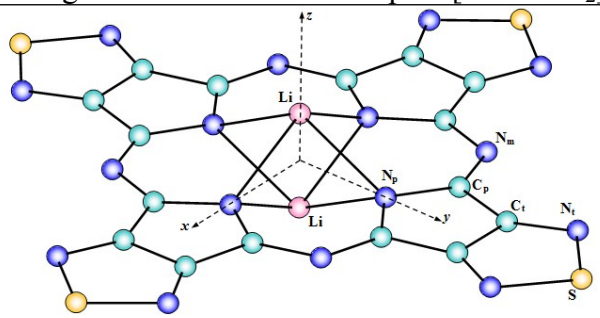
Supporting Information

Tetrakis(1,2,5-thiadiazolo)porphyrazines. 9. Synthesis, spectral and theoretical study of the lithium(I) complex and its unusual behaviour in aprotic solvents in the presence of acids

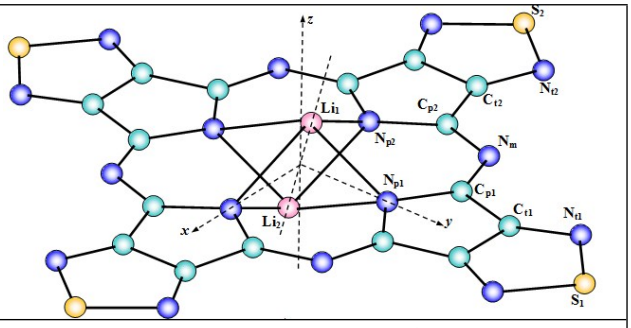
Pavel A. Stuzhin,*[a] Svetlana S. Ivanova, [a] Mahmoud Hamdoush, [a] Gayane A. Kirakosyan, [b] Aleksej Kiselev,[a] Anton Popov, [a] Valerij Sliznev [a] and Claudio Ercolani [c]

[a.] *Research Institute of Macroheterocycles, Ivanovo State University of Chemical Technology, 153000 Ivanovo,Sheremetevskij Pr-t 7, Russia. E-mail: stuzhin@isuct.ru*
[b.] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow 119991, Russia*
[c.] *Dipartimento di Chimica, Università di Roma "Sapienza", P.le A. Moro 5, I-00185 Roma, Italy.*

Table S1. Relative energy (h), geometric parameters (bond length R_e in Å, bond angles α_e) atomic charges (NBO, q) and Vyberg bond indices (Q) for two considered geometrical configurations of dilitium complex [TTDPaLi$_2$].



