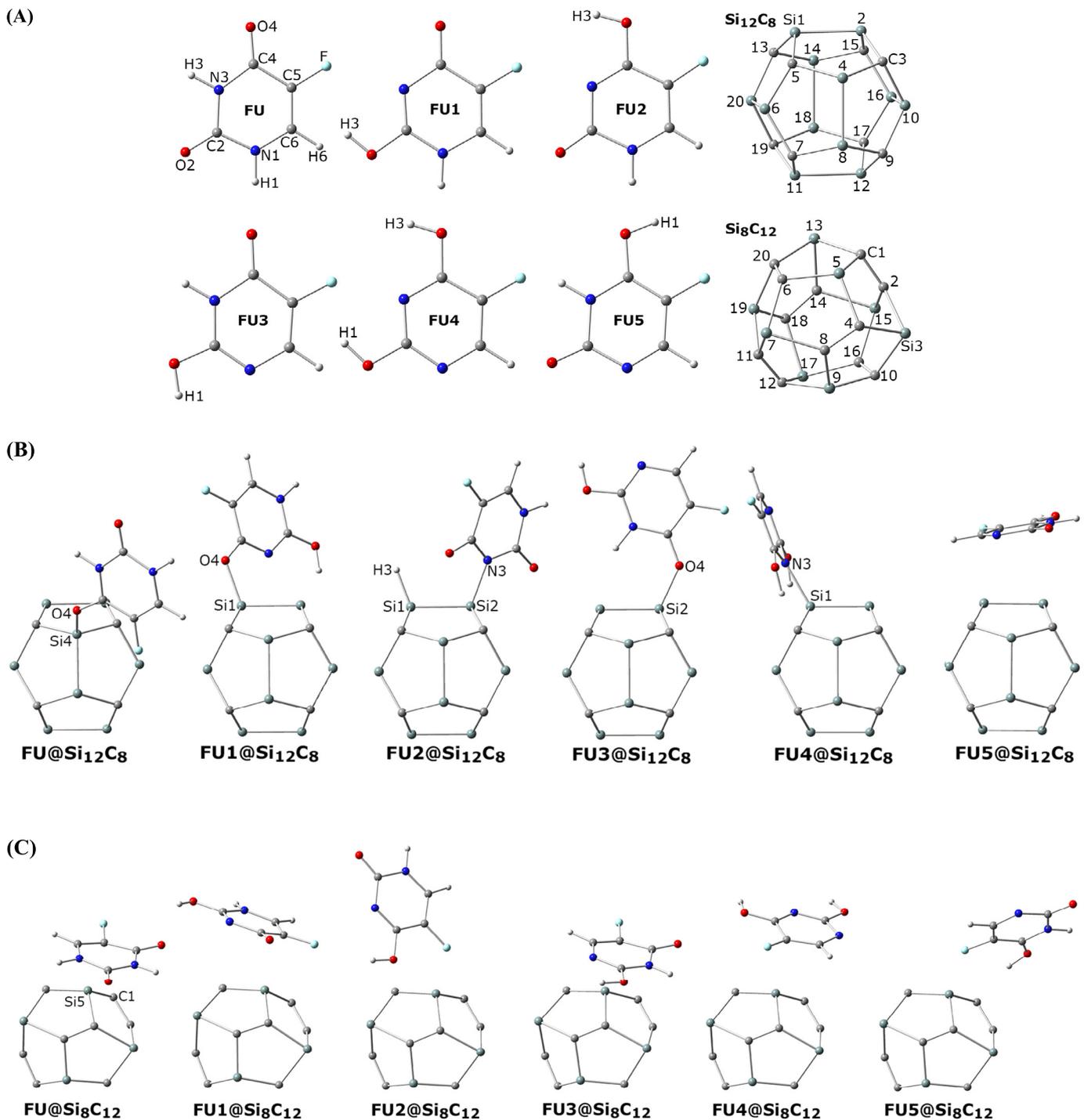


Fig. 1. (A) Individual structures of original and tautomers of FU and also individual SiC fullerene-like nanoparticles. (B) FU@Si₁₂C₈ hybrids. (C) FU@Si₈C₁₂ hybrids.

