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Exploring the electronic, optical, and bioactive properties for new modified fullerenes via molecular modeling

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Abstract

Pristine fullerene characters are highly influenced upon surface decoration by COOH, NH₂, and Li sets. The electronic, vibrational, and optical properties of pristine and modified fullerenes are well tested using DFT. QSAR descriptors are fulfilled via PM6 interface for proposed fullerenes. Results showed that C₆₀-2Li may compete recent kesterite Cu₂ZnGeSe₄ solar cell which have band gap range as 1.5~1.7 eV and efficiency > 14%. The C₆₀-2Li may represent a new row of highly efficient fabricated solar cells. MESP contours found that additive Li possesses a blue shift in Fullerene electronegative behavior towards electrophilic additions whereas additive COOH and NH₂ maintain the original nucleophilic additions. Based upon QSAR values, C₆₀-2NH₂ is acknowledged as potential bioactive substrate for drug delivery. This paves the way toward multidisciplinary application of the studied fullerene system.

Keywords: Modified Fullerenes; IR/Raman, band offsets; MESP; QSAR.

Introduction

Carbon based-nanomaterials such as carbon nanotubes (CNTs) (Ghosh et al. 2021), graphene (Hadad et al. 2021), fullerenes (Puentes Santiago et al. 2021; Waite et al. 2021) and nano-diamonds (Khan et al. 2021; Yu et al. 2021) have surprised researchers by their unbelievable behaviors and extendable potential applications. Carbon quantum

dots (CQDs)(Wu et al. 2021b; Chao et al. 2021) are zero-dimensional quasi-spherical carbon-nanoparticles with very small sizes (1–10 nm) and relatively distinctive fluorescence properties. Graphene quantum dots (GQDs) are nano fragments of graphene with anomalous luminescence behaviors (Shin et al. 2021; Liu et al. 2021a). The nitrogen-doped graphene quantum dots (N-GQDs) have been used for the delivery and fluorescence tracking of doxorubicin. In fact, N-GQDs have lowered 10 times doses of the drug taken by patients to achieve ordinary-like therapeutic effect used in controlling cancer cell growth (Frieler et al. 2021). Also, new fabricated GQDs with humic acid have efficiently acknowledged for Cu²⁺ ions detection (Liu et al. 2021a). In addition, a highly efficient optosensors have been developed using TiO₂/GQDs composited with specified imprinted polymer for cefazolin detection (Chansud 2021). Many computational studies have made graphene quantum dots with metal complexes to improve their optical and non-optical characteristics to foresees more advanced potential applications for GQDs (Permatasari et al. 2021; Zhao et al. 2021; Chen et al. ; Ezzat et al. 2021). Recent molecular modeling researches have focused on constructing electrostatic potential maps (ESP) for proposed chemical compounds (El-Mansy,El-Nahass 2014; Bayoumy et al. 2021; Ibrahim et al. 2013; Ismail et al. 2013). In consequences, ESP becomes a popular tool to provide precise mapping for active functional sites (Bulat et al. 2010; Soliman et al. 2013; El-Nahass et al. 2013) that characterize predominant chemical addition attitude for various structures; either electrophilic or nucleophilic tendency. Several articles were presented previously involve the various definitions of molecular surface (Bayoumy et al. 2020a; Bayoumy et al. 2020c; El-Mansy et al. 2020a; El-Mansy et al. 2020b). One of the common definitions considers MESP maps as the outer area surrounding a chemical structure rising from a group of intersected spheres, whereas their centers are aligned with the nucleus of each species (Connolly 1983; Dunitz et al. 2000; Arteca et al. 1988; Franci et al. 1984); these assumed spheres are produced from forces named Van der Waals radii of the interested atoms (Bondi 1964). On the other side, MESP maps were presented via Bader et al. (Bader et al. 1967; Bader et al. 1987) as the external contour of electrons density $\rho(r)$. Such term is the most popular relative to the first one because it includes more informative details on the chemical properties of the investigated chemical structures, e.g. lone pair electrons, σ -holes presence, and many more. These external

contours have been always ensured to represent nearly 95–98% of the details regarding electronic density of some structures (Geesi et al. 2021; Wu et al. 2021a; Chai et al. 2021). The mapped electrostatic potential $V(r)$ of a structure had been recognized as a major portion in controlling its reactive attitude. Recent physicochemical characteristics aided through QSAR technique have been an efficient tool in mapping pharmaceutical and biological applications for various molecules (Wang et al. 2021; Rosa et al. 2021; Alves et al. 2021; Wu et al. 2021c; Chatterjee, Roy 2021). The aim of intended study is to investigate the effect of COOH, NH₂ as well as Li substituents on electronic, vibrational, and optical properties of fullerene. Moreover, QSAR descriptors are investigated to foresee medicinal applications as well. The modified fullerenes are expected to offer new potential devices for solar cell and memory switches technology.