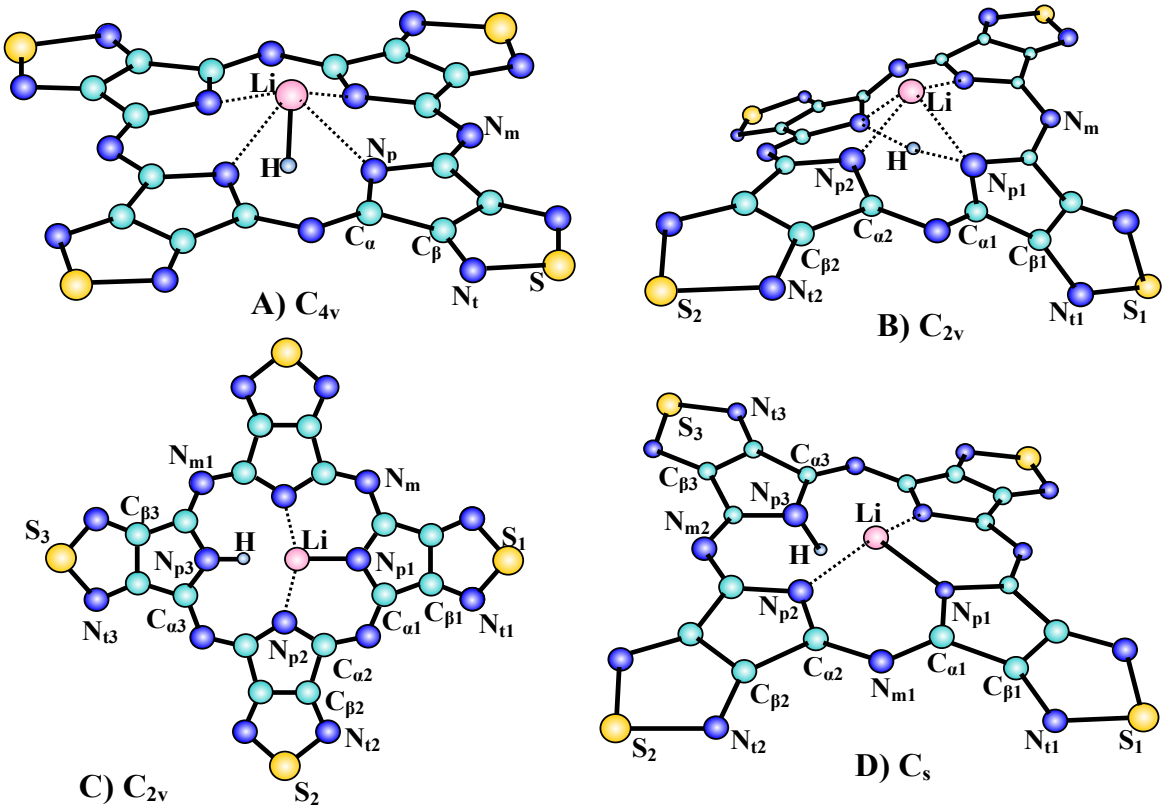
(A) [TTDPaLi$_2$] D_{4h}



(B) [TTDPaLi$_2$] C_{2h}

(A) Symmetry D_{4h} (h =0.035 kJ/mol)					
$R_e(Li\text{-}N_p)$	2.215	$\alpha_e(N_pC_\alpha C_\beta)$	108.6	$q(N_t)$	-0.55
$R_e(N_p\text{-}C_\alpha)$	1.379	$\alpha_e(C_\alpha C_\beta C_\beta)$	106.6	q(S)	0.87
$R_e(C_\alpha\text{-}C_\beta)$	1.457	$\alpha_e(C_\beta C_\beta N_t)$	115.2	$q(N_m)$	-0.43
$R_e(C_{\beta t}\text{-}C_\beta)$	1.418	$\alpha_e(C_\beta N_t S)$	104.7	$Q(Li\text{-}N_p)$	0.04
$R_e(C_\beta\text{-}N_t)$	1.317	$\alpha_e(N_tSN_t)$	100.2	$Q(N_p\text{-}C_\alpha)$	1.24
$R_e(N_t\text{-}S)$	1.654	$\alpha_e(N_pC_\alpha N_m)$	127.9	$Q(C_\alpha\text{-}C_\beta)$	1.06
$R_e(C_\alpha\text{-}N_m)$	1.317	$\alpha_e(C_\alpha N_m C_\alpha)$	123.7	$Q(C_\beta\text{-}C_\beta)$	1.18
$R_e(Li\cdots Li)$	2.016	q(Li)	0.91	$Q(C_\beta\text{-}N_t)$	1.52
$R_e(N_p\cdots N_p)$	3.944	$q(N_p)$	-0.71	$Q(N_t\text{-}S)$	1.20
$\alpha_e(LiN_pLi)$	54.1	$q(C_\alpha)$	0.37	$Q(C_\alpha\text{-}N_m)$	1.39
$\alpha_e(C_\alpha N_p C_\alpha)$	109.5	$q(C_\beta)$	0.09	Q(Li-Li)	0.01
(B) Symmetry C_{2h} (h =0 kJ/mol)					
$R_e(Li_1\text{-}N_{p1})$	2.140	$\alpha_e(C_{\alpha2}N_{p2}C_{\alpha2})$	109.4	$q(N_{t1})$	-0.55
$R_e(Li_2\text{-}N_{p1})$	2.296	$\alpha_e(N_{p1}C_{\alpha1}C_{\beta1})$	108.6	$q(N_{t2})$	-0.55
$R_e(Li_1\text{-}N_{p2})$	2.213	$\alpha_e(N_{p2}C_{\alpha2}C_{\beta2})$	108.6	$q(S_1)$	0.87
$R_e(N_{p1}\text{-}C_{\alpha1})$	1.379	$\alpha_e(C_{\alpha1}C_{\beta1}C_{\beta1})$	106.6	$q(S_2)$	0.87
$R_e(N_{p2}\text{-}C_{\alpha2})$	1.379	$\alpha_e(C_{\alpha2}C_{\beta2}C_{\beta2})$	106.6	$q(N_m)$	-0.43
$R_e(C_{\alpha1}\text{-}C_{\beta1})$	1.457	$\alpha_e(C_{\beta1}C_{\beta1}N_{t1})$	115.2	$Q(Li_1\text{-}N_{p1})$	0.04
$R_e(C_{\alpha2}\text{-}C_{\beta2})$	1.457	$\alpha_e(C_{\beta2}C_{\beta2}N_{t2})$	115.2	$Q(Li_2\text{-}N_{p1})$	0.04
$R_e(C_{\beta1}\text{-}C_{\beta1})$	1.418	$\alpha_e(C_{\beta1}N_{t1}S_1)$	104.7	$Q(Li_1\text{-}N_{p2})$	0.04
$R_e(C_{\beta2}\text{-}C_{\beta2})$	1.418	$\alpha_e(C_{\beta2}N_{t2}S_2)$	104.7	$Q(N_{p1}\text{-}C_{\alpha1})$	1.24
$R_e(C_{\beta1}\text{-}N_{t1})$	1.317	$\alpha_e(N_{t1}S_1N_{t1})$	100.2	$Q(N_{p2}\text{-}C_{\alpha2})$	1.24
$R_e(C_{\beta2}\text{-}N_{t2})$	1.317	$\alpha_e(N_{t2}S_2N_{t2})$	100.2	$Q(C_{\alpha1}\text{-}C_{\beta1})$	1.06
$R_e(N_{t1}\text{-}S_1)$	1.654	$\alpha_e(N_{p1}C_{\alpha1}N_m)$	127.8	$Q(C_{\alpha2}\text{-}C_{\beta2})$	1.06
$R_e(N_{t2}\text{-}S_2)$	1.654	$\alpha_e(N_{p2}C_{\alpha2}N_m)$	127.9	$Q(C_{\beta1}\text{-}C_{\beta1})$	1.18
$R_e(C_{\alpha1}\text{-}N_m)$	1.317	$\alpha_e(C_{\alpha1}N_mC_{\alpha1})$	123.8	$Q(C_{\beta2}\text{-}C_{\beta2})$	1.18
$R_e(C_{\alpha2}\text{-}N_m)$	1.317	q(Li)	0.91	$Q(C_{\beta1}\text{-}N_{t1})$	1.52
$R_e(Li\cdots Li)$	2.020	$q(N_{p1})$	-0.71	$Q(C_{\beta2}\text{-}N_{t2})$	1.52
$R_e(N_{p1}\cdots N_{p1})$	3.953	$q(N_{p2})$	-0.71	$Q(N_{t1}\text{-}S_1)$	1.20
$R_e(N_{p2}\cdots N_{p2})$	3.939	$q(C_{\alpha1})$	0.37	$Q(N_{t2}\text{-}S_2)$	1.20
$\alpha_e(LiN_{p1}Li)$	54.0	$q(C_{\alpha2})$	0.37	$Q(C_{\alpha1}\text{-}N_m)$	1.39
$\alpha_e(LiN_{p2}Li)$	54.3	$q(C_{\beta1})$	0.09	$Q(C_{\alpha2}\text{-}N_m)$	1.39
$\alpha_e(C_{\alpha1}N_{p1}C_{\alpha1})$	109.5	$q(C_{\beta2})$	0.09	Q(Li-Li)	0.01

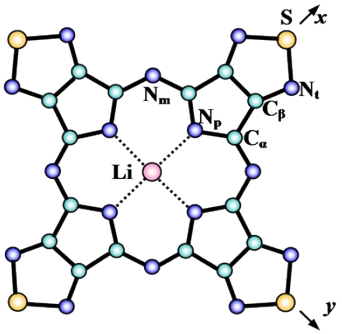
Table S2. Relative energy (h), geometric parameters (bond length R_e in Å, bond angles α_e) for four considered geometrical configurations of monolitium complex [TTDPaHLi]. Atomic charges (NBO, q) and Vyberg bond indices (Q) are given for the most stable C_s structure.