nanoparticles (Fig. 1, panel A). The hydrogen atoms were moved to other proper atomic positions in the FU structure to make keto-enol and di-enol tautomers [27]. To construct the SiC fullerene-like nanoparticles, two systems with twenty atoms for each one, Si₁₂C₈ and Si₈C₁₂, were constructed based on the presence of Si–Si and C–C direct bonds. After constructing the initial models, all individual models were optimized to their minimum-energy levels. Subsequently, the original and tautomeric FU structures were allowed to relax on the surface of each pre-optimized SiC nanoparticles and construct the FU-decorated SiC hybrids (FU@SiC) (Fig. 1, panels B and C). The optimization processes yielded molecular properties (Table 1); dipole moments and various types of energies includ-

ing total energies, binding energies, and energies for the highest occupied molecular orbitals (HOMO) and the lowest unoccupied ones (LUMO). To evaluate binding energies, differences of energies for hybrid structure and singular counterparts are employed; $E_B = E_{FU@SiC} - E_{FU} - E_{SiC}$. It is notes that the basis set superposition error (BSSE) [28] has been corrected for non-covalent interacting FU@SiC hybrids. To evaluate energy gaps, differences of HOMO and LUMO states are employed; $E_G = E_{LUMO} - E_{HOMO}$. Additionally, atomic scale properties were determined by evaluations of chemical shifts (δ) for all atoms of the optimized structures. It is known that the chemical structures of materials could be efficiently detected by nuclear magnetic resonance (NMR) spectroscopy as a

Table 1
Optimized molecular properties^a.

Structure	E_T /eV	E_B /eV	E_{HOMO} /eV	E_{LUMO} /eV	E_G /eV	D_M /Debye
FU	-13987.945	-	-6.786	-1.378	5.408	3.903
FU1	-13987.113	-	-6.617	-0.870	5.747	6.658
FU2	-13987.329	-	-6.518	-1.506	5.012	3.475
FU3	-13987.481	-	-6.494	-1.189	5.305	4.088
FU4	-13987.271	-	-6.718	-1.099	5.619	2.530
FU5	-13986.995	-	-6.360	-1.585	4.775	5.805
Si ₁₂ C ₈	-102815.599	-	-4.741	-3.756	0.985	0.032
Si ₈ C ₁₂	-75450.956	-	-5.502	-4.135	1.367	3.056
FU@Si ₁₂ C ₈	-116804.536	-0.992 C	-3.941	-3.316	0.652	10.783
FU1@Si ₁₂ C ₈	-116804.172	-1.302 C	-3.845	-3.113	0.732	12.761
FU2@Si ₁₂ C ₈	-116805.824	-3.230 C	-4.635	-3.652	0.983	2.749
FU3@Si ₁₂ C ₈	-116804.333	-1.620 C	-4.119	-3.214	0.905	9.842
FU4@Si ₁₂ C ₈	-116804.489	-1.409 C	-4.548	-3.762	0.786	1.753
FU5@Si ₁₂ C ₈	-116802.565	-0.128 nC	-4.859	-3.904	0.955	5.321
FU@Si ₈ C ₁₂	-89438.916	-0.188 nC	-5.241	-3.888	1.353	5.861
FU1@Si ₈ C ₁₂	-89438.149	-0.146 nC	-5.273	-3.901	1.372	5.276
FU2@Si ₈ C ₁₂	-89438.385	-0.133 nC	-5.266	-3.907	1.359	5.879
FU3@Si ₈ C ₁₂	-89438.493	-0.200 nC	-5.140	-3.789	1.351	8.724
FU4@Si ₈ C ₁₂	-89438.247	-0.083 nC	-5.232	-3.865	1.367	4.913
FU5@Si ₈ C ₁₂	-89438.020	-0.175 nC	-5.547	-4.194	1.353	2.253

^a The structures are shown in Fig. 1. The characters C and nC besides binding energies indicate covalent and non-covalent interactions between FU and SiC counterparts. The results for individual FU are comparable with Ref. [27].

versatile technique among the characterizing techniques [29]. To evaluate δ values, chemical shielding tensors (σ_{ii}) were computed based on the gauge-included atomic orbital (GIAO) approach and then converted to isotropic chemical shieldings (σ_{iso}) through the equation: σ_{iso} (ppm) = $(\sigma_{11} + \sigma_{22} + \sigma_{33})/3$ [30]. Subsequently, the obtained σ_{iso} values were converted to δ values using the references of tetramethylsilan (TMS) for Si, C, and H atoms, water (H₂O) for O atoms, and ammonia (NH₃) for N atoms in the equation δ (ppm) = $\sigma_{iso, Reference} - \sigma_{iso, Sample}$ [29]. The chemical shieldings originated from the electronic sites of atoms, could reveal insightful information about the electronic properties of structures [30,31].

