Theoretical Study of p- and n- Doping of Polythiophene and Polypyrrole Based Conjugated Polymers

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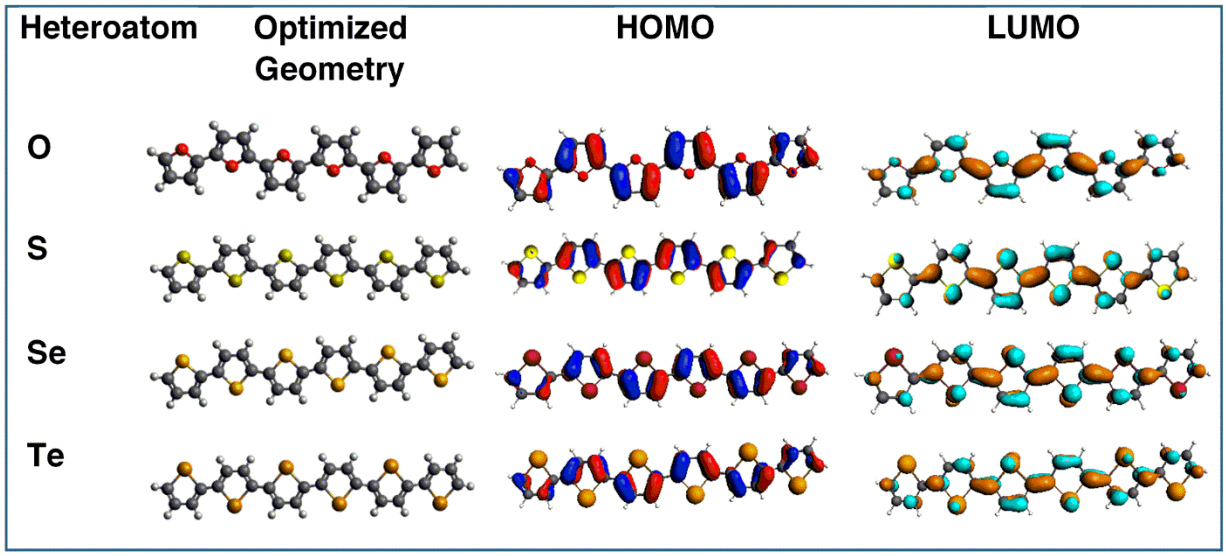

