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Lithium-functionalization of Pyrrole-*n*-carboxylic Acids (*n*=1, 2, 3)



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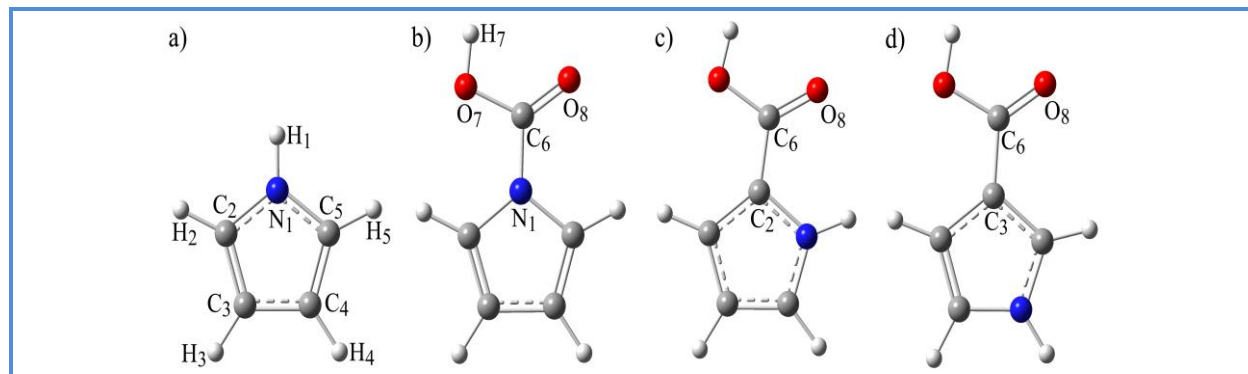
Density functional theory

ABSTRACT

Functionalization processes of neutral and ionic forms of the singular lithium element (Li/Li⁺) by the pyrrole-*n*-carboxylic acid (PnCA; *n*=1, 2, 3) have been investigated based on the quantum chemical density functional theory (DFT) calculations. To this aim, molecular and atomic scales parameters have been obtained for the optimized structures of original and Li/Li⁺ functionalized complex models of PnCA. The results have indicated that the structural shapes and the O8 dominant atom properties are similar to P1CA and P3CA models but different from P2CA model. Moreover, the adsorption energies have indicated that the P3CA model could be considered as the best choice for both of Li and Li⁺ functionalization processes. The orbital distribution patterns and dipole moments have also approved the Li/Li⁺ functionalization by the PnCA species. As a result, the PnCA species could be suggested as suitable adsorbents of neutral and ionic forms of the Li element.

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Graphical Abstract



Introduction

Lithium (Li) is an important element for applications in modern electrical industries, especially for constructing rechargeable Li ion batteries (LIBs), due to the fact that they possess electrochemical properties [1]. There are several types of LIBs in which the sizes of batteries are also varied from large to small sizes [2]. Moreover, the applications of LIBs as power suppliers in biological systems are very much important [3]. Therefore, systematic functionalization containing Li/Li⁺ is crucial for applications in the specific electrical devices [4]. Earlier works have indicated the efficacy of inorganic-based materials for adsorption of Li/Li⁺ for various estimated applications [5–7]. Nanostructures, which have been investigated with tremendous interests during recent decades [8–12], are among the possible candidates for adsorptions of Li/Li⁺ for the desired applications [13–15]. In addition to inorganic-based materials, it is also important to have organic materials for adsorptions of Li/Li⁺, especially for power suppliers of electronic devices in the biological-based medical systems [16]. It is noted that the recovering and recycling of Li element is also important for industries [17]. Earlier studies have indicated that the organic-based materials could also functionalize metal elements by chemical and physical adsorptions [18–20]. Those materials containing functional groups with interacting electron lone-pairs on the atomic sites, such as carboxylic and amide groups are among the choices for metal functionalization [21, 22]. Pyrrole-*n*-carboxylic acid (PnCA; *n*=1, 2, 3) is an important organic-based derivative of pyrrole containing a carboxylic acid functional group with an interacting oxygen atom for metal functionalization (Figure 1). Earlier studies indicated that such carboxylated chemical systems could be employed as proper metal chelators in either pure industries or human-related applications *e.g.*, dietary additives [23, 24]. Pyrrole [25] itself is almost a starting material for synthesizing numbers of chemicals.

