Chemical Methodologies

Supplementary File

Lithium–Functionalization of Pyrrole–n–Carboxylic Acids (n = 1, 2, 3)

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This supplementary file includes the obtained results at the B3LYP/6–311+G** theoretical level for all of investigated PnCA models for making comparison of different levels of calculations between 6–31+G* and 6–311+G** basis sets. The evaluated results have been supported by both theoretical levels with negligible differences; therefore, the results of 6–31+G* basis set have been only listed in the original manuscript. Moreover, according to an earlier year, a new model has been studied here to see the stabilities of different types of Li-functionalized PnCA models. The H atom of carboxylic acid group of PnCA has been replaced by the Li atom to make the Li/H model (Fig. S1). Indeed, the main purpose of this work is keeping the initial carboxylic group and adding the extra Li/Li+. The values of E_{Ads} indicated that the Li/H model is more stable than Li–PnCA models but weaker than Li+–PnCA models. A potential reader could compare the results of this additional job with the results of an earlier work [23].

Table S1: Molecular properties; obtained by the B3LYP/6-311+G** theoretical level*

	P1CA				P2CA				P3CA			
Property	**Orig.**	**–Li**	**–Li+**	**Li/H**	**Orig.**	**–Li**	**–Li+**	**Li/H**	**Orig.**	**–Li**	**–Li+**	**Li/H**
$d_{C_6—O_7}$ Å	1.35	1.32	1.32	1.27	1.36	1.35	1.33	1.28	1.36	1.33	1.33	1.28
$d_{C_6—O_8}$ Å	1.20	1.23	1.24	1.27	1.22	1.26	1.26	1.28	1.21	1.23	1.25	1.28
$d_{O_8—Li}$ Å	—	1.86	1.74	1.87	—	1.75	1.72	1.86	—	1.84	1.72	1.84
$\angle O_7—C_6—O_8$ °	124.32	124.73	122.31	122.70	122.61	120.00	120.67	121.00	121.79	122.10	120.00	120.55
$\angle C_6—O_8—Li$ °	—	130.70	176.28	82.11	—	171.40	172.73	82.93	—	139.16	178.60	82.84
E_T keV	–10.85	–11.06	–11.05	–11.04	–10.85	–11.06	–11.05	–11.04	–10.85	–11.06	–11.05	–11.04
BSSE eV	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.02
E_{Ads} eV	—	–0.58	–1.91	–1.22	—	–0.66	–2.08	–1.61	—	–0.65	–2.27	–1.90
I eV	6.54	2.98	10.10	5.90	6.61	2.79	10.31	5.97	6.54	2.59	10.07	5.95
A eV	1.13	1.83	5.45	1.21	1.31	1.55	5.62	1.02	0.89	1.78	5.37	0.86
E_G eV	5.41	1.15	4.65	4.69	5.30	1.24	4.69	4.95	5.65	0.81	4.70	5.09
D_M Debye	1.53	4.043	11.40	4.80	1.45	1.26	11.45	3.77	3.554	8.24	10.41	1.69

*See the models in Fig. (S1).

Table S2: Atomic charges *Q*; obtained by the B3LYP/6-311+G** theoretical level*

	P1CA				P2CA				P3CA			
Atom	**Orig.**	**–Li**	**–Li+**	**Li/H**	**Orig.**	**–Li**	**–Li+**	**Li/H**	**Orig.**	**–Li**	**–Li+**	**Li/H**
N_1	–0.46	–0.46	–0.44	–0.46	–0.50	–0.52	–0.50	–0.51	–0.52	–0.51	–0.49	–0.53
C_2	–0.03	–0.02	–0.02	–0.02	–0.01	–0.01	–0.03	0.02	0.03	0.04	0.06	0.01
C_3	–0.26	–0.25	–0.22	–0.28	–0.22	–0.22	–0.15	–0.22	–0.24	–0.25	–0.26	–0.23
C_4	–0.26	–0.26	–0.21	–0.28	–0.29	–0.29	–0.27	–0.30	–0.25	–0.24	–0.22	–0.25
C_5	–0.02	–0.18	–0.03	–0.02	–0.01	–0.01	0.06	–0.02	–0.05	–0.04	–0.02	–0.06
C_6	0.94	0.98	1.00	0.91	0.76	0.73	0.81	0.74	0.78	0.83	0.85	0.76
O_7	–0.69	–0.66	–0.63	–0.81	–0.68	–0.67	–0.63	–0.81	–0.69	–0.66	–0.62	–0.82
O_8	–0.60	–0.74	–0.86	–0.81	–0.63	–0.86	–0.89	–0.84	–0.62	–0.75	–0.87	–0.83
Li	—	0.04	0.96	0.90	—	0.28	0.96	0.89	—	0.01	0.96	0.88
H_1	—	—	—	—	0.43	0.42	0.42	0.42	0.41	0.41	0.43	0.40
H_2	0.23	0.23	0.24	0.23	—	—	—	—	0.22	0.23	0.22	0.22
H_3	0.22	0.22	0.24	0.21	0.23	0.23	0.24	0.23	—	—	—	—
H_4	0.22	0.22	0.24	0.21	0.22	0.22	0.24	0.21	0.23	0.24	0.25	0.23
H_5	0.23	0.23	0.22	0.23	0.21	0.21	0.23	0.20	0.21	0.21	0.23	0.20
H_7	0.50	0.48	0.51	—	0.48	0.48	0.42	—	0.48	0.48	0.50	—