Figure S1. Optimized geometries, HOMO and LUMO of undoped PTh and analogs

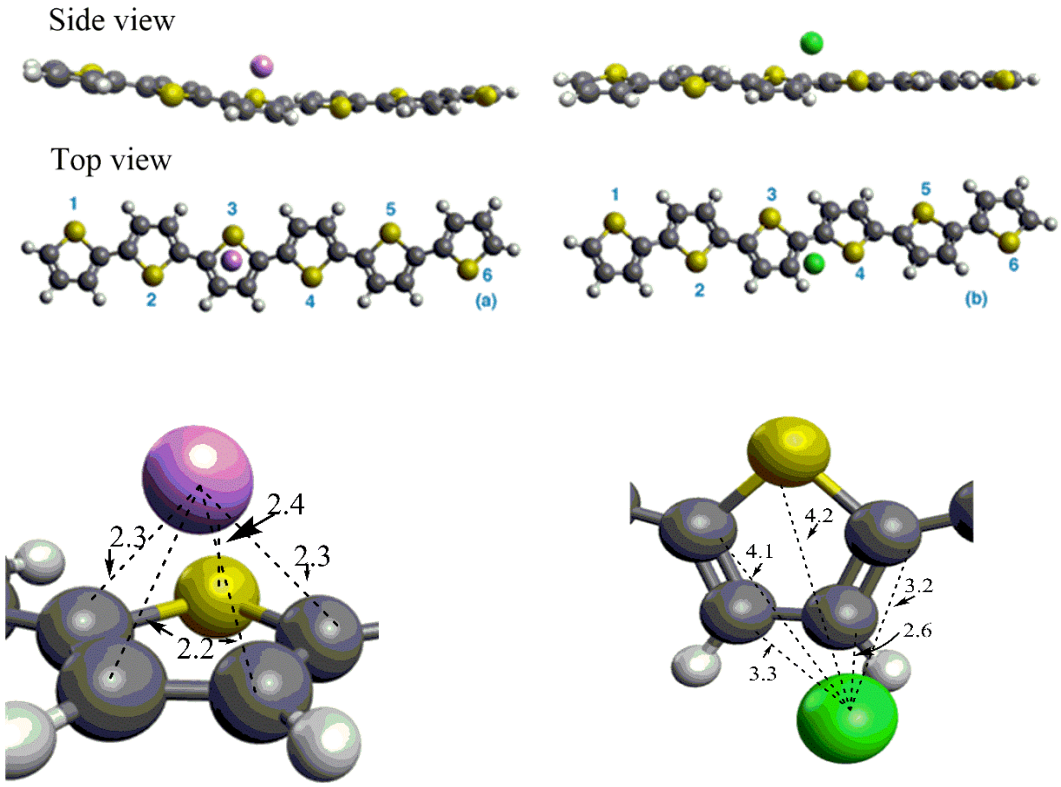

Figure S2. Top and side view of optimized geometries (a) PTh doped with Li (b) PTh doped with Cl in molecular calculations. Distance (in Å) to the dopant from atoms in 3rd ring is also shown.