Moreover, pyrrole is an important building block of biologically active compounds such as hemoglobin and chlorophyll [26]. Therefore, it could be an interesting topic to investigate Li/Li⁺-functionalization capability of PnCA as a very well-known originated structure.

Within this work, we have investigated the Li/Li⁺ functionalization by the carboxyl acid functional group of PnCA (n=1, 2, 3) species (Figures 1 and 2) based on quantum chemical computations. We have considered both of neutral and ionic forms of Li element to be adsorbed by the PnCA (n=1, 2, 3) species. In an earlier work [23], the H atom of carboxylic group of P2CA was replaced by the Li atom, in which the Li was relaxed between the two O atoms after optimization. It is worth mentioning that the small molecule of PnCA could show different properties shown in an earlier work by their different interactions with nanostructures [27]. Within this work, the singular Li/Li⁺ functionalization of PnCA models has been performed in the presence of the initial H atom of carboxyl group, in which the original carboxyl acid group of PnCA has been unchanged. The optimized geometries, molecular properties, and atomic scale charges have been evaluated to provide an answer for possible assistance of PnCA (n=1, 2, 3) species for Li/Li⁺ functionalization (Tables 1 and 2, Figures 1–3).

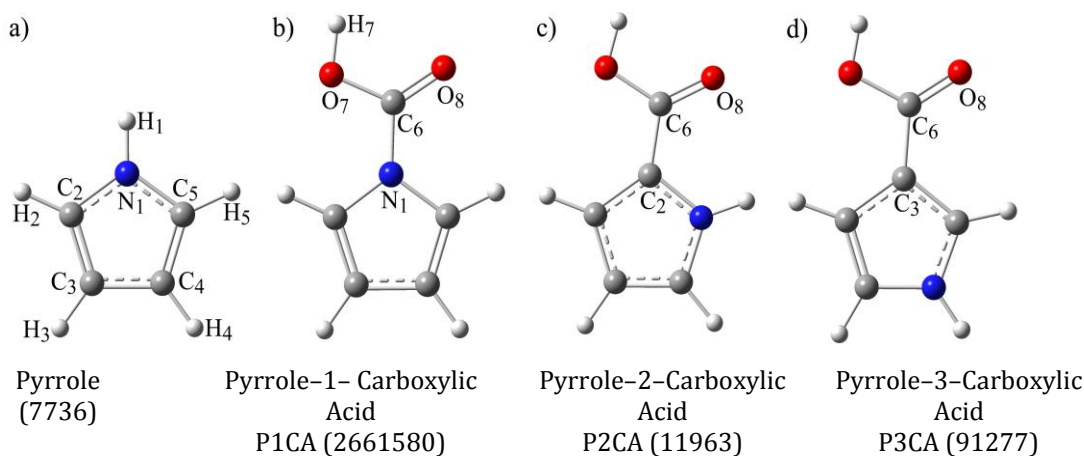


Figure 1. Pyrrole and the carboxylic acid derivatives; their abbreviations and (ChemSpider IDs)

Experimental

Computational details

Quantum chemical calculations have been performed within this work based on density functional theory (DFT) methodologies employing the B3LYP functional and the 6-31+G* basis set as implemented in the Gaussian package [28-31]. First, all of the original PnCA (pyrrole-*n*-carboxylic acid; n=1, 2, 3) structures (Figure 1) have been geometrically optimized to obtain

the minimized energy structures. It is noted that the carboxylic acid group is respectively bonded to N, C-alpha and C-beta positions of PnCA resulting the P1CA, P2CA and P3CA models. Second, Li/Li+-contained models of the already optimized PnCA species have been re-optimized to obtain the best functionalization geometries of the complex structures (Figure 2). By the optimization processes, optimized geometries, total energies (E_T) and dipole moments (D_M) have been directly evaluated for the investigated original and complex model systems (Table 1 and Figure 2). To validate the obtained E_T values, the basis set superposition error (BSSE) correction energies have been calculated for the optimized structures based on the Counterpoise method [32]. Further molecular properties have been indirectly evaluated using eqs. (1-4); representing adsorption energies (E_{Ads}), ionization energies (I), electron affinities (A), and molecular energy gaps (E_G), respectively (Table 1). The values for I and A have been evaluated based on Koopmans' theorem, in which so many works have been dedicated to validate it [33, 34]. It is noted that the HOMO and LUMO implied for the calculated energy levels of the highest occupied and the lowest unoccupied molecular orbitals (eqs. 2 and 3) have been illustrated in Figure 3.