3. Results and discussion

3.1. Optimized molecular properties

Optimized molecular properties including total energies (E_T), binding energies (E_B), energies of the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals (E_{HOMO} and E_{LUMO}), and dipole moments (D_M) for the individual and hybrid models of this work (Fig. 1) are listed in Table 1. The individual models are the original and tautomeric forms of FU and two models of SiC fullerene-like nanoparticles include Si₁₂C₈ and Si₈C₁₂. The criterion of making two nanoparticles is to consider existence of Si–Si bond in the Si₁₂C₈ model and C–C bond in the Si₈C₁₂ one as well as Si–C bond in both models. The tautomeric structures are constructed based on movement of H atoms among N₁, N₃, O₂, and O₄ atomic positions. The hybrid structures are constructed through decorations of Si₁₂C₈ and Si₈C₁₂ nanoparticles by the available FU structures to make FU@SiC hybrids (Fig. 1, panels B and C). The results of optimized energies indicate that the most stable structure is the original di-keto form of FU and the most unstable structure is FU₅, a keto–enol form with movement of H₁ to O₄ atomic position. Comparing the results of total energies indicates that the stabilities for other tautomers are ordered as FU₃ > FU₂ > FU₄ > FU₁. The results are in agreement with earlier results on uracil and FU tautomeric structures [27]. The results for E_{HOMO} and E_{LUMO} also demonstrated that the orbital levels and the gaps between them are changed due to tautomerizations, in which the results reveal the changes of electronic properties for molecular systems of tautomers. Different magnitudes for E_{HOMO} and E_{LUMO} are seen for the SiC nanoparticles and different gaps are also seen

for the two structures based on their atomic components. Different magnitudes for dipole moments are also obvious for the individual tautomers and also for two SiC nanoparticles, in which the value of D_M for Si₈C₁₂ is larger than Si₁₂C₈ structure.

There are two sets of FU@SiC hybrids based on the components of SiC nanoparticles; Si₁₂C₈ and Si₈C₁₂. A quick look at the B and C panels of Fig. 1 indicates that the situations of interactions are different for the FU tautomers on the surface of two SiC nanoparticles. After optimizations, covalent attachments are seen for the Si₁₂C₈ nanoparticles, whereas only non-covalent interactions are seen for the Si₈C₁₂ nanoparticles. The trend shows the importance of atomic components in the structural behaviors of molecular interactions. Comparing the values of E_T for FU@Si₁₂C₈ and FU@Si₈C₁₂ hybrids indicates that the stabilities are different for the two hybrid systems, in which stronger interactions are seen for the FU@Si₁₂C₈ hybrids in panel B of Fig. 1 rather than the FU@Si₈C₁₂ hybrids in panel C. The results for FU@Si₁₂C₈ hybrids indicate that the obtained stabilities are different for the hybrid structures as could be seen by the magnitudes of E_T , in which the most stable hybrid structure is FU₂@Si₁₂C₈ among the investigated hybrids. Interestingly, the H atom of O₄ is moved to Si₁ atom of SiC nanoparticle and also the covalent attachment is seen for N₃ and Si₂ atom in the hybrid structure. With the exception of FU₅@Si₁₂C₈, all other hybrids in this set include covalent bonds with almost similar strengths. However, physical interactions are only seen for FU₅@Si₁₂C₈ and the results of E_T show the least stability for this structure among available hybrids. As it was shown earlier, the results of E_T for individual tautomers indicated FU₅ is the least stable structure, in which the same result is also detected for FU₅@Si₁₂C₈ hybrid. However, the stability for the original FU structure in the hybrid form is lowered in comparison with the original individual FU structure. Due to the special properties of Si₁₂C₈ nanoparticle, the stability for FU₂ is increased in the FU₂@Si₁₂C₈ hybrid. Magnitudes of E_B also approve the values of stabilities, in which the most stable structure is FU₂@Si₁₂C₈ and the least stable structure is FU₅@Si₁₂C₈. The stabilities for other FU@Si₁₂C₈ hybrids are almost similar. Different magnitudes for energies of HOMO and LUMO levels and also their gaps were observed for the hybrid structures, meaning changes of electronic properties of molecular orbitals of the investigated structures. The values of D_M indicate that the polarities are significantly changed during the hybridizations, in which remarkable magnitudes are seen for FU₁@, FU@, and FU₃@Si₁₂C₈

Table 2
Atomic chemical shifts (δ /ppm) for FU species^a.