Calculations Details

All the studied structures were calculated with GAUSSIAN 09W soft code (Tomberg 2020; Frisch et al. 2010) at Spectroscopy Department, National Research Centre, Egypt. Each structure is optimized with DFT@B3LYP/6-31G(d,p) (Singh et al. 2021; Sultan et al. 2021; Liu et al. 2021b) and then both IR and Raman spectra are reproduced as well. Also, QSAR descriptors are computed via semiempirical PM6 interface (Wen et al. 2021; Alotaibi et al. 2021) provided by implemented SCIGRESS 3.0 (Badry et al. 2021; Elfiky, Azzam 2020) software at the same facility. Some QSAR indices are highlighted as total energy (E), resultant formation heat (FH), ionization potential (IP), partition coefficient (logP), molar-refractivity (M_R), molecule weight (M_w), and finally polarizability (P).

Results and Discussion

Building Model Molecules

Fullerene is studied as a model molecule as indicated in **Fig. 1**, at sites 4 and 5 one bond is broken then two units of COOH, NH₂ as well as Li are attached as complex through 4 and 5 atoms of fullerene forming C₆₀-2COOH, C₆₀-2NH₂ and C₆₀-2Li, respectively as indicated in **Figs. 2, a, b and c.**

Fig. 1 Fullerene model molecule.

Fig. 2 Model molecules for fullerene-2X whereas a- $x=2\text{COOH}$; b- $x=2\text{NH}_2$ and C- $X=2\text{Li}$.

Table 1 Computed Frontiers parameters for pristine and modified fullerenes.

	C_{60}	$\text{C}_{60-2\text{COOH}}$	$\text{C}_{60-2\text{NH}_2}$	$\text{C}_{60-2\text{Li}}$
E_{HOMO}	-3.23	-3.23	-3.13	-2.73
E_{LUMO}	-5.99	-5.79	-5.68	-4.14
Energy Gap	2.76	2.56	2.56	1.41
$I = -E_{\text{HOMO}}$	3.23	0.12	3.13	0.10
$A = -E_{\text{LUMO}}$	5.99	0.21	5.68	0.15
$\kappa = 1/2(E_{\text{LUMO}} - E_{\text{HOMO}})$	1.38	1.28	1.28	0.70
$\chi = 1/2(E_{\text{LUMO}} + E_{\text{HOMO}})$	-4.61	-4.51	-4.40	-3.44
$\phi = \chi^2/2\kappa$	7.69	7.95	7.59	8.38
$S = 1/\kappa$	0.72	0.78	0.78	1.42

98

99 **1. Frontier molecular orbitals (FMOs) analyses**

100 As structural reactivity and reactants selective pathways are clarified by FMOs theorem
 101 (El-Mansy 2017; El-Mansy et al. 2017; Gulácsi et al. 2016; El-Mansy,Yahia 2014).
 102 Almost researchers determine reactivity and pathway-selectivity through how strong the
 103 interplays are among conduction (LUMOs) and valence (HOMOs) domains (El-Barbary
 104 et al. 2009; Ibrahim et al. 2012). Constructively, FMOs indices are calculated like optical
 105 band offset, ionizing-potential $I = -E_{HOMO}$, electron-affinity $A = -E_{LUMO}$, chemical
 106 potential $\chi = (E_{LUMO} + E_{HOMO})/2$, hardness $\kappa = (E_{LUMO} - E_{HOMO})/2$, electrophile-
 107 index $\phi = \chi^2/2\kappa$, softness $S = 1/\kappa$ and aggregated dipole moment and registered in
 108 **Table 1** for studied configurations. Results showed that designed C₆₀-2Li configuration
 109 have high total dipole moment (12.74 Debye) and optical energy gap (1.41 eV). The
 110 modified C₆₀-2Li solar efficiency may compete recent kesterite Cu₂ZnGeSe₄ solar cell
 111 which have band gap range as 1.5~1.7 eV and efficiency > 14% (Khelifi et al. 2021).
 112 **Fig. 3** represent HOMO/LUMO offsets for designed C₆₀ configurations at B3LYP/6-
 113 31G(d,p).