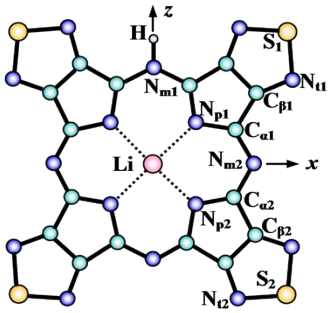
(A) Symmetry C_{4v} (h =360 kJ/mol)					
$R_e(Li\text{-}N_p)$	2.191	$R_e(C_\alpha\text{-}N_m)$	1.311	$\alpha_e(C_\beta C_\beta N_t)$	115.3
$R_e(N_p\text{-}C_\alpha)$	1.382	$R_e(Li\text{-}H)$	1.648	$\alpha_e(C_\beta N_t S)$	104.6
$R_e(C_\alpha\text{-}C_\beta)$	1.455	$\alpha_e(N_pLiN_p)$	126.0	$\alpha_e(N_tSN_t)$	100.3
$R_e(C_\beta\text{-}C_\beta)$	1.413	$\alpha_e(C_\alpha N_p C_\alpha)$	108.6	$\alpha_e(N_pC_\alpha N_m)$	128.0
$R_e(C_\beta\text{-}N_t)$	1.318	$\alpha_e(N_pC_\alpha C_\beta)$	109.0	$\alpha_e(C_\alpha N_m C_\alpha)$	123.0
$R_e(N_t\text{-}S)$	1.654	$\alpha_e(C_\alpha C_\beta C_\beta)$	106.6	$\chi_e(LiN_pN_pN_m)$	147.8
(B) Symmetry C_{2v} (h =330 kJ/mol)					
$R_e(Li\text{-}N_{p1})$	2.089	$R_e(C_{\alpha1}\text{-}N_m)$	1.315	$\alpha_e(C_{\beta2}N_{t2}S_2)$	105.0
$R_e(Li\text{-}N_{p2})$	2.203	$R_e(C_{\alpha2}\text{-}N_m)$	1.316	$\alpha_e(N_{t1}S_1N_{t1})$	100.6
$R_e(Li\text{-}H)$	1.657	$\alpha_e(N_{p1}LiN_{p1})$	94.8	$\alpha_e(N_{t2}S_2N_{t2})$	99.9
$R_e(N_{p1}\text{-}C_{\alpha1})$	1.428	$\alpha_e(N_{p2}LiN_{p2})$	144.8	$\alpha_e(N_{p1}C_{\alpha1}N_m)$	132.2
$R_e(N_{p2}\text{-}C_{\alpha2})$	1.350	$\alpha_e(C_{\alpha1}N_{p1}C_{\alpha1})$	106.2	$\alpha_e(N_{p2}C_{\alpha2}N_m)$	121.9
$R_e(C_{\alpha1}\text{-}C_{\beta1})$	1.445	$\alpha_e(C_{\alpha2}N_{p2}C_{\alpha2})$	109.6	$\alpha_e(C_{\alpha1}N_mC_{\alpha2})$	121.8
$R_e(C_{\alpha2}\text{-}C_{\beta2})$	1.463	$\alpha_e(N_{p1}C_{\alpha1}C_{\beta1})$	108.5	$\chi_e(C_{\alpha1}\cdots C_{\alpha1})$	169.3
$R_e(C_{\beta1}\text{-}C_{\beta1})$	1.404	$\alpha_e(N_{p2}C_{\alpha2}C_{\beta2})$	108.9	$\chi_e(C_{\alpha2}\cdots C_{\alpha2})$	166.7
$R_e(C_{\beta2}\text{-}C_{\beta2})$	1.429	$\alpha_e(C_{\alpha1}C_{\beta1}C_{\beta1})$	107.7	$\chi_e(C_{\alpha1}C_{\beta1}C_{\beta1}N_{t1})$	177.0
$R_e(C_{\beta1}\text{-}N_{t1})$	1.322	$\alpha_e(C_{\alpha2}C_{\beta2}C_{\beta2})$	105.4	$\chi_e(C_{\alpha2}C_{\beta2}C_{\beta2}N_{t2})$	177.0
$R_e(C_{\beta2}\text{-}N_{t2})$	1.312	$\alpha_e(C_{\beta1}C_{\beta1}N_{t1})$	115.3	$\chi_e(C_{\beta1}C_{\alpha1}N_mC_{\alpha2})$	178.9
$R_e(N_{t1}\text{-}S_1)$	1.648	$\alpha_e(C_{\beta2}C_{\beta2}N_{t2})$	115.0	$\chi_e(C_{\beta2}C_{\alpha2}N_mC_{\alpha1})$	165.0
$R_e(N_{t2}\text{-}S_2)$	1.659	$\alpha_e(C_{\beta1}N_{t1}S_1)$	104.4		
(C) Symmetry C_{2v} (h =32 kJ/mol)					
$R_e(Li\text{-}N_{p1})$	1.757	$R_e(N_{t2}\text{-}S_2)$	1.656	$\alpha_e(C_{\beta1}C_{\beta1}N_{t1})$	114.9
$R_e(Li\text{-}N_{p2})$	1.963	$R_e(N_{t3}\text{-}S_3)$	1.647	$\alpha_e(C_{\beta2}C_{\beta2}N_{t2})$	115.3

