Table S1. Final ζ , κ and κ' values for all atoms.

atom	ζ ($Å^{-1}$; $bohr^{-1}$)	κ	κ'
P (monopole)	29.4145; 15.5655	-	1.02(2)
P (dipoles-octapoles)	9.8048; 5.1885	0.996(6)	1.02(2)
O	8.4395; 4.4660	0.957(3)	0.84(7)
OW	8.4395; 4.4660	0.968(3)	0.99(4)
Li1, Li2	2.4173; 1.2792	1.0	1.0
H1, H2	3.7795; 2.0000	1.2	1.2

Table S2. Theoretical Bader (Q_B) and Hirshfeld (Q_H) charges for the cluster (cl) (see Experimental Part, Theoretical Calculations).

atom	functional	Q_B(cl)	Q_H(cl)
P	*PW91*	2.92	0.33
	BLYP	2.93	0.35
	PBE	2.92	0.32
	mPW	2.92	0.33
	B3LYP	2.99	0.37
	B1PW91	3.02	0.36
	TPSS	2.95	0.33
O	*PW91*	-1.56	-0.39
	BLYP	-1.56	-0.39
	PBE	-1.56	-0.39
	mPW	-1.56	-0.39
	B3LYP	-1.59	-0.42
	B1PW91	-1.61	-0.42
	TPSS	-1.57	-0.40
OW	*PW91*	-1.32	-0.26
	BLYP	-1.30	-0.26
	PBE	-1.32	-0.26
	mPW	-1.32	-0.26
	B3LYP	-1.34	-0.28
	B1PW91	-1.36	-0.29
	TPSS	-1.32	-0.26
H1	*PW91*	0.60	0.12
	BLYP	0.60	0.12
	PBE	0.61	0.12
	mPW	0.60	0.12
	B3LYP	0.62	0.13
	B1PW91	0.63	0.13
	TPSS	0.61	0.12
H2	*PW91*	0.61	0.11
	BLYP	0.60	0.11
	PBE	0.61	0.11
	mPW	0.61	0.11
	B3LYP	0.63	0.12
	B1PW91	0.64	0.12
	TPSS	0.61	0.11
Li1(4)	*PW91*	0.90	0.20

	BLYP	0.90	0.20
	PBE	0.90	0.20
	mPW	0.90	0.20
	B3LYP	0.90	0.22
	B1PW1	0.91	0.23
	TPSS	0.91	0.20
Li2(6)	*PW91*	0.92	0.21
	BLYP	0.92	0.22
	PBE	0.92	0.21
	mPW	0.92	0.21
	B3LYP	0.92	0.24
	B1PW91	0.93	0.24
	TPSS	0.92	0.22

Table S3. Comparison of experimental and theoretical (for the clusters) values of ρ_c ($e \cdot Å^{-3}$) and $\nabla^2\rho_c$ ($e \cdot Å^{-5}$), as well as the Hessian eigenvalues ($e \cdot Å^{-5}$).

bond	functional	ρ_c	$\nabla^2\rho_c$	λ_1	λ_2	λ_3
P-P[i]	*experiment*	0.927(4)	-4.017(2)	-3.94	-3.94	3.86
	PW91	0.938	-5.446	-4.155	-4.123	2.834
	BLYP	0.948	-5.485	-4.263	-4.227	3.005
	PBE	0.938	-5.468	-4.138	-4.106	2.776
	mPW	0.941	-5.466	-4.171	-4.140	2.846
	B3LYP	0.970	-5.919	-4.429	-4.388	2.899
	B1PW91	0.968	-6.013	-4.374	-4.338	2.701
	TPSS	0.954	-5.690	-4.249	-4.215	2.774
P-O	*experiment*	1.500(5)	21.86(2)	-9.21	-8.76	39.83
	PW91	1.481	22.115	-9.370	-8.955	40.438
	BLYP	1.483	21.771	-9.473	-9.042	40.293
	PBE	1.479	22.337	-9.343	-8.936	40.606
	mPW	1.480	22.161	-9.379	-8.962	40.510
	B3LYP	1.492	22.164	-9.719	-9.292	41.185
	B1PW91	1.489	22.768	-9.676	-9.264	41.715
	TPSS	1.465	23.149	-9.288	-8.897	41.329
OW-H1	*experiment*	2.22(7)	-31.7(4)	-31.66	-30.82	31.42
	PW91	2.13	-47.6	-37.401	-36.510	26.340
	BLYP	2.14	-46.7	-37.305	-36.389	26.966
	PBE	2.13	-47.7	-37.449	-36.558	26.292
	mPW	2.14	-47.4	-37.401	-36.486	26.485
	B3LYP	2.13	-47.9	-37.907	-36.967	26.942
	B1PW91	2.13	-49.2	-38.221	-	26.292