Atom	FU@	FU1@	FU2@	FU3@	FU4@	FU5@
H ₁	4.995	5.439	5.780	4.986	5.017	4.976
	(5.906)	(6.446)	(5.182)	(5.886)	(12.822)	(5.189)
	[6.225]	[6.027]	[5.935]	[5.952]	[5.834]	[7.074]
H ₃	6.078	4.791	5.325	6.806	4.776	6.083
	(7.167)	(7.755)	(5.595)	(15.732)	(16.819)	(6.156)
	[6.619]	[5.282]	[5.840]	[7.499]	[5.533]	[6.253]
H ₆	6.382	6.215	6.664	7.072	7.899	8.163
	(6.578)	(6.624)	(6.368)	(7.943)	(8.133)	(8.249)
	[8.062]	[7.124]	[6.969]	[8.502]	[8.809]	[8.443]
C ₂	136.627	142.291	139.971	142.662	151.906	140.097
	(134.621)	(144.275)	(140.678)	(142.637)	(150.228)	(140.180)
	[135.529]	[144.466]	[139.029]	[149.689]	[155.634]	[140.189]
C ₄	146.779	151.802	153.592	143.802	149.995	143.254
	(160.498)	(154.796)	(154.613)	(150.177)	(155.099)	(143.748)
	[146.776]	[149.459]	[150.775]	[144.805]	[154.424]	[143.387]
C ₅	136.895	143.568	129.162	143.432	135.706	126.438
	(136.348)	(139.437)	(135.406)	(140.461)	(136.077)	(125.979)
	[124.781]	[138.386]	[132.313]	[133.408]	[129.173]	[136.944]
C ₆	117.069	111.918	122.796	130.951	142.045	147.789
	(123.377)	(114.706)	(117.356)	(141.124)	(143.544)	(148.463)
	[137.046]	[125.641]	[125.324]	[149.874]	[148.893]	[146.812]
N ₁	113.702	100.533	136.860	185.268	237.755	240.960
	(130.549)	(118.372)	(117.586)	(215.294)	(230.848)	(241.019)
	[134.089]	[110.321]	[139.704]	[199.828]	[246.889]	[238.571]
N ₃	156.102	220.437	226.799	150.767	213.058	136.042
	(157.998)	(233.683)	(168.429)	(154.119)	(162.900)	(136.741)
	[154.613]	[225.434]	[227.906]	[155.032]	[212.268]	[139.109]
O ₂	287.284	119.704	312.088	120.142	134.512	301.441
	(300.942)	(137.276)	(312.897)	(127.032)	(181.156)	(300.135)
	[309.969]	[126.647]	[296.703]	[136.121]	[148.729]	[114.628]
O ₄	257.208	205.977	135.973	290.683	117.923	92.839
	(239.329)	(232.281)	(246.053)	(185.180)	(187.226)	(99.819)
	[228.632]	[177.710]	[132.936]	[249.089]	[131.516]	[286.319]
F	50.037	63.269	42.277	57.608	46.768	10.490
	(68.604)	(64.739)	(48.723)	(61.462)	(53.738)	(18.268)
	[38.816]	[57.746]	[41.247]	[46.412]	[38.939]	[33.169]

^a The structures are shown in Fig. 1. The results for individual FU are comparable with Ref. [27]. In each column, the free number belongs to individual structure, the number in parenthesis belongs to FU@Si₁₂C₈ hybrids, and the number in brackets belongs to FU@Si₈C₁₂ hybrids.