$$E_{Ads} = E_{Complex} - E_{Li/Li+} - E_{PnCA} \quad (1)$$

$$I = -E_{HOMO} \quad (2)$$

$$A = -E_{LUMO} \quad (3)$$

$$E_G = E_{LUMO} - E_{HOMO} \quad (4)$$

In addition to the evaluated molecular parameters, atomic scale parameters have been obtained for the investigated original and complex model systems for better interpretations of Li/Li+ functionalization processes by the PnCA species (Table 2). The net atomic charges (Q) have been evaluated based on the performed natural bond orbital (NBO) population calculations for all of the optimized model systems [35]. It is important to investigate the properties of molecular systems at the atomic scale, because the atomic properties could dictate the general activity of molecules. Herein, the Q parameters could help to provide insightful information for the investigations of molecular systems at the atomic scales.

In order to compare the calculated results for a potential reader, all of the described computations of this work have been repeated based on the B3LYP/6-311+G** theoretical level as included in an electronic supplementary file. Since the differences in the obtained parameters are almost negligible, the B3LYP/6-31+G* results are only listed here.

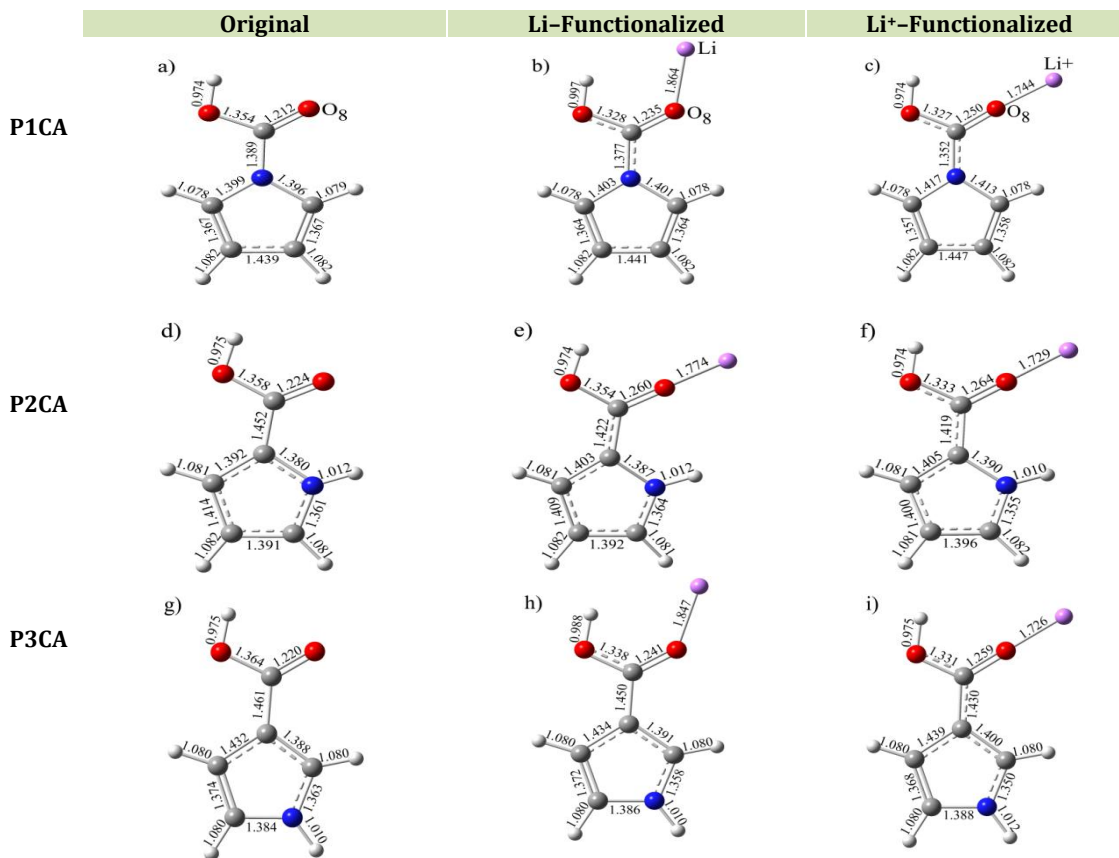


Figure 2. The optimized structures of original and singular Li/Li⁺-Functionalized PnCA (n=1–3)

Results and discussion

Optimizations

Within this work, the capability of PnCA (pyrrole-*n*-carboxylic acid; n=1, 2, 3) species for the functionalization of Li/Li⁺ (Figures 1–3) has been investigated based on the DFT calculated parameters (Tables 1 and 2). A quick look at the obtained optimized structures (Figure 2) could indicate that the geometrical parameters of the original PnCA species are different from each other. Moreover, the geometries are also different in each of the n=1, 2, 3 of PnCA-Li/Li⁺ complexes. Careful analyzing the representative bond lengths and angles of Table 1. can reveal that there are different O–Li bonds in each of the complex systems. All of the Li⁺-complexes have shorter O–Li⁺ bond lengths in comparison to O–Li bond lengths in all of Li-complexes. The magnitudes of O–Li bond lengths are identical for the P1CA and P3CA complexes but different from the P2CA complex. Interestingly, the magnitudes of O–Li⁺ bond lengths are identical for all of PnCA complexes. Comparing the magnitudes of the representative bond angles can indicate that the C6–O8–Li of P1CA and P3CA complexes are identical but different from P2CA complex. As a concluding remark

