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**Original Research Article** 

# DFT Studies on 10 Chromenes Derivatives Performance as Sensing Materials for Electrochemical Detection of Lithium (I)

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## ABSTRACT

In this study, we have conducted a detailed analysis of 10 recently synthesized chromen derivatives to evaluate their performance as electrocatalytic sensing materials for the detection of Li<sup>+</sup> ions. Our investigation involved the use of Infra-red (IR) and frontier molecular orbital (FMO) computations to gain insights into the interactions between these derivatives and Li<sup>+</sup> ions. The results obtained from our analysis revealed that the derivative with  $NO_2$  substitution in the meta position of the benzene ring exhibited the strongest interaction with Li<sup>+</sup> ions. This was observed in both vacuum and aqueous phases, with K<sub>f</sub> values of  $5.429 \times 10^{+48}$  and  $1.036 \times 10^{+23}$ , respectively. Such a strong interaction suggests that this derivative has the potential to be an excellent candidate for the development of electrochemical sensors for the detection of Li<sup>+</sup> ions. Furthermore, we also investigated the changes in the bandgap of this derivative during the complexation process. Our findings indicated that this particular derivative experienced the most significant changes in its bandgap, with a percentage decrease of -50.824. This observation highlights its potential as a selective and sensitive recognition element for the detection of Li<sup>+</sup> ions. Overall, our research provides valuable insights into the performance of these chromen derivatives as electrocatalytic sensing materials for Li<sup>+</sup> ion detection. The derivative with NO<sub>2</sub> substitution in the meta position of the benzene ring emerges as a promising candidate due to its strong interaction with Li<sup>+</sup> ions and significant changes in its bandgap during complexation. These findings pave the way for the development of new and improved electrochemical sensors for the detection of Li<sup>+</sup> ions, which can have significant implications in various fields such as energy storage and battery technologies.

Keywords: Chromenes, Density functional theory, Sensor, Complexation, Li<sup>+</sup>

# Introduction

 $Li^+$  is a psychotropic medicine which is available as carbonate salt ( $Li_2(CO_3)$ ) for the treatment of bipolar disorder and acute mania [1, 2]. Li<sup>+</sup> is on the World Health Organization's list of essential medicines and is prescribed widely by physicians [3]. However, there is a narrow border between the appendix and toxic dosages of  $Li^+$  and in high dosages it is associated with severe side effects including convulsion, ataxia, tremor, diarrhea, nausea, kidney failure, liver damage, and even death [4, 5]. Therefore, development a simple, accurate and precise analytical method for Li<sup>+</sup> determination is of great importance. To date, various techniques have been reported for the determination of Li<sup>+</sup> such as spectrophotometry [6], flame and graphite furnace atomic absorption spectroscopy (AAS) [7, 8]. Unfortunately, the above-mentioned methods have several disadvantages like expensive and complicated instrumentations, being time-consuming, requiring experienced operators, and consuming large amounts of toxic organic solvents in the sample pretreatment step [9]. Electrochemical sensors can be an ideal alternative for the aforementioned analytical methods owing to their simplicity, economic instrumentation, being portable, high sensitivity, short analysis time and wide linear range [10]. But, the main step in the fabrication of an electrochemical sensor is finding an electrocatalytic modifier that interacts with the analyte selectively and this interaction should lead to a significant change in electronic properties of the modifier like conductivity (which will be employed as an analytical signal for the detection of analyte) [11]. On the other hand, the chromen based synthesized derivatives in this research has several oxygen atoms in their structure which facilitate their interaction with hard metals like Li<sup>+</sup>. In this respect, 10 different chromen derivatives that were recently, their complexation with  $\mathrm{Li}^{\scriptscriptstyle +}$  was scrutinized by density functional theory computations in order to find

out which derivative acts as the best sensing material for the electrochemical detection of Li<sup>+</sup>.

#### **COMPUTATIONAL METHODS**

Software GuassView 6 [12] was used to design the structures of chromen derivatives, *Li*<sup>+</sup>, and their complexes. Each of the structures that were designed first underwent geometric optimization. After that, computations for infra-red (IR), and frontier molecular orbital (FMO) were performed on designed structures. The density functional theory (DFT) method was used throughout the computations by Gaussian 16 [13] software at the B3LYP/6-31G (d) level of theory. This level was selected since the findings obtained from earlier studies were acceptable and were consistent with experimental results [14]. All computations were performed in the vacuum and aqueous phases at 298.15 K. The PCM solvation method was selected for modelling the aqueous phase.