114

Fig. 3 HOMO/LUMO offsets for pristine and modified fullerenes

2. IR and Raman Analyses

Both calculated IR and Raman wavenumbers and the corresponding assignments for designed C₆₀ configurations are collected in **Table 2**. Computed IR and Raman spectra for proposed C₆₀ configurations at B3LYP/6-31G(d,p) in **Fig. 4**. Results showed that more indexed peaks have been recorded in C₆₀-2Li configuration due to its large reactivity (TDM=12.74 Debye) and lower band gap offset (1.41 eV). The assignments are briefly disused as the following:

The O-H and N-H stretch modes are observed in the region 3400-3800 cm⁻¹ (Branca et al. 2016; Karimi-Maleh et al. 2021). The O-H stretch for C₆₀-2COOH is observed at 3746 cm⁻¹ for both IR and Raman spectra. The O-H plane-in bend for C₆₀-2COOH is noticed at 1194 cm⁻¹ for both IR and Raman pattern. While O-H Plane-out bend for C₆₀-2COOH is detected at 712 and 624 cm⁻¹ for IR and Raman charts, respectively.

The N-H stretch for C₆₀-2NH₂ is seen at 3572 and 3482 cm⁻¹ in IR and Raman spectra, respectively. The N-H plane-in bend for C₆₀-2COOH is assigned at 1098 and 1135 cm⁻¹ for IR and Raman pattern, respectively. Whereas N-H Plane-out bend for C₆₀-2COOH is detected at 893 and 795 cm⁻¹ for IR and Raman charts, respectively.

The C=O and C=C stretch modes are scanned in spectral range 1850-1300 cm⁻¹ (Dos Santos et al. 2021; Lin et al. 2021; Zhou et al. 2021). The C=O stretch for C₆₀-2COOH is observed at 1828 cm⁻¹ for both IR and Raman spectra. The Original C=C stretch for C₆₀ is found at 1436 and 1617 cm⁻¹ for IR and Raman, respectively. The C=C stretch for C₆₀-2COOH is seen at 1330 and 1609 cm⁻¹ in IR and Raman, respectively. The C=C stretch for C₆₀-2NH₂ is recorded at 1495 and 1603 cm⁻¹ in IR and Raman plots, respectively. The C=C stretch for C₆₀-2Li is indexed at 1607 and 1567 cm⁻¹ in IR and Raman, respectively.

The C-C stretch is observed at 969 and 1072 cm⁻¹ for C₆₀-2COOH at IR and Raman peaks, respectively. Similarly, The C-C stretch is observed at 965 and 988 cm⁻¹ for C₆₀-2Li in IR and Raman, respectively.

The C-O plane-in bend is observed at 665 and 560 cm^{-1} for $\text{C}_{60}\text{-2COOH}$ at IR and Raman peaks, respectively. The C-N plane-in bend is observed at 599 cm^{-1} for $\text{C}_{60}\text{-2NH}_2$ in both IR and Raman, respectively. Finally, The C-Li plane-in bend is observed at 593, 558 cm^{-1} for $\text{C}_{60}\text{-2Li}$ in IR and Raman, respectively.

Table 2 Calculated IR and Raman wavenumbers and corresponding assignments for pristine and modified fullerenes.