hybrids. As mentioned earlier, the interactions between FU tautomers and Si₈C₁₂ nanoparticles are all non-covalent (Fig. 1, panel C), in which the stabilities of FU@Si₈C₁₂ are lower than the stabilities of FU@Si₁₂C₈ hybrids. Among the FU@Si₈C₁₂ hybrids, the most stable structure is seen for the original FU on the Si₈C₁₂ nanoparticle. The results of E_B also approve that the interaction between FU and Si₈C₁₂ nanoparticle is stronger than other hybrid structures of FU₁–FU₅@Si₈C₁₂. The stabilities and interaction strengths are almost similar for other hybrid structures. The levels for HOMO and LUMO still detect the effects of hybridizations in the FU@Si₈C₁₂ hybrids but the magnitudes of gaps are larger in comparison with the FU@Si₁₂C₈ hybrids. However, the magnitudes of D_M for FU@Si₈C₁₂ hybrids are smaller than FU@Si₁₂C₈ ones. Comparing the results for individual SiC nanoparticles and hybrids, reveals the influence of functionalizations on the properties of nanoparticles, in which the magnitudes of D_M for individual nanoparticles were significantly changed in the hybrid structures. As a remarkable conclusion, it could be mentioned that the existence of Si–Si bonds in SiC nanoparticles make the formation of covalent bonds possible for FU tautomers, whereas the existence of C–C bonds only show possibilities for formation of non-covalent interactions. In a very recent work [32], adsorption studies of FU at the surface of original and doped C₆₀ fullerene nanostructures indicated that the interactions are non-covalent for original C₆₀ whereas covalent interactions are observed for doped C₆₀s. In another work [27], the tautomeric structures of FU contribute to non-covalent interactions with original silicon sheets. These results and the results of current research could indicate that the heterogeneous nanostructures show better tendency to interact with FU

structures in comparison with original nanostructures. The type of heterogeneous nanostructure is also important, in which the interactions of FU with Si₈C₁₂ are all non-covalent comparing with Si₁₂C₈ nanostructure.

3.2. Atomic chemical shifts

The evaluated chemical shifts (δ) for the atoms of optimized individual and hybrid structures of FU, SiC, and FU@SiC (Fig. 1) are listed in Tables 2–4. The chemical shielding (σ) tensors are originated from the electronic sites of atoms; therefore, they could reveal insightful information about the electronic properties of matters [29]. A quick look at the results for atoms of FU counterparts (Table 2) in both individual and hybrid forms indicates that the electronic environment for each atom is changed from the original structure to tautomer or from individual structure to hybrid forms. Moreover, each atom of FU structure detects a different environment in two hybrid systems, based on different components of SiC fullerene-like particles. Two H atoms of FU, H₁ and H₃, are moving through tautomerization processes; but the position for H₆ is kept frozen. Since the magnitudes of δ show the discrepancy of electronic properties of the sample atom from the reference atom, so these magnitudes could show significant changes of electronic properties of each atom from the reference point to current situation. Although the position of H₆ is kept frozen through tautomers, the electronic properties are still changed in different structures due to indirect side effects, as could be seen by the magnitudes of δ . In all cases, the effects for H₆ atoms of FU@Si₈C₁₂ are much more significant than the other hybrid and individual structures.

Table 3
Atomic chemical shifts (δ /ppm) for Si₁₂C₈ fullerene-like nanoparticles^a.

Atom	Individual	FU@	FU1@	FU2@	FU3@	FU4@	FU5@
Si ₁	408.569	365.038	102.839	48.725	42.657	180.863	360.514
Si ₂	407.044	318.628	188.457	22.520	117.825	215.926	395.336
Si ₄	414.081	120.6949	411.389	396.223	393.728	410.542	413.469
Si ₆	413.793	406.252	374.864	362.364	386.881	376.509	404.659
Si ₈	413.883	201.790	385.899	382.337	385.204	393.673	407.878
Si ₁₀	412.404	389.504	355.536	352.660	369.679	388.532	408.777
Si ₁₁	407.433	372.346	377.234	144.527	105.776	349.269	394.081
Si ₁₂	406.456	406.548	124.476	208.131	329.246	401.831	366.396
Si ₁₄	413.883	338.765	365.960	403.791	394.030	392.047	409.662
Si ₁₆	411.931	357.869	410.318	356.101	365.290	391.467	412.858
Si ₁₈	413.059	81.291	384.708	379.759	384.263	407.747	413.242
Si ₂₀	410.065	370.899	280.675	381.705	391.468	371.745	400.820
C ₃	123.991	113.729	111.581	170.655	141.639	72.408	119.365
C ₅	126.333	127.636	154.641	187.161	121.404	55.756	136.137
C ₇	126.421	123.072	143.402	137.286	123.777	113.249	128.134
C ₉	123.991	94.284	143.253	143.123	125.975	161.987	125.624
C ₁₃	125.603	135.439	91.897	186.083	120.421	84.048	128.339
C ₁₅	123.144	127.885	124.988	177.736	141.918	85.321	113.929
C ₁₇	125.603	121.524	119.160	143.390	152.283	178.631	124.181
C ₁₉	123.144	146.383	115.894	137.168	122.817	109.176	128.889

^a The structures are shown in Fig. 1. The structures indicated by FU@ imply for the properties of Si₁₂C₈ in FU@Si₁₂C₈ hybrids (Fig. 1, panel B).