*See the models in Fig. (S1).

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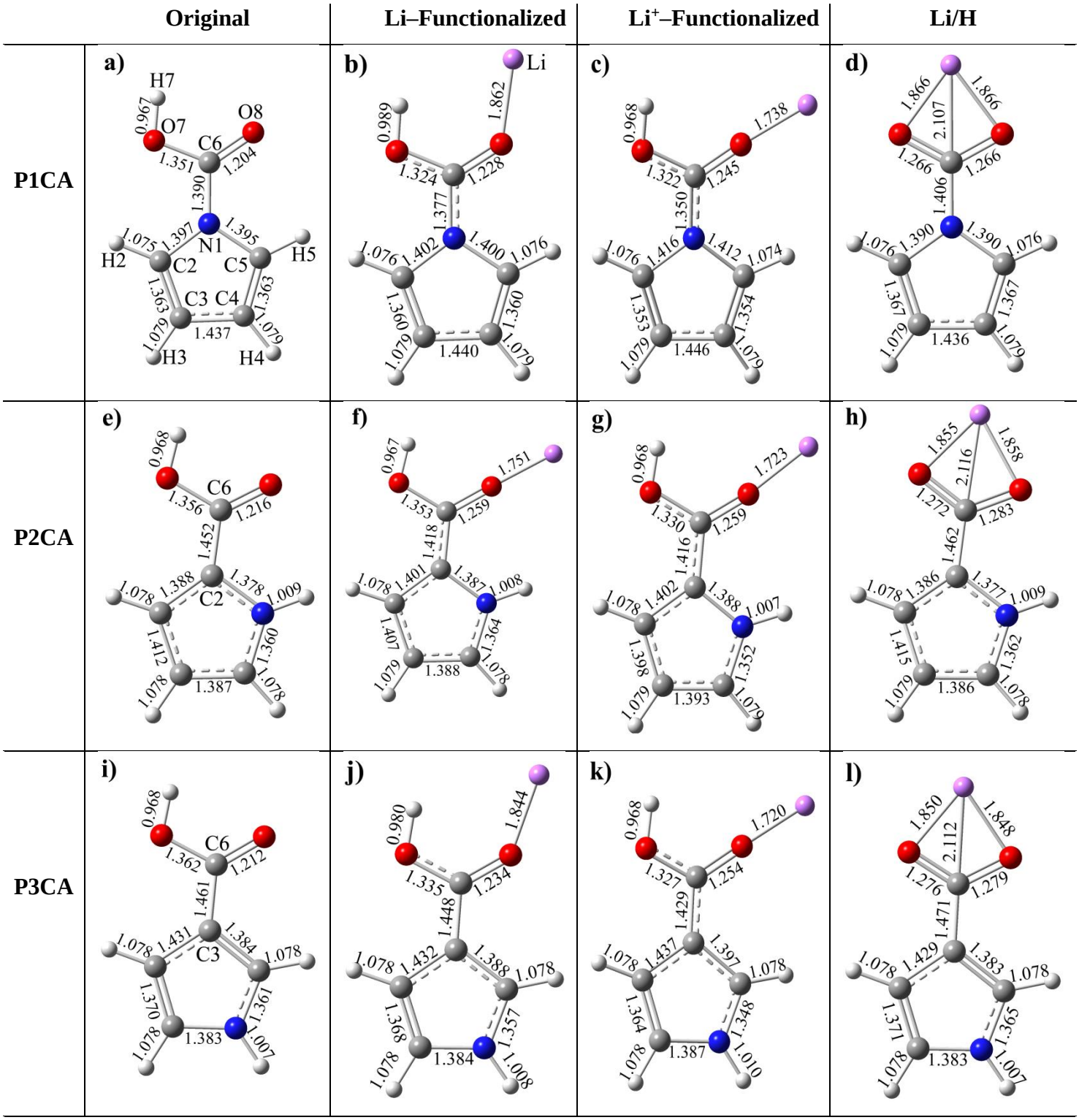