The following processes were investigated:

$$Li^+ + Ligand \rightarrow Complex$$
 (1)

complexation energy values ( $E_{Complexation}$ ) and thermodynamic parameters, such as enthalpy changes ( $\Delta H_f$ ), Gibbs free energy changes ( $\Delta G_f$ ), entropy changes ( $\Delta S_{th}$ ), and thermodynamic equilibrium constant ( $K_f$ ), were calculated using equations 2–6 [15].

$$E_{\text{Complexation}} = \left( E_{(\text{Complex})} - \left( E_{(\text{Cation})} + E_{(\text{Ligand})+} E_{(\text{BSSE})} \right) \right)$$
(2)

$$\Delta H_{f} = \left(H_{(Complex)} - \left(H_{(Cation)} + H_{(Ligand)}\right)\right)$$
(3)

$$\Delta G_{f} = \left(G_{(Complex)} - \left(G_{(Cation)} + G_{(Ligand)}\right)\right)$$
(4)

$$\Delta S_{\rm th} = \left(S_{\rm (Complex)} - \left(H_{\rm (Cation)} + H_{\rm (Ligand)}\right)\right)$$
(5)

$$K_{f} = \exp\left(-\frac{\Delta G_{ad}}{RT}\right) \tag{6}$$

In the equations above, E stands for the total electronic energy for every structure,  $E_{BSSE}$  stands for the basis set superposition correction, and H represents the total energy of the evaluated materials plus the thermal correction of enthalpy. For each structure under study, the G denotes the total energy plus the thermal correction of the Gibbs free energy [16]. R represents the constant of the ideal gas, S is the thermal correction entropy for the studied structures, and T stands for temperature [17].

Equations 7–12 were used to calculate the bandgap ( $E_g$ ), chemical hardness ( $\eta$ ), chemical potential ( $\mu$ ), maximum charge capacity ( $\Delta N_{max}$ ), and the electrophilicity ( $\omega$ ) of frontier molecular orbitals [18].

$$E_g = E_{LUMO} - E_{HOMO} \tag{7}$$

$$\%\Delta E_g = \frac{E_{g2} - E_{g1}}{E_{g1}} \times 100 \tag{8}$$

$$\eta = \frac{(E_{LUMO} - E_{HOMO})}{2}$$
<sup>(9)</sup>

$$\mu = \frac{(E_{LUMO} + E_{HOMO})}{2}$$

$$\tag{10}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{11}$$

$$\Delta N_{max} = -\frac{\mu}{\eta} \tag{12}$$

 $E_{LUMO}$ , in the equations above, is the energy of the lowest unoccupied molecular orbital, and  $E_{HOMO}$  is the energy of the highest occupied molecular orbital. The bandgaps of the ligand and formed complexes are shown as  $E_{g1}$  and  $E_{g2}$ , respectively [19, 20].

#### 3. Results and discussion

The initial structure of  $Li^+$  complexes with chromen derivatives is shown in Fig. 8. As can be seen,  $Li^+$  ion was inserted between the oxygen atom of chromen ring and the substituent group in each derivative with the distance of 2.5 (Å). The complexation phenomenon was only

investigated in this configuration because in all of the synthesized derivatives other parts of the skeletal formula is completely similar to each other and their only difference is the nature and position of substituent group on the top of the central ring. Consequently, the interactions of Li<sup>+</sup> with other parts of the synthesized derivatives would be similar to each other and in this respect, the complexation procedure was scrutinized only in one conformer in order to check the influence of nature and position of substituent group on the interactions [20].



Figure 8. The initial structure of Li<sup>+</sup> complexes with synthesized chromen derivatives (X is the symbol of different substituents in the synthesized derivatives)

The optimized structures of complexes are provided in Fig. 9. As it is clear, Li<sup>+</sup> has strong interactions with all of the synthesized derivatives because of occurrence a little structural distortion in most optimized structures and the formation of some chemical bonds between Li<sup>+</sup> ion and electron donor atoms [19]. After geometrical optimization, IR computations also were done on the structures and the obtained minimum IR frequencies are given in Tables 5 and 6. As the provided data show clearly, no negative frequency was observed in the structures indicating all of the scrutinized structures are true local minimums [18]. The highly negative calculated values of complexation energies that are reported in Tables 5 and 6, revealed that the complexation process is experimentally possible in all of the synthesized derivatives and the presence of water as the solvent does not have a tangible effect on the interactions because the

values are also negative in the aqueous phase [20]. The highly negative values of  $\Delta H_f$  and  $\Delta G_f$  show the complexation process is exothermic and spontaneous for all of the synthesized derivatives in both vacuum and aqueous phases [20]. The negative values of  $\Delta S_{th}$  exhibit the complexation process is not appropriate in terms of entropy and the chaos declined during the interactions [19]. The great values of  $K_f$  show the complexation process is one-sided and non-equilibrium for all of the studied structures [19]. Among all of the evaluated synthesized derivatives, 4g has the strongest interaction with Li<sup>+</sup> because 4g-Li<sup>+</sup> complex has the lowest values of  $\Delta H_f$  and  $\Delta G_f$  and the highest values of  $K_f$  in comparison to other complexes in both investigated phases. Therefore, 4g derivative can be a more selective electrochemical recognition element for the detection of Li<sup>+</sup> [18].