IR Wavenumber (cm^{-1})				Assignments
C_{60}	$\text{C}_{60}\text{-2COOH}$	$\text{C}_{60}\text{-2NH}_2$	$\text{C}_{60}\text{-2Li}$	
	3746			$\nu\text{O-H}$
		3572		$\nu\text{N-H}$
	1828			$\nu\text{C=O}$
			1607	
	1330	1495	1584	$\nu\text{C=C}$
1436			1444	
	1194			$\beta\text{O-H}$
		1098		$\beta\text{N-H}$
		969	965	$\nu\text{C-C}$
		893		$\gamma\text{N-H}$
	712			$\gamma\text{O-H}$
	665 $_{(\text{X=O})}$	599 $_{(\text{X=N})}$	593 $_{(\text{X=Li})}$	$\beta\text{C-X}$
588	619 $_{(\text{X=O})}$	557 $_{(\text{X=N})}$	550 $_{(\text{X=Li})}$	$\beta\text{C-C}+\beta\text{C-X}$
537	536 $_{(\text{X=O})}$	506 $_{(\text{X=N})}$	537 $_{(\text{X=Li})}$	$\gamma\text{C-C}+\gamma\text{C-X}$
Raman Wavenumber (cm^{-1})				Assignments
C_{60}	$\text{C}_{60}\text{-2COOH}$	$\text{C}_{60}\text{-2NH}_2$	$\text{C}_{60}\text{-2Li}$	
	3746			$\nu\text{O-H}$
		3482		$\nu\text{N-H}$
	1828			$\nu\text{C=O}$
1617	1609	1603	1567	
1503	1497	1476	1433	$\nu\text{C=C}$
	1194			$\beta\text{O-H}$
		1135		$\beta\text{N-H}$
	994	1072	988	$\nu\text{C-C}$
		795		$\gamma\text{N-H}$
	624			$\gamma\text{O-H}$
787	560	599 $_{(\text{X=N})}$	585 $_{(\text{X=Li})}$	$\beta\text{C-X}$
	536 $_{(\text{X=O})}$	539 $_{(\text{X=N})}$	554 $_{(\text{X=Li})}$	$\beta\text{C-C}+\beta\text{C-X}$
490	492 $_{(\text{X=O})}$	467 $_{(\text{X=N})}$	478 $_{(\text{X=Li})}$	$\gamma\text{C-C}+\gamma\text{C-X}$

3. Molecular Electrostatic Potential (MESP)

Geometry optimization calculations are performed for fullerene structure as well as its proposed derivatives to show their MESP distribution. Generally, MESP maps appear in several color gradients indicating regions of different electronegativity. These colors

always go from red to dark blue spectrum, the red one corresponds to sites of extreme negativity while the blue is for positive regions. The full colors range is red, yellow, green, light blue and dark blue representing the most negative and most positive, respectively. MESP colors are always attributed, in some way, to the electronegativity of the shared atoms where atoms having high electronegativity will appear in red at bonding to others of lower electronegative values. Therefore, presence of species of similar electronegativity creates narrow color distribution and green color may be predominant.

Fig. 4 Predicted IR and Raman spectra for pristine and modified fullerenes.

Fig. 5 shows the calculated MESP maps of fullerene and its suggested derivatives. The illustrated MESP maps are characterized by the presence of some colors of the previously mentioned ones. A spherical red elliptical region can be noticed obviously at the central region of fullerene structure that attributed previously (Bayoumy et al. 2020b) for the strong electron delocalization resonance for multiple benzene moieties forming fullerene.

176 **Fig. 5** Calculated MESP maps for (a) C_{60} , (b) $C_{60}-2COOH$, (c) $C_{60}-2NH_2$ and (d) $C_{60}-$
 177 $2Li$.

178 Such light blue color is the main color in all proposed derivatives especially for $C_{60}-2Li$
 179 in which Li addition affect significantly both circumference and red ellipse inside
 180 fullerene ball, that appear in very faint red flag. Small dark blue regions appear as well
 181 around the additive Li atoms. However, additive COOH and NH_2 groups has no
 182 noticeable impact on this red elliptical sphere inside fullerene ball. New mapped regions
 183 arising upon additive COOH. Firstly, a yellow region around O atoms indicating the

withdrawing electrons quarrel occurs between COOH group and fullerene sphere. toward each other. Presence of yellow instead of red color around O represent success of fullerene to attract electrons from O. Dark blue color appears in the vicinity of terminal H atoms of COOH groups due to electrons attraction via O atoms. Similarly, MESP map of C₆₀-2NH₂ has the same pattern of C₆₀-2COOH, however the yellow color around N atoms is light not dark which may be due to that O is more electronegative than N atom. Eventually, Additive Li possesses a blue shift in Fullerene electronegative behavior towards electrophilic additions whereas additive COOH and NH₂ maintain the same intrinsic nucleophilic additions.