of geometrical optimizations, the structural representations of P1CA and P3CA complexes are almost similar to each other but different from the structural representation of P2CA complex. The values of E_T (total energy) indicated that all three of the PnCA species have the same possibility of formations in both of the original and complex systems. Careful examinations of values of E_{Ads} (adsorption energy) can demonstrate that the Li+-functionalization is more favourable than the Li-functionalization for all of the PnCA species. Comparing the obtained magnitudes of adsorption energies of this work with the reported standard value of ~ 3 eV for Li-O bond [36] and also with an earlier work on Li-adsorption with graphene-fullerene hybrid species ($E_{\text{Ads}} = \sim 2.3$ eV [37] demonstrates the remarkable ability of the PnCA small molecule for Li adsorption). Analysing the evaluated parameters from the HOMO and LUMO energies showed that the orbitals could dictate different electronic properties for the corresponding systems. Moreover, the influence of Li/Li+-functionalization could change the electronic environment of PnCA cyclic structures, which could also reveal the effects of the functionalization on the aromaticity of PnCA.

Table 1. Molecular properties*

Property	P1CA			P2CA			P3CA		
	Original	-Li	-Li+	Original	-Li	-Li+	Original	-Li	-Li+
C ₆ -O ₇ Å	1.35	1.33	1.33	1.36	1.35	1.33	1.36	1.34	1.33
C ₆ -O ₈ Å	1.21	1.24	1.25	1.22	1.26	1.26	1.22	1.24	1.26
O ₈ -Li Å	—	1.86	1.74	—	1.77	1.73	—	1.85	1.73
O ₇ -C ₆ -O ₈ °	124	124	122	122	120	120	121	122	119
C ₆ -O ₈ -Li °	—	129	176	—	167	179	—	137	179
E_T keV	-10.85	-11.06	-11.05	-10.85	-11.06	-11.05	-10.85	-11.06	-11.05
BSSE eV	0.05	0.02	0.02	0.05	0.02	0.02	0.04	0.02	0.02
E_{Ads} eV	—	-0.55	-1.88	—	-0.61	-2.03	—	-0.62	-2.23
I eV	6.47	2.98	10.02	6.55	2.77	10.26	6.47	2.59	9.98
A eV	1.10	1.78	5.39	1.26	1.59	5.55	0.84	1.72	5.28
E_G eV	5.37	1.20	4.63	5.29	1.18	4.71	5.63	0.88	4.70
D_M Debye	1.56	3.98	11.50	1.48	1.79	11.46	3.62	8.21	10.53