Table 4
Atomic chemical shifts (δ /ppm) for Si₈C₁₂ nanoparticles^a.

Atom	Individual	FU@	FU1@	FU2@	FU3@	FU4@	FU5@
Si ₃	2.157	5.279	0.489	0.0567	8.334	5.451	4.733
Si ₅	232.811	277.643	354.226	373.269	296.581	373.330	297.163
Si ₇	342.473	356.042	340.057	347.788	354.738	346.907	326.439
Si ₉	233.433	297.236	245.538	266.704	285.973	270.142	258.055
Si ₁₃	344.484	296.434	-312.628	313.691	306.282	310.871	290.416
Si ₁₅	233.489	289.726	279.468	270.884	280.474	275.685	270.463
Si ₁₇	345.683	230.173	249.514	259.097	230.511	270.165	247.346
Si ₁₉	292.918	166.026	216.477	209.326	174.927	207.272	199.459
C ₁	128.417	127.309	126.709	127.408	129.252	129.039	136.177
C ₂	121.377	101.589	105.286	108.689	108.175	111.786	91.379
C ₄	120.772	117.892	121.579	118.861	121.084	121.166	121.337
C ₆	129.845	160.748	151.017	146.359	156.411	148.175	143.191
C ₈	128.571	129.929	134.298	133.192	130.456	133.672	129.338
C ₁₀	121.377	119.294	119.324	119.141	124.637	120.959	141.273
C ₁₁	97.843	113.136	113.573	108.248	110.372	106.466	112.187
C ₁₂	129.759	122.139	124.479	122.317	122.727	125.806	124.239
C ₁₄	129.420	147.876	138.156	139.861	145.776	141.019	138.428
C ₁₆	128.663	132.075	138.867	131.875	137.516	135.543	141.649
C ₁₈	98.349	105.893	106.361	102.949	106.118	106.631	115.506
C ₂₀	98.726	73.774	74.893	83.106	79.786	85.087	81.361

^a The structures are shown in Fig. 1. The structures indicated by FU@ imply for the properties of Si₈C₁₂ in FU@Si₈C₁₂ hybrids (Fig. 1, panel C).

However, a clear harmony of changes are not seen for H₁ and H₃ atoms, which are moving through nitrogen and oxygen atomic sites. Interestingly, H₃ from O₄ is moved to Si₁ atomic site in FU₂@Si₁₂C₈ hybrid, which is seen as an unusual observation among the investigated model systems. The small magnitudes of δ for hydrogen atoms are due to existence of weak electronic environment for this atom in comparison with larger magnitudes for other heavier atoms.

The results of Table 2 for carbon atoms also show different electronic environments for different atomic positions. Although the carbon atoms do not directly participate in tautomerizations, they can detect effects of these processes as could be seen by their magnitudes of δ . The properties for each atom among three models indicate that the changes of δ are significant due to being in different structural situations. For nitrogen atoms, many more significant effects are seen especially for that atom which is directly participated in the tautomerizations. In the original structure, both of N₁ and N₃ are hydrogenated, whereas in the tautomers the hydrogen atoms are removed from one or both of nitrogen atoms. Interesting observations are obtained for FU₂@Si₁₂C₈ and FU₄@Si₁₂C₈