					37.305	
	TPSS	2.13	-47.4	-37.329	-36.413	26.340
OW-H2	*experiment*	2.18(7)	-33.6(5)	-31.90	-30.72	29.00
	PW91	2.03	-43.5	-34.726	-33.979	25.255
	BLYP	2.04	-42.6	-34.630	-33.859	25.930
	PBE	2.03	-43.6	-34.774	-34.003	25.207
	mPW	2.04	-43.4	-34.726	-33.955	25.400
	B3LYP	2.03	-43.8	-35.281	-34.534	26.051
	B1PW91	2.02	-45.1	-35.594	-34.871	25.352
	TPSS	2.03	-43.3	-34.678	-33.883	25.255
H1···O^{iv}	*experiment*	0.22(3)	3.03(5)	-1.39	-1.34	5.76
	PW91	0.28	2.26	-1.646	-1.640	5.543
	BLYP	0.28	2.29	-1.645	-1.639	5.576
	PBE	0.28	2.26	-1.644	-1.638	5.545
	mPW	0.28	2.27	-1.650	-1.644	5.562
	B3LYP	0.27	2.32	-1.609	-1.604	5.535
	B1PW91	0.27	2.31	-1.609	-1.604	5.526
	TPSS	0.28	2.29	-1.649	-1.641	5.576
H2···O^{v}	*experiment*	0.26(3)	3.34(7)	-1.98	-1.67	6.99
	PW91	0.35	2.32	-2.204	-2.179	6.707
	BLYP	0.35	2.37	-2.207	-2.179	6.760
	PBE	0.35	2.33	-2.204	-2.178	6.709
	mPW	0.35	2.34	-2.210	-2.184	6.731
	B3LYP	0.34	2.42	-2.164	-2.135	6.712
	B1PW91	0.34	2.39	-2.162	-2.135	6.685
	TPSS	0.35	2.37	-2.200	-2.174	6.740
Li···O	*experiment*	0.174(1)	5.216(1)	-1.08	-1.07	7.37
	PW91	0.206	4.827	-1.269	-1.254	7.348
	BLYP	0.208	4.779	-1.279	-1.262	7.321
	PBE	0.207	4.827	-1.270	-1.255	7.350
	mPW	0.205	4.834	-1.268	-1.253	7.355
	B3LYP	0.205	4.890	-1.274	-1.257	7.420
	B1PW91	0.202	4.972	-1.265	-1.249	7.485
	TPSS	0.204	4.899	-1.269	-1.253	7.422
Li2···OW	*experiment*	0.090(1)	2.396(1)	-0.41	-0.40	3.20
	PW91	0.107	2.271	-0.561	-0.545	3.376

	BLYP	0.108	2.262	-0.566	-0.549	3.376
	PBE	0.108	2.266	-0.563	-0.548	3.376
	mPW	0.106	2.276	-0.559	-0.544	3.379
	B3LYP	0.106	2.303	-0.568	-0.552	3.424
	B1PW91	0.104	2.331	-0.562	-0.546	3.439
	TPSS	0.104	2.317	-0.554	-0.538	3.408
Li1···OW[iii]	*experiment*	0.147(1)	4.369(1)	-0.86	-0.85	6.08
	PW91	0.191	3.957	-1.185	-1.134	6.275
	BLYP	0.193	3.916	-1.190	-1.140	6.246
	PBE	0.192	3.952	-1.188	-1.137	6.278
	mPW	0.191	3.962	-1.188	-1.136	6.285
	B3LYP	0.190	4.003	-1.193	-1.144	6.338
	B1PW91	0.187	4.075	-1.191	-1.141	6.405
	TPSS	0.190	4.024	-1.193	-1.142	6.360

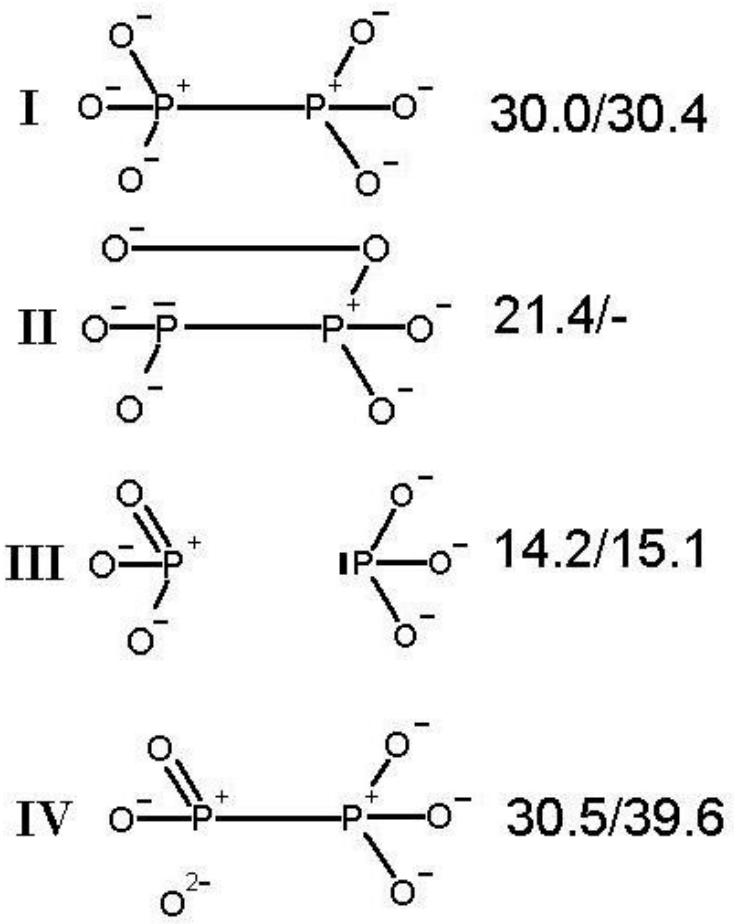

Figure 1 Fig. S1. The basic Lewis structures with their shares (%) in the electronic structure of the $P_2O_6^{4-}$ anion *in vacuo* (the first number) and in the $Li_6P_2O_6^{2+}$ cluster (the last number). For the sake of simplicity all the O atoms are treated as equivalent; consequently the numbers for forms **II**-**IV** represent the sums of shares of 6 (**II** and **III**) or 12 equivalent forms affecting different O atoms. Form **II** appeared only for the anion *in vacuo*, the O-O bond is probably a computational artefact brought about by expansion of atomic wavefunctions in the highly negative anion.