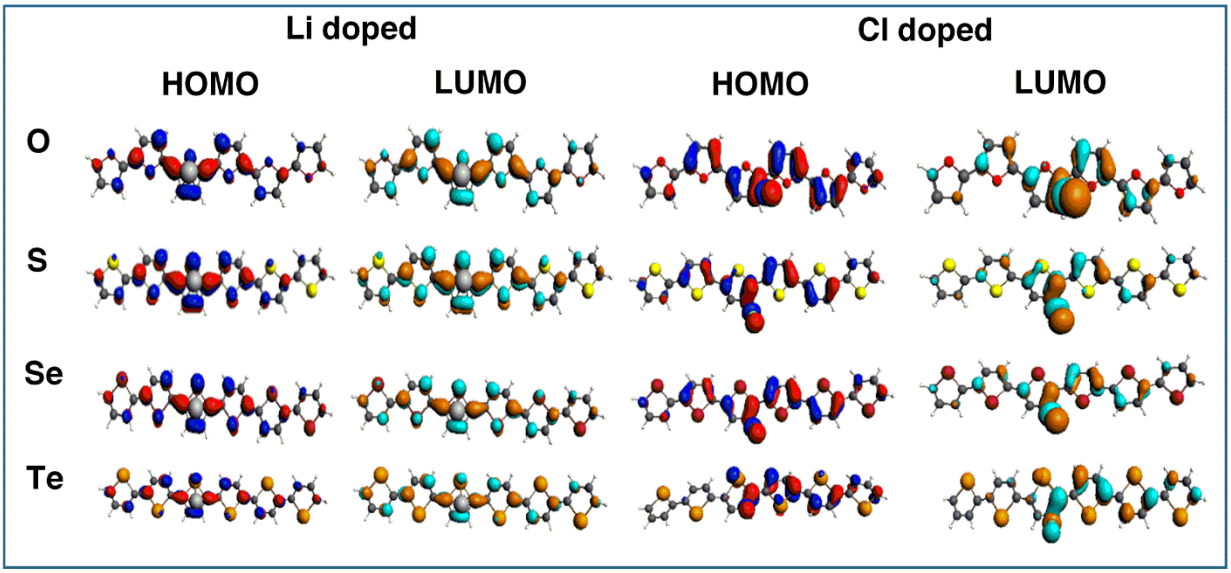

Figure S3. HOMO and LUMO of PTh and analogs after doping

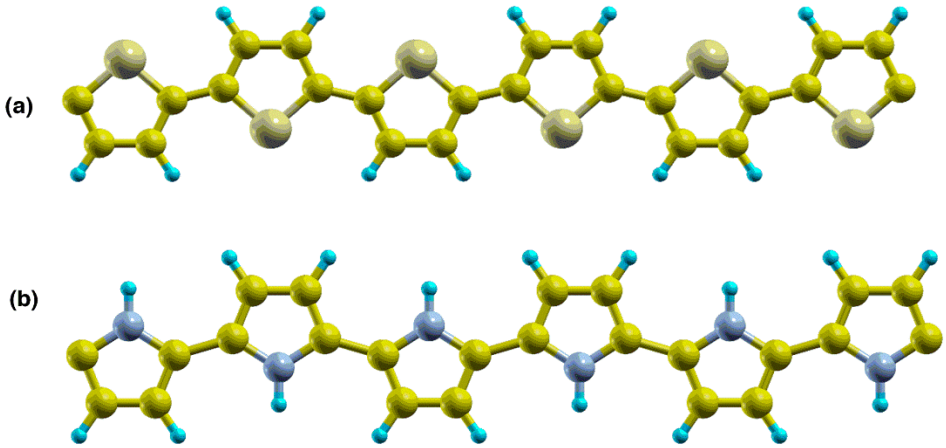

Figure S4. Optimized structures of (a) periodic PTh (one supercell): S was replaced by O, Se, Te to get the analogs, (b) periodic PPy (one supercell): N was replaced by P, As, Se to get the analogs.

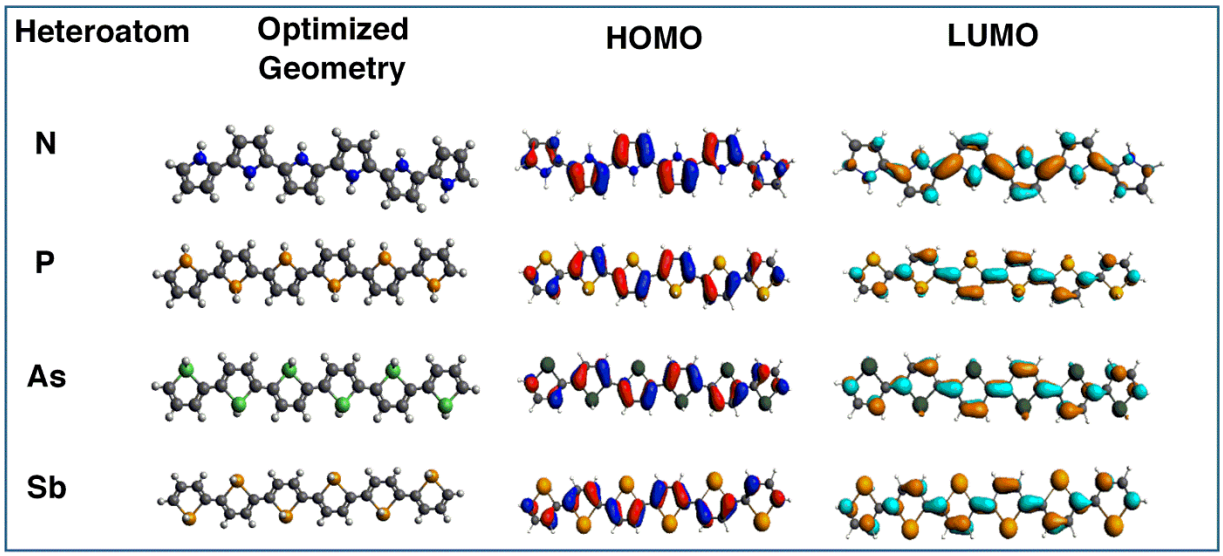

Figure S5. Optimized geometries, HOMO and LUMO of PPy and analogs before doping

Table S1. Calculated HOMO-LUMO gap (eV) in PTh and PPy analogs before and after doping with Cl or Li, using PBE, B3LYP, PBE0 and M06 functionals (molecular calculations)