Both of the ionization potential (I) and electron affinity (A) parameters are different in each of the original PnCA models and also in the corresponding complexes. Interestingly, the values of energy gaps (E_G) are significantly decreased in the PnCA-Li complexes in comparison to both of the original PnCA and complex PnCA-Li+ models. The HOMO and LUMO distribution patterns (Figure 3) also indicate that the orbital properties of the investigated model systems detect different environment in comparison to each other. The trend could mean that the effects of Li/Li+-functionalization could be very well detected by the orbital patterns. Comparing the values of dipole moments (D_M) also indicates that the n position of carboxylic acid group could change the polarity of structures, in which the polarity of P3CA is in the highest stage whereas that of P2CA is in the lowest stage. The polarities of PnCA-Li/Li+ complexes have been increased in comparison to

the original PnCA models, in which the polarities of PnCA-Li⁺ complexes are in the highest stage. As a concluding remark of this section, it could be mentioned that the PnCA models could adsorb both of the Li/Li⁺ forms of element, which could be very well monitored by the molecular properties. All geometrical, energetically and orbital parameters indicated the effects of adsorption processes on the original properties of PnCA counterparts, in which the magnitudes of effects have been varied in different magnitudes for different complex model systems.

Table 2. Atomic charges Q

Atom	P1CA			P2CA			P3CA		
	Original	-Li	-Li ⁺	Original	-Li	-Li ⁺	Original	-Li	-Li ⁺
N ₁	-0.46	-0.45	-0.44	-0.53	-0.54	-0.53	-0.55	-0.54	-0.52
C ₂	-0.06	-0.05	-0.05	-0.01	-0.02	-0.04	-0.01	0.02	0.03
C ₃	-0.30	-0.29	-0.26	-0.24	-0.24	-0.18	-0.25	-0.26	-0.27
C ₄	-0.30	-0.29	-0.25	-0.33	-0.32	-0.30	-0.28	-0.26	-0.25
C ₅	-0.05	-0.05	-0.06	-0.04	-0.04	0.03	-0.08	-0.08	-0.05
C ₆	0.95	0.99	1.01	0.77	0.75	0.81	0.80	0.84	0.86
O ₇	-0.72	-0.69	-0.66	-0.71	-0.70	-0.66	-0.72	-0.69	-0.66
O ₈	-0.62	-0.75	-0.86	-0.64	-0.84	-0.88	-0.62	-0.75	-0.87
Li	—	0.05	0.96	—	0.23	0.96	—	0.01	0.96
H ₁	—	—	—	0.46	0.45	0.45	0.45	0.45	0.46
H ₂	0.26	0.26	0.27	—	—	—	0.26	0.26	0.25
H ₃	0.25	0.26	0.28	0.26	0.26	0.28	—	—	—
H ₄	0.25	0.26	0.24	0.25	0.25	0.28	0.26	0.27	0.28
H ₅	0.26	0.26	0.27	0.24	0.24	0.26	0.24	0.25	0.26
H ₇	0.53	0.48	0.54	0.52	0.23	0.53	0.51	0.50	0.53