R_e(Li-H)	1.636	R_e($C_{\alpha1}$-N_m)	1.320	α_e($C_{\beta3}C_{\beta3}N_{t3}$)	114.5
R_e(N_{p1}-$C_{\alpha1}$)	1.350	R_e($C_{\alpha2}$-N_m)	1.328	α_e($C_{\beta1}N_{t1}S_1$)	105.2
R_e(N_{p2}-$C_{\alpha2}$)	1.386	R_e($C_{\alpha2}$-N_{m1})	1.327	α_e($C_{\beta2}N_{t2}S_2$)	104.8
R_e(N_{p3}-$C_{\alpha3}$)	1.375	R_e($C_{\alpha3}$-N_{m1})	1.309	α_e($C_{\beta3}N_{t3}S_3$)	105.2
R_e($C_{\alpha1}$-$C_{\beta1}$)	1.471	R_e(N_{p3}-H)	0.984	α_e($N_{t1}S_1N_{t1}$)	99.8
R_e($C_{\alpha2}$-$C_{\beta2}$)	1.463	α_e($C_{\alpha1}N_{p1}C_{\alpha1}$)	113.9	α_e($N_{t2}S_2N_{t2}$)	100.0
R_e($C_{\alpha3}$-$C_{\beta3}$)	1.453	α_e($C_{\alpha2}N_{p2}C_{\alpha2}$)	110.1	α_e($N_{t3}S_3N_{t3}$)	100.5
R_e($C_{\beta1}$-$C_{\beta1}$)	1.433	α_e($C_{\alpha3}N_{p3}C_{\alpha3}$)	117.9	α_e($N_{p1}C_{\alpha1}N_m$)	125.4
R_e($C_{\beta2}$-$C_{\beta2}$)	1.417	α_e($N_{p1}C_{\alpha1}C_{\beta1}$)	106.7	α_e($N_{p2}C_{\alpha2}N_m$)	131.0
R_e($C_{\beta3}$-$C_{\beta3}$)	1.440	α_e($N_{p2}C_{\alpha2}C_{\beta2}$)	107.7	α_e($N_{p2}C_{\alpha2}N_{m1}$)	129.8
R_e($C_{\beta1}$-N_{t1})	1.311	α_e($N_{p3}C_{\alpha3}C_{\beta3}$)	102.7	α_e($N_{p3}C_{\alpha3}N_{m1}$)	126.5
R_e($C_{\beta2}$-N_{t2})	1.315	α_e($C_{\alpha1}C_{\beta1}C_{\beta1}$)	106.3	α_e($C_{\alpha1}N_mC_{\alpha2}$)	126.3
R_e($C_{\beta3}$-N_{t3})	1.318	α_e($C_{\alpha2}C_{\beta2}C_{\beta2}$)	107.1	α_e($C_{\alpha2}N_{m1}C_{\alpha3}$)	127.0
R_e(N_{t1}-S_1)	1.659	α_e($C_{\alpha3}C_{\beta3}C_{\beta3}$)	108.4		
(D) Symmetry C_s (h =0 kJ/mol)					
R_e(Li-N_{p1})	1.874	R_e($C_{\alpha2}$-N_{m1})	1.323	α_e($C_{\beta1}N_{t1}S_1$)	104.9
R_e(Li-N_{p2})	2.035	R_e($C_{\alpha2}$-N_{m2})	1.324	α_e($C_{\beta2}N_{t2}S_2$)	104.8/104.7
R_e(Li-H)	1.976	R_e($C_{\alpha3}$-N_{m2})	1.306	α_e($C_{\beta3}N_{t3}S_3$)	105.0
R_e(N_{p1}-$C_{\alpha1}$)	1.359	R_e(N_{p3}-H)	1.009	α_e($N_{t1}S_1N_{t1}$)	99.8
R_e(N_{p2}-$C_{\alpha2}$)	1.376/1.375	α_e(Li$N_{p1}C_{\alpha1}$)	124.2	α_e($N_{t2}S_2N_{t2}$)	100.0
R_e(N_{p3}-$C_{\alpha3}$)	1.397	α_e(N_{p2}LiN_{p2})	149.2	α_e($N_{t3}S_3N_{t3}$)	100.8
R_e($C_{\alpha1}$-$C_{\beta1}$)	1.468	α_e(N_{p3}HLi)	103.8	α_e($N_{p1}C_{\alpha1}N_{m1}$)	126.9
R_e($C_{\alpha2}$-$C_{\beta2}$)	1.463/1.459	α_e($C_{\alpha1}N_{p1}C_{\alpha1}$)	111.6	α_e($N_{p2}C_{\alpha2}N_{m1}$)	129.8
R_e($C_{\alpha3}$-$C_{\beta3}$)	1.443	α_e($C_{\alpha2}N_{p2}C_{\alpha2}$)	109.8	α_e($N_{p2}C_{\alpha2}N_{m2}$)	127.9
R_e($C_{\beta1}$-$C_{\beta1}$)	1.424	α_e($C_{\alpha3}N_{p3}C_{\alpha3}$)	114.5	α_e($N_{p3}C_{\alpha3}N_{m2}$)	127.7
R_e($C_{\beta2}$-$C_{\beta2}$)	1.417	α_e($N_{p1}C_{\alpha1}C_{\beta1}$)	107.9	α_e($C_{\alpha1}N_{m1}C_{\alpha2}$)	125.2
R_e($C_{\beta3}$-$C_{\beta3}$)	1.431	α_e($N_{p2}C_{\alpha2}C_{\beta2}$)	108.2/108.8	α_e($C_{\alpha2}N_{m2}C_{\alpha3}$)	125.4
R_e($C_{\beta1}$-N_{t1})	1.312	α_e($N_{p3}C_{\alpha3}C_{\beta3}$)	104.1	α_e(H$N_{p3}C_{\alpha3}$)	120.3
R_e($C_{\beta2}$-N_{t2})	1.314/1.315	α_e($C_{\alpha1}C_{\beta1}C_{\beta1}$)	106.3	χ_e($C_{\alpha1}\cdots C_{\alpha1}$)	176.7
R_e($C_{\beta3}$-N_{t3})	1.322	α_e($C_{\alpha2}C_{\beta2}C_{\beta2}$)	106.8/106.3	χ_e($C_{\beta1}C_{\alpha1}N_{m1}C_{\alpha2}$)	173.4
R_e(N_{t1}-S_1)	1.659	α_e($C_{\alpha3}C_{\beta3}C_{\beta3}$)	108.6	χ_e($C_{\beta2}C_{\alpha2}N_{m1}C_{\alpha1}$)	176.7
R_e(N_{t2}-S_2)	1.656/1.657	α_e($C_{\beta1}C_{\beta1}N_{t1}$)	115.1	χ_e($C_{\beta2}C_{\alpha2}N_{m2}C_{\alpha3}$)	177.3
R_e(N_{t3}-S_3)	1.643	α_e($C_{\beta2}C_{\beta2}N_{t2}$)	115.2/115.3	χ_e($C_{\beta3}C_{\alpha3}N_{m2}C_{\alpha2}$)	165.6
R_e($C_{\alpha1}$-N_{m1})	1.318	α_e($C_{\beta3}C_{\beta3}N_{t3}$)	114.6		
q(Li)	0.87	q(N_{t3})	-0.55	Q($C_{\beta1}$-$C_{\beta1}$)	1.17
q(H)	0.42	q(S_1)	0.85	Q($C_{\beta2}$-$C_{\beta2}$)	1.18
q(N_{p1})	-0.63	q(S_2)	0.86	Q($C_{\beta3}$-$C_{\beta3}$)	1.16
q(N_{p2})	-0.64	q(S_3)	0.92	Q($C_{\beta1}$-N_{t1})	1.55
q(N_{p3})	-0.60	Q(Li-N_{p1})	0.06	Q($C_{\beta2}$-N_{t2})	1.53/1.53
q($C_{\alpha1}$)	0.39	Q(Li-N_{p2})	0.07	Q($C_{\beta3}$-N_{t3})	1.48
q($C_{\alpha2}$)	0.39/0.37	Q(Li-H)	0.004	Q(N_{t1}-S_1)	1.19
q($C_{\alpha3}$)	0.37	Q(N_{p1}-$C_{\alpha1}$)	1.27	Q(N_{t2}-S_2)	1.20/1.19
q($C_{\beta1}$)	0.09	Q(N_{p2}-$C_{\alpha2}$)	1.27/1.26	Q(N_{t3}-S_3)	1.23
q($C_{\beta2}$)	0.09/0.08	Q(N_{p3}-$C_{\alpha3}$)	1.10	Q($C_{\alpha1}$-N_{m1})	1.39
q($C_{\beta3}$)	0.09	Q($C_{\alpha1}$-$C_{\beta1}$)	1.04	Q($C_{\alpha2}$-N_{m1})	1.38
q(N_{t1})	-0.54	Q($C_{\alpha2}$-$C_{\beta2}$)	1.04/1.05	Q($C_{\alpha2}$-N_{m2})	1.37
q(N_{t2})	-0.54/-0.55	Q($C_{\alpha3}$-$C_{\beta3}$)	1.10	Q($C_{\alpha3}$-N_{m2})	1.44
q(N_{t3})	-0.55			Q(N_{p3}-H)	0.78