 Table 5: The values compexation energy, enthalpy changes, Gibbs free energy changes, entropy variations, thermodynamic formation constants, and the maximum IR frequencies for Li<sup>+</sup> complexes with chrommen derivatives in the vacuum

NO	ΔEComplexation	ΔH <sub>f</sub> (kJ/mol)	ΔG <sub>f</sub> (kJ/mol)	$\Delta S_{th} (J/mol)$	K <sub>f</sub>	$v_{\min}$ (cm <sup>-1</sup> )
	(kJ/mol)					
4a-Complex	-202.072	-191.230	-150.432	-116.908	2.270×10 <sup>+26</sup>	2.334
4b-Complex	-220.114	-209.140	-168.376	-128.018	3.161×10 <sup>+29</sup>	3.145
4c-Complex	-219.526	-219.940	-183.187	-123.333	1.244×10 <sup>+32</sup>	4.951
4d-Complex	-167.428	-160.726	-121.455	-131.780	1.902×10 <sup>+21</sup>	2.095
4e-Complex	-137.500	-129.048	-88.622	-135.660	3.363×10 <sup>+15</sup>	1.948
4f-Complex	-228.870	-214.501	-173.108	-138.903	2.133×10 <sup>+30</sup>	2.630
4g-Complex	-328.361	-319.678	-278.163	-139.314	5.429×10 <sup>+48</sup>	3.492
4h-Complex	-179.164	-177.269	-139.525	-126.658	2.787×10 <sup>+24</sup>	4.104
41-Complex	-234.297	-226.899	-189.201	-126.506	1.407×10 <sup>+33</sup>	5.621
4m-Complex	-173.950	-164.530	-125.620	-130.571	1.021×10 <sup>+22</sup>	2.741



**Figure 9.** Optimized structures of complexes (oxygen: red, nitrogen: blue, carbon: gray, hydrogen: white, lithium: purple, chorine: green, iodide: brown)

 Table 6: The values compexation energy, enthalpy changes, Gibbs free energy changes, entropy variations, thermodynamic formation constants, and the maximum IR frequencies for Li<sup>+</sup> complexes with chrommen derivatives in the aquoeus phase

NO	ΔEComplexation	ΔH <sub>f</sub> (kJ/mol)	ΔG <sub>f</sub> (kJ/mol)	$\Delta S_{th}(J/mol)$	K <sub>f</sub>	v <sub>min</sub> (cm <sup>-1</sup> )
	(kJ/mol)					
4a-Complex	-122.222	-111.381	-70.582	-139.827	2.324×10 <sup>+12</sup>	1.835
4b-Complex	-107.659	-96.817	-56.019	-136.792	6.525×10 <sup>+09</sup>	4.729
4c-Complex	-72.498	-61.656	-20.858	-136.908	4.512×10 <sup>+03</sup>	3.619
4d-Complex	-101.218	-90.377	-49.578	-131.780	4.855×10 <sup>+08</sup>	7.210
4e-Complex	-68.633	-57.792	-16.993	-136.908	9.490×10 <sup>+02</sup>	5.917
4f-Complex	-94.970	-84.128	-43.330	-139.192	3.903×10 <sup>+07</sup>	4.760
4g-Complex	-181.564	-172.881	-131.366	140.124	1.036×10 <sup>+23</sup>	2.115
4h-Complex	-67.551	-56.710	-15.911	-136.908	6.134×10 <sup>+02</sup>	8.619
41-Complex	-80.214	-69.373	-28.574	-136.908	1.015×10 <sup>+05</sup>	3.968
4m-Complex	-93.342	-82.500	-41.702	-136.908	2.024×10 <sup>+07</sup>	4.174

The difference between the HOMO and LUMO orbital energies is the band gap, which is inversely related to the electrical conductivity of materials [20]. The electrical conductivity of materials with a narrow band gap is higher than of materials with a wide one [18]. Therefore, to assess the efficiency of the synthesized derivatives as an electrochemical sensor for measuring Li<sup>+</sup>, this parameter was computed for the each of individual structures and the obtained results are presented in Table 3. As it is clear, the Eg of all of the synthesized derivatives are in the range of 9.980-13.440 (eV) indicating the synthesized ligands do not have a remarkable discrepancy in their conductivity [19]. But, the variation of  $E_g$  (% $\Delta E_g$ ) during the complexation process of Li<sup>+</sup> is more tangible in the case of 4g derivative because when Li<sup>+</sup> interacts with 4g its bandgap declines (%-50.824) from 12.750 (eV) to 6.270 (eV). In other words, 4g derivative not only has the strongest interaction with Li<sup>+</sup> but also its electrical conductivity experiences the sharpest enhancement during the complexation process [33]. Hence, among all of the synthesized derivatives 4g seems to be the best candidate for electrochemical recognition of  $Li^+$  [20].