Figure S1: The B3LYP/6-311+G** optimized structures of original and singular Li/Li+–Functionalized and Li/H PnCA (n=1–3) models. The H atom of carboxylic acid group is replaced by the Li atom in the Li/H model.

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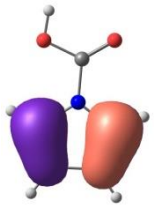
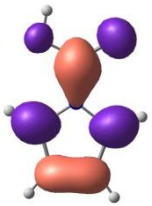
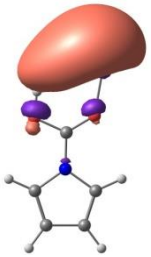
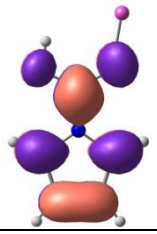
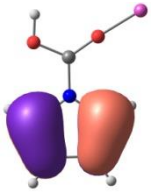
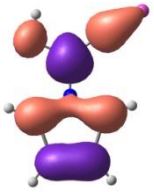
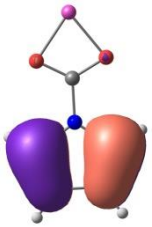
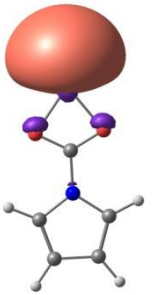
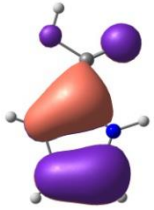
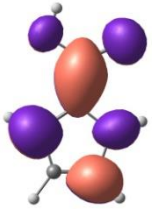
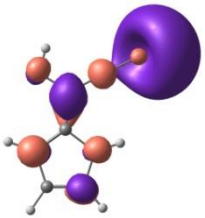
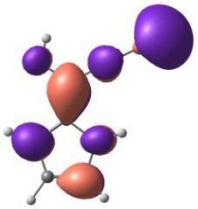
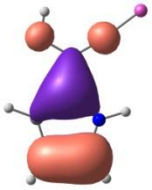
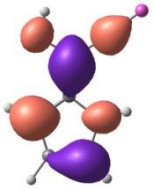
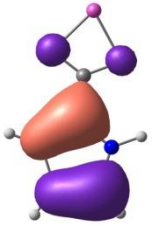
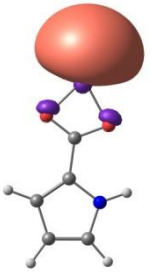
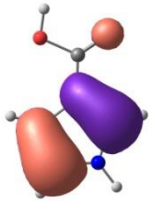
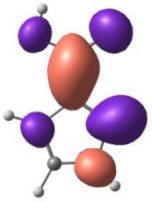
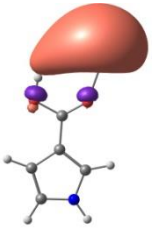
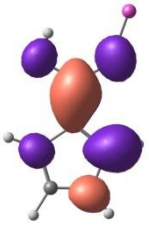
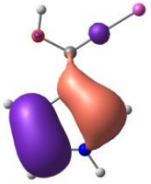
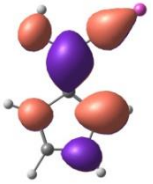
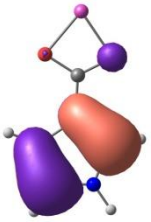
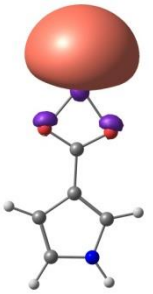
	Original		Li–Functionalized		Li^+–Functionalized		Li/H	
	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
P1CA								
P2CA								
P3CA								

Figure S2: The B3LYP/6-311+G** HOMO and LUMO distribution patterns of original and singular Li/Li+–Functionalized and Li/H PnCA (n=1–3) models. The H atom of carboxylic acid group is replaced by the Li atom in the Li/H model.

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