Table S3. Geometric parameters (bond length R_e in Å, bond angles α_e) atomic charges (NBO, q) and Vyberg bond indices (Q) for lithate complex $[TTDPaLi]^-$ and its *meso*-protonated form H[TTDPaLi]



$[TTDPaLi]^-$, D_{4h}

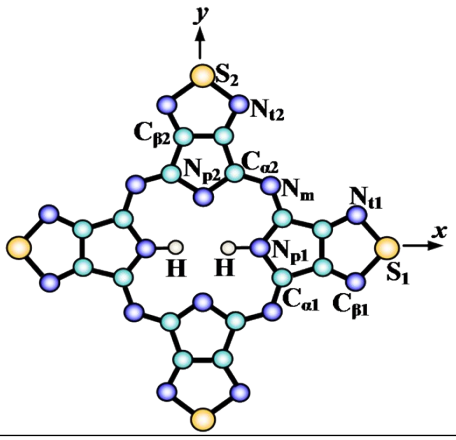
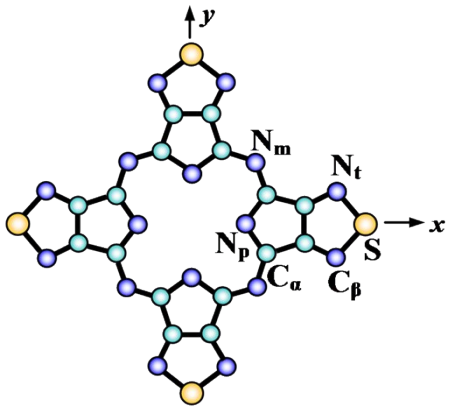


H[TTDPaLi], C_{2v}

		$[TTDPaLi]^-$	**D_{4h}**		
$R_e(Li\text{-}N_p)$	2.011	$\alpha_e(C_\alpha C_\beta C_\beta)$	106.3	$q(N_t)$	-0.56
$R_e(N_p\text{-}C_\alpha)$	1.363	$\alpha_e(C_\beta C_\beta N_t)$	115.2	q(S)	0.78
$R_e(C_\alpha\text{-}C_\beta)$	1.466	$\alpha_e(C_\beta N_t S)$	104.9	$q(N_m)$	-0.45
$R_e(C_\beta\text{-}C_\beta)$	1.428	$\alpha_e(N_t S N_t)$	99.8	$Q(Li\text{-}N_p)$	0.06
$R_e(C_\beta\text{-}N_t)$	1.313	$\alpha_e(N_p C_\alpha N_m)$	128.4	$Q(N_p\text{-}C_\alpha)$	1.28
$R_e(N_t\text{-}S)$	1.664	$\alpha_e(C_\alpha N_m C_\alpha)$	124.5	$Q(C_\alpha\text{-}C_\beta)$	1.04
$R_e(C_\alpha\text{-}N_m)$	1.323	q(Li)	0.85	$Q(C_\beta\text{-}C_\beta)$	1.16
$R_e(N_p\cdots N_p)$	4.022	$q(N_p)$	-0.57	$Q(C_\beta\text{-}N_t)$	1.55
$\alpha_e(C_\alpha N_p C_\alpha)$	111.3	$q(C_\alpha)$	0.35	$Q(N_t\text{-}S)$	1.16
$\alpha_e(N_p C_\alpha C_\beta)$	108.1	$q(C_\beta)$	0.10	$Q(C_\alpha\text{-}N_m)$	1.38