hybrids, in which N₃ is respectively connected to Si₂ and Si₁ atoms through covalent bonds. In comparison with individual structures, the changes of δ for N₃ atoms in two hybrids also indicate that FU₂@Si₁₂C₈ and FU₄@Si₁₂C₈ are in strong interactions. It seems that the position of N₃ between two types of oxygen atoms, O₂ is urea type and O₄ is amide type, makes it a proper atom to undergo stronger interactions in comparison with N₁. The stability of SiC nanoparticle is also important, in which strong interactions with FU counterparts are seen with Si₁₂C₈ (more stability) but not with Si₈C₁₂ (less stability). Two oxygen atoms of urea type (O₂) and amide type (O₄) show different behaviors in the tautomeric systems and also in interaction with SiC nanoparticles. Parallel to the results for N₃, the interaction for O₄ is strong with Si₁₂C₈ nanoparticles especially in FU₁@Si₁₂C₈ and FU₃@Si₁₂C₈ hybrids, in which covalent bonds with Si₁ and Si₂ are formed. Combinations of the results for N₃ and O₄ could reveal that the amide part of FU is more proper for interactions with SiC nanoparticles than the urea part (N₁ and O₂). Moreover, N₃ is the winner of strong interactions, in which O₄ releases its hydrogen in FU₂@Si₁₂C₈ to make better possibility of strong interactions of N₃ with Si₂ atoms. The

oxygen atom has two lone pairs of electrons in the electronic site, which could be floated during the interactions to yield different properties. Similar situations of electron lone pairs are observed for the fluorine atom, in which the magnitudes of δ indicate different properties in the investigated individual and hybrid models. Since the F atom does not directly contribute to tautomerization, the magnitudes of changes of δ are not significant as much as nitrogen and oxygen atoms, but they are still notable. By examining the magnitudes of δ for F atom in FU₅ and hybrids, it could be proposed that there is an intramolecular hydrogen bond interaction between H₁ and F atoms at individual and FU₅@Si₁₂C₈ hybrid, whereas this interaction is protected in FU₅@Si₈C₁₂ hybrid. This result could be more approved by the magnitudes of δ for H₁ in FU₅ and related hybrids, in which the magnitude is increased in FU₅@Si₈C₁₂ in comparison with individual FU and FU₅@Si₁₂C₈ hybrid.

The obtained δ for atoms of optimized Si₁₂C₈ and Si₈C₁₂ fullerene-like nanoparticles (Fig. 1) in the forms of individual and hybrids are listed in Tables 3 and 4. The tautomeric structures do not similarly interact with the SiC counterparts; therefore, the results for Si₁₂C₈ and Si₈C₁₂ and also for each SiC counterpart in the tautomeric interacting systems are different. Comparing the atomic parameters between the individual particle and tautomeric interacting counterparts indicate that the properties are significantly highlighted for the atoms of interaction regions. Furthermore, the results of other atoms also show the effects of interactions in other atomic regions are far from the exact interaction regions. Significant effects are observed for the atoms of interaction regions in the FU@Si₁₂C₈ hybrids more than the FU@Si₈C₁₂ hybrids. As mentioned earlier for the optimized properties, the FU@Si₁₂C₈ hybrids were seen more stable than the FU@Si₈C₁₂ hybrids with respect to energies. The atomic results for the hybrids and their counterparts also show that there are proper interactions in the FU@Si₁₂C₈ hybrids more significant than FU@Si₈C₁₂ hybrids. The atomic results for individual nanoparticles also indicated different properties, which could determine their characteristics for desired applications as could be seen by different situations of interactions in the investigated hybrids.

4. Conclusions

Within this work, we have investigated the properties of interactions between FU tautomers and SiC fullerene-like nanoparticles through DFT calculations of molecular and atomic properties. The results indicated that the properties of FU@SiC hybrids and also for each of SiC particles are different. The energetic properties indicated that FU@Si₁₂C₈ hybrids are more stable than FU@Si₈C₁₂ hybrids, in which the atomic properties also indicated that the interactions between the counterparts of former hybrids are many more significant than the latter ones. Comparing the results for individual SiC particles and hybrids indicated that the most significant effects of interactions could be seen for the atoms of interaction regions, but the effects for other atoms are still notable. In the cases of FU@Si₁₂C₈ hybrids, formations of covalent bonds were also detected between the FU tautomers and Si₁₂C₈ nanoparticle, in which only non-covalent interactions were seen for FU@Si₈C₁₂ hybrids. Distances between the HOMO and LUMO levels for FU@Si₁₂C₈ hybrids are smaller than FU@Si₈C₁₂ hybrids in agreement with the smaller distance for individual Si₁₂C₈ than individual Si₈C₁₂ particles. And finally, the stabilities and interactions of FU tautomers could be investigated by SiC fullerene-like nanoparticles, in which Si₁₂C₈ fullerene-like nanoparticle could be better than Si₈C₁₂ one.

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