	PBE			B3LYP			PBE0			M06		
X	Before	Li	Cl	Before	Li	Cl	Before	Li	Cl	Before	Li	Cl
O	1.77	0.78	1.58	2.79	1.24	1.24	3.08	1.55	1.52	3.17	1.06	1.53
S	1.55	0.77	1.38	2.50	1.11	1.23	2.78	1.40	1.52	2.90	1.39	1.53
Se	1.41	0.78	1.26	2.30	1.08	1.16	2.57	1.37	1.38	2.67	1.35	1.36
Te	1.15	0.77	0.99	2.00	1.05	1.37	2.25	1.35	1.74	2.35	1.36	1.73
N-H	2.29	1.94	2.07	3.39	1.16	1.18	3.71	1.49	1.45	3.77	1.23	1.40
P-H	0.88	0.85	1.01	1.70	1.16	1.67	2.23	1.50	2.11	2.07	1.53	2.05
As-H	0.81	0.86	0.93	1.60	1.21	1.67	1.84	1.60	2.11	1.94	1.57	2.09
Sb-H	0.74	0.89	0.98	1.47	1.23	1.68	1.70	1.64	2.13	1.80	1.60	2.09

Table S2. Distance (in Å) to the dopant (Cl/Li) from atoms in the 3rd ring (Figure S2)

Heteroatom	Distance to the dopant	
	Li	Cl
O	2.1-2.2	2.7-4.0
S	2.2-2.4	2.6-4.2
Se	2.2-2.6	2.7-4.5
Te	2.2-2.8	2.1-4.3

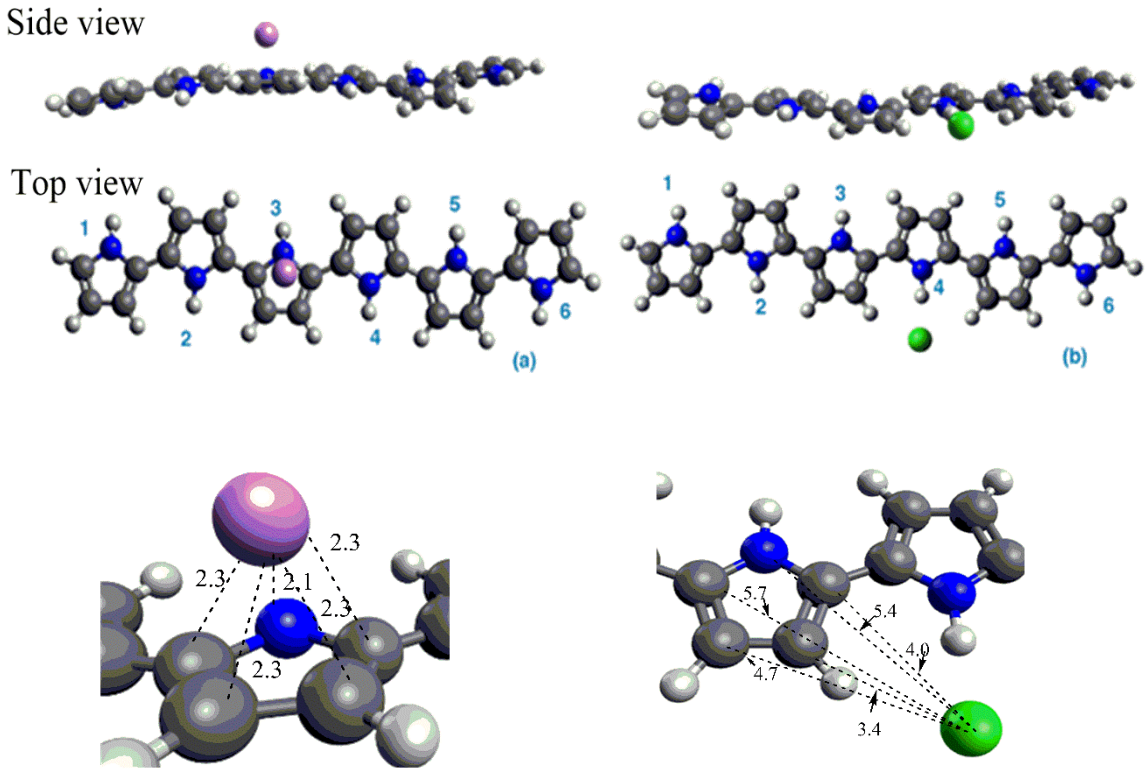

Figure S6. Top and side view of optimized geometries (a) PPy doped with Li (b) PPy doped with Cl in molecular calculations. Distance (in Å) to the dopant from atoms in 3rd ring is also shown.