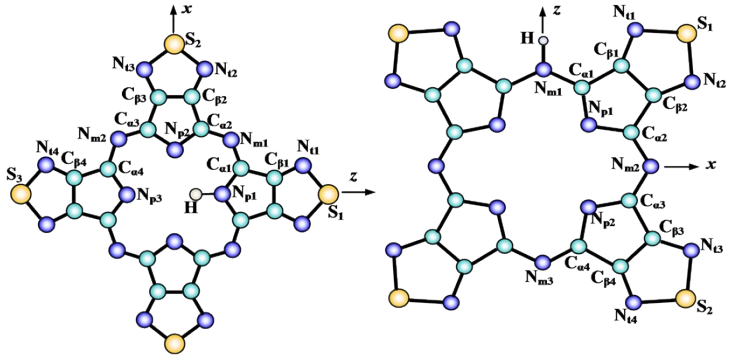
***meso*-Protonated form H[TTDPaLi] (symmetry C_{2v}) (h = -67.4 kJ/mol as compared to [TTDPaHLi] (C_s)**					
$R_e(Li\text{-}N_{p1})$	2.032	$R_e(N_{t2}\text{-}S_2)$	1.660/1.660	$\alpha_e(C_{\beta1}C_{\beta1}N_{t1})$	114.1/116.0
$R_e(Li\text{-}N_{p2})$	1.994	$R_e(C_{\alpha1}\text{-}N_{m1})$	1.354	$\alpha_e(C_{\beta2}C_{\beta2}N_{t2})$	115.2/115.3
$R_e(N_{m1}\text{-}H)$	1.013	$R_e(C_{\alpha1}\text{-}N_{m2})$	1.315	$\alpha_e(C_{\beta1}N_{t1}S_1)$	105.6/104.4
$R_e(N_{p1}\text{-}C_{\alpha1})$	1.377/1.336	$R_e(C_{\alpha2}\text{-}N_{m2})$	1.323	$\alpha_e(C_{\beta2}N_{t2}S_2)$	104.9/104.8
$R_e(N_{p2}\text{-}C_{\alpha2})$	1.363/1.363	$R_e(N_{p1}\cdots N_{p2})$	4.026	$\alpha_e(N_{t1}S_1N_{t1})$	99.8
$R_e(C_{\alpha1}\text{-}C_{\beta1})$	1.466/1.447	$\alpha_e(N_{p1}LiN_{p2})$	89.6	$\alpha_e(N_{t2}S_2N_{t2})$	99.8
$R_e(C_{\alpha2}\text{-}C_{\beta2})$	1.469/1.467	$\alpha_e(C_{\alpha1}N_{p1}C_{\alpha1})$	109.8	$\alpha_e(N_{p1}C_{\alpha1}N_{m1})$	124.5
$R_e(C_{\beta1}\text{-}C_{\beta1})$	1.424	$\alpha_e(C_{\alpha2}N_{p2}C_{\alpha2})$	110.7	$\alpha_e(N_{p1}C_{\alpha1}N_{m2})$	127.9
$R_e(C_{\beta2}\text{-}C_{\beta2})$	1.421	$\alpha_e(N_{p1}C_{\alpha1}C_{\beta1})$	107.7/110.7	$\alpha_e(N_{p2}C_{\alpha2}N_{m2})$	127.9
$R_e(C_{\beta1}\text{-}N_{t1})$	1.314/1.314	$\alpha_e(N_{p2}C_{\alpha2}C_{\beta2})$	108.3/108.5	$\alpha_e(C_{\alpha1}N_{m1}C_{\alpha1})$	129.1
$R_e(C_{\beta2}\text{-}N_{t2})$	1.312/1.312	$\alpha_e(C_{\alpha1}C_{\beta1}C_{\beta1})$	106.5/105.2	$\alpha_e(C_{\alpha1}N_{m2}C_{\alpha2})$	125.0
$R_e(N_{t1}\text{-}S_1)$	1.655/1.662	$\alpha_e(C_{\alpha2}C_{\beta2}C_{\beta2})$	106.3/106.2		
q(Li)	0.86	$q(S_1)$	0.86	$Q(C_{\alpha2}\text{-}C_{\beta2})$	1.29/1.29
q(H)	0.43	$q(S_2)$	0.84	$Q(C_{\beta1}\text{-}C_{\beta1})$	1.16
$q(N_{p1})$	-0.55	$q(N_{m1})$	-0.45	$Q(C_{\beta2}\text{-}C_{\beta2})$	1.17
$q(N_{p2})$	-0.58	$q(N_{m2})$	-0.42	$Q(C_{\beta1}\text{-}N_{t1})$	1.54/1.52
$q(C_{\alpha1})$	0.37/0.36	$Q(Li\text{-}N_{p1})$	0.06	$Q(C_{\beta2}\text{-}N_{t2})$	1.55/1.55
$q(C_{\alpha2})$	0.39/0.38	$Q(Li\text{-}N_{p2})$	0.06	$Q(N_{t1}\text{-}S_1)$	1.20/1.17
$q(C_{\beta1})$	0.10/0.07	$Q(N_{m1}\text{-}H)$	0.78	$Q(N_{t2}\text{-}S_2)$	1.18/1.18
$q(C_{\beta2})$	0.09/0.09	$Q(N_{p1}\text{-}C_{\alpha1})$	1.23/1.37	$Q(C_{\alpha1}\text{-}N_{m1})$	1.19
$q(N_{t1})$	-0.54/-0.58	$Q(N_{p2}\text{-}C_{\alpha2})$	1.29/1.29	$Q(C_{\alpha1}\text{-}N_{m2})$	1.41
$q(N_{t2})$	-0.54/-0.54	$Q(C_{\alpha1}\text{-}C_{\beta1})$	1.05/1.07	$Q(C_{\alpha2}\text{-}N_{m2})$	1.37

Table S4. Geometric parameters (bond length R_e in Å, bond angles α_e) atomic charges (NBO, q) and Vyberg bond indices (Q) for [$TTDPaH_2$] and corresponding dianion [TTDPa]$^{2-}$

	
[$TTDPaH_2$], D_{2h}	**[TTDPa]$^{2-}$, D_{4h}**