4. QSAR analyses

QSAR technique provides a clear and extensive scheme for potential biological sharings of target biostructures. QSAR has been acknowledged as the most valuable tool for mapping structures bioactivities (Shylaja et al. 2021; Ojha et al. 2021). **Table 3** lists the PM6 QSAR characters such as overall energy (E) (stability index), resultant formation heat (FH) (enthalpy change during a chemical formation process), ionizing-potential (IP), partition-coefficient (logP), molar-refractivity (M_R), molecule-weight (M_W), and polarizability (P).

Table 3 Calculated PM6 QSAR descriptors for C₆₀, C₆₀-2COOH, C₆₀-2NH₂, and C₆₀-2Li.

Chemical Structure	E (kcal/mol)	FH (kcal/mol)	IP (eV)	log P	M _R	M _W (a.u)	P (Å ³)
C ₆₀	-209054.076	811.464	-9.666	9.600	232.926	720.642	62.018
C ₆₀ -2COOH	-247391.847	616.475	-9.569	8.766	244.841	810.677	68.690
C ₆₀ -2NH ₂	-221896.003	783.445	-9.378	7.134	238.212	752.687	64.910
C ₆₀ -2Li	-209692.038	778.903	-6.999	8.200	229.768	734.524	66.995

Results showed that additive Li has no significant impact on fullerene stability whereas both additives NH₂ and COOH are highly lower its stability. The FH for C₆₀-2COOH, C₆₀-2NH₂ and C₆₀-2Li are 616.475, 783.445 and 778.903 kcal/mol, respectively. The electric conductivity is improved a little bit for both C₆₀-2NH₂ and C₆₀-2COOH than pristine fullerene. Unfortunately, the lack in C₆₀-2Li conductivity may be attributed to Li

mono-valence nature. Regarding log P values, both pristine and modified fullerenes ensure a dominant hydrophobic character. The C₆₀ hydrophobicity seems to be down grading upon additive 2COOH, 2Li, and 2NH₂ as C₆₀ > C₆₀-2COOH > C₆₀-2Li > C₆₀-2NH₂. The low C₆₀-2NH₂ hydrophobic character emphasize that more attached amino antennae would drag the original fullerene towards improved bioactivities. Molar-refractivity of C₆₀ has improved positively by additive 2COOH and 2NH₂ in contradict to 2Li. Polarizability index for pristine fullerene has improved slightly by additive 2COOH, 2NH₂, and 2Li groups. Hereby, the C₆₀-2NH₂ is acknowledged as potential bioactive substrate for drug delivery.

Conclusion

Molecular modelling for modified fullerenes is completed by DFT BELYP 6-31G(d,p) through G09 software to show substituents (COOH, NH₂, Li) effect on electronic, vibrational, optical characteristics for pristine fullerene. Both calculated IR and Raman spectra and corresponding assignments for designed C₆₀ configurations are calculated at the same level. Additive Li possesses a blue shift in Fullerene electronegative behavior towards electrophilic additions whereas additive COOH and NH₂ maintain the same intrinsic nucleophilic additions. Also, C₆₀-2Li have high total dipole moment (12.74 Debye) and band offset (1.41 eV). Hopefully, the upcoming modified C₆₀-2Li solar efficiency may compete recent kesterite Cu₂ZnGeSe₄ solar cell which have band gap range as 1.5~1.7 eV and efficiency > 14%. QSAR descriptors for modified fullerenes showed that additive 2NH₂ implies bioactivities of pristine fullerenes than 2COOH and 2Li sets. Hereby, the C₆₀-2NH₂ is acknowledged as potential bioactive substrate for drug delivery.

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Figures

Figure 1

Fullerene model molecule.

Figure 2

Model molecules for fullerene-2X whereas a- $x=2\text{COOH}$; b- $x=2\text{NH}_2$ and c- $X=2\text{Li}$.

Figure 3

HOMO/LUMO offsets for pristine and modified fullerenes

Figure 4

Predicted IR and Raman spectra for pristine and modified fullerenes.

Figure 5

Calculated MESP maps for (a) C60, (b) C60-2COOH, (c) C60-2NH2 and (d) C60-2Li.