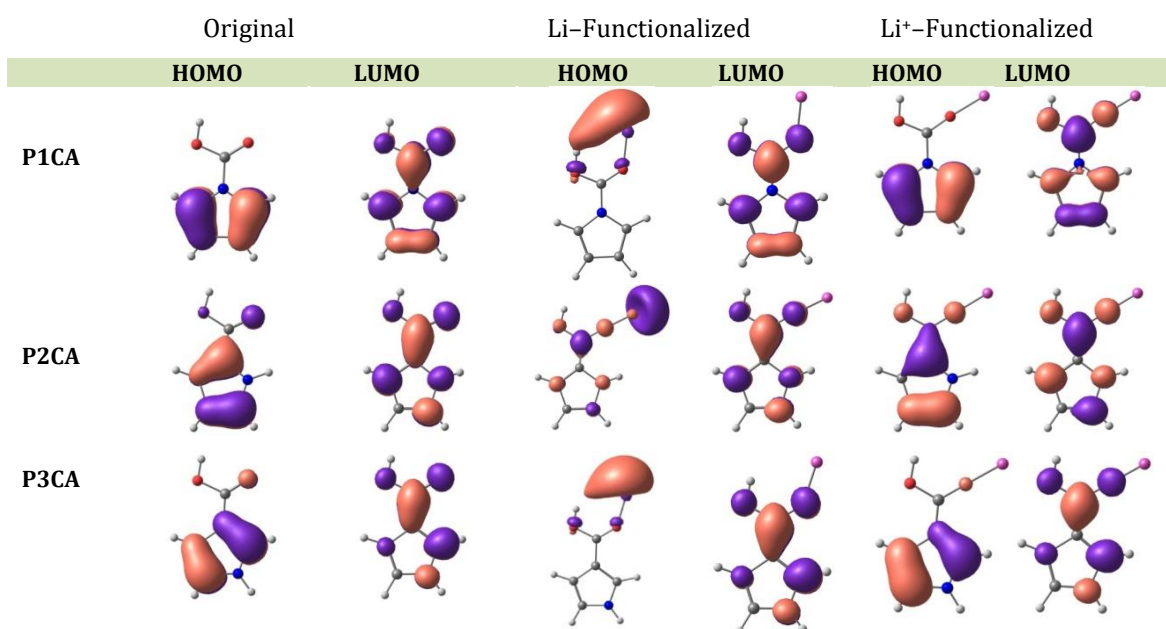


Figure 3. The HOMO and LUMO distribution patterns of original and Li/Li⁺-Functionalized PnCA (n=1-3)

Atomic Charges

Atomic scale parameters including net atomic charges (Q) have been summarized in Table 2. for all of the original and complex model systems (Figure 2). According to the obtained results for five types of atoms of the structures, the effects of functionalization are significant for the O8 atom, which is in direct connection to the functionalized Li/Li+. No real effects have been observed for other atoms when compared to the results of the original PnCA with the complex model systems. Interestingly, the O8 atoms of P1CA and P3CA complex models detect similar environments but different from P2CA complex models. Regarding the geometrical properties, a parallel trend for similarities of P1CA and P3CA complex models have been obtained earlier. Further analysis of the Q results can indicate that the O8 and Li atoms do not share electrons in the P1CA–Li and P3CA–Li models whereas they share electrons in the P2CA model. The net charges of Li atoms are almost zero in the two models but it is a meaningful non-zero value in the P2CA model. Corresponding results for the O8 atoms show that the changes in net charges are very much significant for the O8 of P2CA–Li model in comparison to the other P1CA–Li and P3CA–Li complex models. For the O8 and Li atoms of PnCA–Li+ complex model systems, similar results have been obtained for all of three complex structures. As a concluding remark of this section, it could be mentioned that the O8 atom is dominant for determining the properties of PnCA–Li/Li+ complex model systems.

Conclusions

DFT calculations have been performed to investigate the Li/Li+ functionalization processes by the PnCA ($n=1, 2, 3$) species. Based on the obtained molecular and atomic properties, it can be concluded that the Li/Li+ functionalization took place by the PnCA counterparts yielding different structural shapes for the PnCA–Li/Li+ complex model systems. Interestingly, the structural shapes for Li/Li+– functionalized P1CA and P3CA complex models were identical but different from the Li/Li+– functionalized P2CA complex model. The trend was approved by the changes of Q properties for the dominant O8 atoms of PnCA model systems. Based on the EAdS values, the P3CA was the best choice for Li/Li+ functionalization among the model systems. The HOMO and LUMO distribution patterns indicated that the orbital properties could detect the effects of Li/Li+ functionalization, in which the changes of patterns and the corresponding energy levels were significant among the original and complex models of PnCA. Moreover, the polarities of models were significantly changed for the complex systems. As a final conclusion, the approval of Li/Li+ functionalization by the PnCA species could lead to suggest the PnCA species as suitable adsorbents of the neutral and ionic forms of the Li element.

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