Table S3. Distance (in Å) to the dopant (Cl/Li) from atoms in the 3rd ring as marked in Figure S6

Heteroatom	Distance to the dopant	
	Li	Cl
N	2.1-2.3	3.4-5.7
P	2.2-2.6	1.9-4.1
As	2.2-2.7	1.9-3.8
Sb	2.2-2.9	2.0-4.3

Table S4. Charge of the counterion (e^-) in molecular calculations

	Mulliken		NPA		Voronoi		Hirshfeld	
Heteroatom	Cl	Li	Cl	Li	Cl	Li	Cl	Li
O	-0.48	0.60	-0.52	0.96	-0.43	0.44	-0.40	0.48
S	-0.45	0.50	-0.40	0.93	-0.40	0.40	-0.37	0.43
Se	-0.49	0.51	-0.43	0.47	-0.44	0.44	-0.41	0.42
Te	-0.26	0.48	-0.28	0.92	-0.22	0.38	-0.19	0.40
N	-0.65	0.26	-0.75	0.55	-0.48	0.16	-0.46	0.18
P	-0.18	0.49	-0.17	0.95	-0.15	0.43	-0.12	0.45
As	-0.20	0.55	-0.19	0.95	-0.17	0.42	-0.13	0.44
Sb	-0.12	0.42	-0.19	0.95	-0.16	0.41	-0.12	0.42

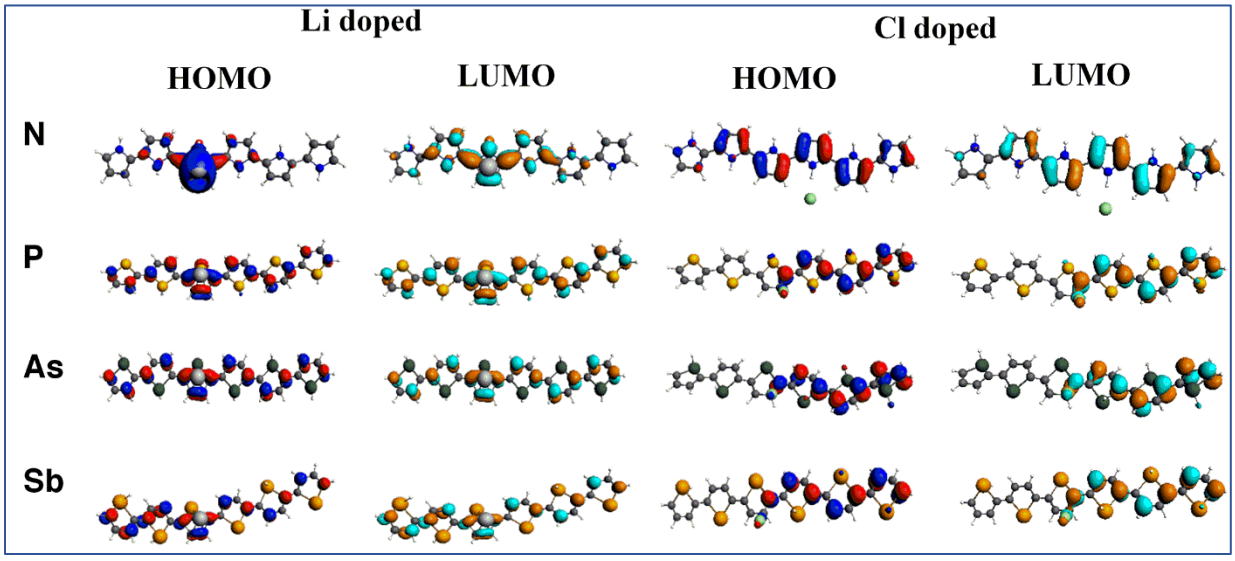

Figure S7. HOMO and LUMO of PPy and analogs after doping