NO	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)	Eg (eV)	%ΔE <sub>g</sub>	η (eV)	μ (eV)	ω (eV)	ΔN <sub>max</sub> (eV)
Li <sup>+</sup>	-64.000	-6.950	57.050		28.525	-35.475	22.059	1.244
49	-5 710	4.430	10.140		5.070	-0.640	0.040	0.126
74	-5.710	4.450	10.140		5.070	-0.040	0.040	0.120
4a-Complex	-8.640	0.190	8.830	-12.919	4.415	-4.225	2.022	0.957
4b	-9.800	0.180	9.980		4.990	-4.810	2.318	0.964
4b-Complex	-6.690	5.120	11.810	18.337	5.905	-0.785	0.052	0.133
4c	-7.530	5.220	12.750		6.375	-1.155	0.105	0.181
4C-Complex	-11.600	-2.050	9.550	-25.098	4.775	-6.825	4.878	1.429
4d	-5.990	5.800	11.790		5.895	-0.095	0.001	0.016
4d-Complex	-8.760	-0.300	8.460	-28.244	4.230	-4.530	2.426	1.071
4e	-5.850	5.380	11.230		5.615	-0.235	0.005	0.042
4e-Complex	-8.880	0.370	9.250	-17.631	4.625	-4.255	1.957	0.920
4f	-5.830	4.400	10.230		5.115	-0.715	0.050	0.140
4f-Complex	-9.040	0.050	9.090	-11.144	4.545	-4.495	2.223	0.989
4g	-7.540	5.210	12.750		6.375	-1.165	0.106	0.183
4g-Complex	-8.390	-2.120	6.270	-50.824	3.135	-5.255	4.404	1.676
4h	-6.600	5.190	11.790		5.895	-0.705	0.042	0.120
4h-Complex	-8.680	-0.750	7.930	-32.740	3.965	-4.715	2.803	1.189
41	-5.890	4.340	10.230		5.115	-0.775	0.059	0.152
41-Complex	-8.650	-0.700	7.950	-22.287	3.975	-4.675	2.749	1.176
4m	-7.030	6.410	13.440		6.720	-0.310	0.007	0.046
4m-Complex	-10.840	0.100	10.940	-18.601	5.470	-5.370	2.636	0.982

Other FMO parameters including the electrophilicity, chemical hardness, maximum transferred charge capacity, and chemical potential were also calculated and the results are shown in Table 3. It reveals that the  $Li^+$  chemical hardness decreases significantly after interacting with all of the synthesized derivatives indicating the complexes are softer and more chemically reactive than the pure cation without chromen based ligands because electron transfers that are essential for the implementation of a chemical reaction can be done in complexes more conveniently [20]. All investigated structures have a negative measured chemical potential, suggesting that they all have thermodynamic stability [20]. Electrophilicity and maximum transferred charge capacity are two indices that show the tendency of a compound towards electron [19]. Indeed, a compound with higher values of both parameters tends to absorb electron more than a material with lower values of  $\omega$  and  $\Delta N_{max}$ . As the presented results show clearly Li<sup>+</sup> has a high tendency for absorbing electrons because of its high values of  $\omega$  and  $\Delta N_{max}$  (22.059 and 1.244 (eV) respectively). On the other hand, the low values of both indices in all of the investigated chromen derivatives prefers to donate electron and as a result, electron transfer between the cation and ligands can occur easily indicating the capability of the synthesized derivatives to form a complex with Li<sup>+</sup> and playing the role of an ionophore for potentiometric determination of Li<sup>+</sup> [20].

## Conclusion

In conclusion, DFT simulations were employed to scrutinize the interaction of  $Li^+$  with the synthesized derivatives in order to check if any of them can be employed as an electrocatalytic modifier for the development of a novel electrochemical sensor for  $Li^+$  determination or not. The achieved results demonstrated among all of the synthesized derivatives, the one with a NO<sub>2</sub> substitution in meta position of benzene ring has the strongest interaction with  $Li^+$ . In addition, the electrochemical conductivity of this derivative experiences the most improvement during complexing with  $Li^+$ . Therefore, this compound seems to be the most ideal candidate to be chosen as a sensing material for electrochemical detection of  $Li^+$ .

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