		[$TTDPaH_2$]	**D_{2h}**		
$R_e(H\text{-}N_{p1})$	1.011	$\alpha_e(C_{\alpha1}C_{\beta1}C_{\beta1})$	108.1	$q(N_{t1})$	-0.54
$R_e(N_{p1}\text{-}C_{\alpha1})$	1.382	$\alpha_e(C_{\alpha2}C_{\beta2}C_{\beta2})$	106.1	$q(N_{t2})$	-0.54
$R_e(N_{p2}\text{-}C_{\alpha2})$	1.365	$\alpha_e(C_{\beta1}C_{\beta1}N_{t1})$	114.9	$q(S_1)$	0.90
$R_e(C_{\alpha1}\text{-}C_{\beta1})$	1.452	$\alpha_e(C_{\beta2}C_{\beta2}N_{t2})$	115.3	$q(S_2)$	0.85
$R_e(C_{\alpha2}\text{-}C_{\beta2})$	1.464	$\alpha_e(C_{\beta1}N_{t1}S_1)$	104.9	$q(N_m)$	-0.42
$R_e(C_{\beta1}\text{-}C_{\beta1})$	1.425	$\alpha_e(C_{\beta2}N_{t2}S_2)$	104.8	$Q(H\text{-}N_{p1})$	0.73
$R_e(C_{\beta2}\text{-}C_{\beta2})$	1.417	$\alpha_e(N_{t1}S_1N_{t1})$	100.4	$Q(N_{p1}\text{-}C_{\alpha1})$	1.15
$R_e(C_{\beta1}\text{-}N_{t1})$	1.318	$\alpha_e(N_{t2}S_2N_{t2})$	99.8	$Q(N_{p2}\text{-}C_{\alpha2})$	1.30
$R_e(C_{\beta2}\text{-}N_{t2})$	1.313	$\alpha_e(N_{p1}C_{\alpha1}N_m)$	128.7	$Q(C_{\alpha1}\text{-}C_{\beta1})$	1.08
$R_e(N_{t1}\text{-}S_1)$	1.649	$\alpha_e(N_{p2}C_{\alpha2}N_m)$	128.1	$Q(C_{\alpha2}\text{-}C_{\beta2})$	1.04
$R_e(N_{t2}\text{-}S_2)$	1.659	$\alpha_e(C_{\alpha1}N_mC_{\alpha2})$	125.3	$Q(C_{\beta1}\text{-}C_{\beta1})$	1.17
$R_e(C_{\alpha1}\text{-}N_m)$	1.305	q(H)	0.46	$Q(C_{\beta2}\text{-}C_{\beta2})$	1.17
$R_e(C_{\alpha2}\text{-}N_m)$	1.325	$q(N_{p1})$	-0.51	$Q(C_{\beta1}\text{-}N_{t1})$	1.51
$R_e(N_{p1}\cdots N_{p1})$	4.115	$q(N_{p2})$	-0.57	$Q(C_{\beta2}\text{-}N_{t2})$	1.54
$R_e(N_{p2}\cdots N_{p2})$	3.984	$q(C_{\alpha1})$	0.39	$Q(N_{t1}\text{-}S_1)$	1.21
$\alpha_e(C_{\alpha1}N_{p1}C_{\alpha1})$	114.8	$q(C_{\alpha2})$	0.38	$Q(N_{t2}\text{-}S_2)$	1.19
$\alpha_e(C_{\alpha2}N_{p2}C_{\alpha2})$	109.5	$q(C_{\beta1})$	0.09	$Q(C_{\alpha1}\text{-}N_m)$	1.44
$\alpha_e(N_{p1}C_{\alpha1}C_{\beta1})$	104.5	$q(C_{\beta2})$	0.09	$Q(C_{\alpha2}\text{-}N_m)$	1.35
$\alpha_e(N_{p2}C_{\alpha2}C_{\beta2})$	109.1				
		[TTDPa]$^{2-}$	**D_{4h}**		
$R_e(N_p\text{-}C_\alpha)$	1.352	$\alpha_e(C_\alpha C_\beta C_\beta)$	105.7	$q(N_t)$	-0.58
$R_e(C_\alpha\text{-}C_\beta)$	1.475	$\alpha_e(C_\beta C_\beta N_t)$	115.2	q(S)	0.68
$R_e(C_\beta\text{-}C_\beta)$	1.438	$\alpha_e(C_\beta N_t S)$	105.1	$q(N_m)$	-0.47
$R_e(C_\beta\text{-}N_t)$	1.311	$\alpha_e(N_tSN_t)$	99.4	$Q(N_p\text{-}C_\alpha)$	1.33
$R_e(N_t\text{-}S)$	1.676	$\alpha_e(N_pC_\alpha N_m)$	128.9	$Q(C_\alpha\text{-}C_\beta)$	1.03
$R_e(C_\alpha\text{-}N_m)$	1.329	$\alpha_e(C_\alpha N_m C_\alpha)$	124.1	$Q(C_\beta\text{-}C_\beta)$	1.13
$R_e(N_p\cdots N_p)$	4.042	$q(N_p)$	-0.41	$Q(C_\beta\text{-}N_t)$	1.57
$\alpha_e(C_\alpha N_p C_\alpha)$	111.8	$q(C_\alpha)$	0.33	$Q(N_t\text{-}S)$	1.13
$\alpha_e(N_pC_\alpha C_\beta)$	108.4	$q(C_\beta)$	0.11	$Q(C_\alpha\text{-}N_m)$	1.36

Table S5. Geometric parameters (bond length R_e in Å, bond angles α_e) atomic charges (NBO, q) and Vyberg bond indices (Q) for monoanions $[TTDPaH]^-$ (protonated N_p) and $\{H[TTPA]\}^-$ (protonated N_m)



$[TTDPaH]^-$ (symmetry C_{2v}) protonation of N_p

$\{H[TTDPa]\}^-$ (symmetry C_{2v}) protonation of N_m

Protonation of N_p: h=0					
$R_e(N_{p1}\text{-}H)$	1.023	$R_e(C_{\alpha3}\text{-}N_{m2})$	1.323	$\alpha_e(N_{p2}C_{\alpha2}C_{\beta2})$	109.3
$R_e(N_{p1}\text{-}C_{\alpha1})$	1.390	$R_e(C_{\alpha4}\text{-}N_{m2})$	1.324	$\alpha_e(N_{p2}C_{\alpha3}C_{\beta3})$	108.3
$R_e(C_{\alpha1}\text{-}C_{\beta1})$	1.448	$R_e(N_{p3}\text{-}C_{\alpha4})$	1.352	$\alpha_e(C_{\alpha2}C_{\beta2}C_{\beta3})$	105.5
$R_e(C_{\beta1}\text{-}C_{\beta1})$	1.428	$R_e(C_{\alpha4}\text{-}C_{\beta4})$	1.476	$\alpha_e(C_{\beta3}C_{\beta2}N_{t2})$	115.4
$R_e(C_{\beta1}\text{-}N_{t1})$	1.320	$R_e(C_{\beta4}\text{-}C_{\beta4})$	1.427	$\alpha_e(C_{\beta2}C_{\beta3}N_{t3})$	115.2
$R_e(N_{t1}\text{-}S_1)$	1.652	$R_e(C_{\beta4}\text{-}N_{t4})$	1.310	$\alpha_e(C_{\beta2}N_{t2}S_2)$	104.8
$R_e(C_{\alpha1}\text{-}N_{m1})$	1.311	$R_e(N_{t4}\text{-}S_3)$	1.669	$\alpha_e(N_{t2}S_2N_{t3})$	99.6
$R_e(C_{\alpha2}\text{-}N_{m1})$	1.326	$\alpha_e(C_{\alpha1}N_{p1}C_{\alpha1})$	114.2	$\alpha_e(N_{p2}C_{\alpha3}N_{m2})$	129.4
$R_e(N_{p2}\text{-}C_{\alpha2})$	1.352	$\alpha_e(N_{p1}C_{\alpha1}C_{\beta1})$	104.7	$\alpha_e(C_{\alpha3}N_{m2}C_{\alpha4})$	124.4
$R_e(N_{p2}\text{-}C_{\alpha3})$	1.359	$\alpha_e(C_{\alpha1}C_{\beta1}C_{\beta1})$	108.2	$\alpha_e(N_{p3}C_{\alpha4}N_{m2})$	128.2
$R_e(C_{\alpha2}\text{-}C_{\beta2})$	1.466	$\alpha_e(C_{\beta1}C_{\beta1}N_{t1})$	114.9	$\alpha_e(C_{\alpha4}N_{p3}C_{\alpha4})$	110.8
$R_e(C_{\alpha3}\text{-}C_{\beta3})$	1.474	$\alpha_e(C_{\beta1}N_{t1}S_1)$	104.8	$\alpha_e(N_{p3}C_{\alpha4}C_{\beta4})$	108.9
$R_e(C_{\beta2}\text{-}C_{\beta3})$	1.427	$\alpha_e(N_{t1}S_1N_{t1})$	100.5	$\alpha_e(C_{\alpha4}C_{\beta4}C_{\beta4})$	105.7
$R_e(C_{\beta2}\text{-}N_{t2})$	1.312	$\alpha_e(N_{p1}C_{\alpha1}N_{m1})$	130.4	$\alpha_e(C_{\beta4}C_{\beta4}N_{t4})$	115.3
$R_e(C_{\beta3}\text{-}N_{t3})$	1.311	$\alpha_e(C_{\alpha1}N_{m1}C_{\alpha2})$	124.1	$\alpha_e(C_{\beta4}N_{t4}S_3)$	104.9
$R_e(N_{t2}\text{-}S_2)$	1.667	$\alpha_e(N_{p2}C_{\alpha2}N_{m1})$	126.5	$\alpha_e(N_{t4}S_3N_{t4})$	99.5
$R_e(N_{t3}\text{-}S_2)$	1.666	$\alpha_e(C_{\alpha2}N_{p2}C_{\alpha3})$	110.7		
Protonation of N_m: h=104.7 kJ/mol					
$R_e(N_{m1}\text{-}H)$	1.010	$R_e(C_{\alpha4}\text{-}C_{\beta4})$	1.478	$\alpha_e(N_{p1}C_{\alpha1}N_{m1})$	124.9
$R_e(N_{p1}\text{-}C_{\alpha1})$	1.320	$R_e(C_{\beta3}\text{-}C_{\beta4})$	1.429	$\alpha_e(C_{\alpha1}N_{m1}C_{\alpha1})$	129.3
$R_e(N_{p1}\text{-}C_{\alpha2})$	1.368	$R_e(C_{\beta3}\text{-}N_{t3})$	1.310	$\alpha_e(N_{p1}C_{\alpha2}N_{m2})$	128.2
$R_e(C_{\alpha1}\text{-}C_{\beta1})$	1.456	$R_e(C_{\beta4}\text{-}N_{t4})$	1.310	$\alpha_e(C_{\alpha2}N_{m2}C_{\alpha3})$	124.3
$R_e(C_{\alpha2}\text{-}C_{\beta2})$	1.475	$R_e(N_{t3}\text{-}S_2)$	1.671	$\alpha_e(N_{p2}C_{\alpha3}N_{m2})$	128.2
$R_e(C_{\beta1}\text{-}C_{\beta2})$	1.433	$R_e(N_{t4}\text{-}S_2)$	1.670	$\alpha_e(C_{\alpha3}N_{p2}C_{\alpha4})$	111.1
$R_e(C_{\beta1}\text{-}N_{t1})$	1.311	$R_e(C_{\alpha4}\text{-}N_{m3})$	1.326	$\alpha_e(N_{p2}C_{\alpha3}C_{\beta3})$	109.0
$R_e(C_{\beta2}\text{-}N_{t2})$	1.312	$\alpha_e(C_{\alpha1}N_{p1}C_{\alpha2})$	110.3	$\alpha_e(N_{p2}C_{\alpha4}C_{\beta4})$	108.6
$R_e(N_{t1}\text{-}S_1)$	1.673	$\alpha_e(N_{p1}C_{\alpha1}C_{\beta1})$	111.2	$\alpha_e(C_{\alpha3}C_{\beta3}C_{\beta4})$	105.6
$R_e(N_{t2}\text{-}S_1)$	1.665	$\alpha_e(N_{p1}C_{\alpha2}C_{\beta2})$	107.9	$\alpha_e(C_{\beta4}C_{\beta3}N_{t3})$	115.4
$R_e(C_{\alpha1}\text{-}N_{m1})$	1.361	$\alpha_e(C_{\alpha1}C_{\beta1}C_{\beta2})$	104.7	$\alpha_e(C_{\beta3}C_{\beta4}N_{t4})$	115.3
$R_e(C_{\alpha2}\text{-}N_{m2})$	1.317	$\alpha_e(C_{\beta2}C_{\beta1}N_{t1})$	116.0	$\alpha_e(C_{\beta3}N_{t3}S_2)$	104.9
$R_e(C_{\alpha3}\text{-}N_{m2})$	1.331	$\alpha_e(C_{\beta1}C_{\beta2}N_{t2})$	114.2	$\alpha_e(C_{\beta4}N_{t4}S_2)$	105.0
$R_e(N_{p2}\text{-}C_{\alpha3})$	1.349	$\alpha_e(C_{\beta1}N_{t1}S_1)$	104.5	$\alpha_e(N_{t3}S_1N_{t4})$	99.4
$R_e(N_{p2}\text{-}C_{\alpha4})$	1.352	$\alpha_e(C_{\beta2}N_{t2}S_1)$	105.8	$\alpha_e(N_{p2}C_{\alpha4}N_{m3})$	128.7
$R_e(C_{\alpha3}\text{-}C_{\beta3})$	1.475	$\alpha_e(N_{t1}S_1N_{t2})$	99.5	$\alpha_e(C_{\alpha4}N_{m3}C_{\alpha4})$	125.0

Table S6. Cartesian coordinates (in Å) of atoms and total energies for optimized molecular structures.

1. [TTDPaLi$_2$], D_{4h} structure

Charge	X	Y	Z
3	0.000000000	0.000000000	-1.007889151
3	0.000000000	0.000000000	1.007889151
7	0.000000000	1.972077549	0.000000000
7	-1.972077549	0.000000000	0.000000000
7	0.000000000	-1.972077549	0.000000000
7	1.972077549	0.000000000	0.000000000
6	-1.125868606	2.768444196	0.000000000
6	-2.768444196	-1.125868606	0.000000000
6	1.125868606	-2.768444196	0.000000000
6	2.768444196	-1.125868606	0.000000000
6	1.125868606	2.768444196	0.000000000
6	-2.768444196	1.125868606	0.000000000
6	-1.125868606	-2.768444196	0.000000000
6	2.768444196	1.125868606	0.000000000
6	-0.708865954	4.164256249	0.000000000
6	-4.164256249	-0.708865954	0.000000000
6	0.708865954	-4.164256249	0.000000000
6	4.164256249	-0.708865954	0.000000000
6	0.708865954	4.164256249	0.000000000
6	-4.164256249	0.708865954	0.000000000
6	-0.708865954	-4.164256249	0.000000000
6	4.164256249	0.708865954	0.000000000
7	-1.269056864	5.356362132	0.000000000
7	-5.356362132	-1.269056864	0.000000000
7	1.269056864	-5.356362132	0.000000000
7	5.356362132	-1.269056864	0.000000000
7	1.269056864	5.356362132	0.000000000
7	-5.356362132	1.269056864	0.000000000
7	-1.269056864	-5.356362132	0.000000000
7	5.356362132	1.269056864	0.000000000
16	0.000000000	6.417416663	0.000000000
16	-6.417416663	0.000000000	0.000000000
16	0.000000000	-6.417416663	0.000000000
16	6.417416663	0.000000000	0.000000000
7	-2.386210636	2.386210636	0.000000000
7	-2.386210636	-2.386210636	0.000000000
7	2.386210636	-2.386210636	0.000000000
7	2.386210636	2.386210636	0.000000000

TOTAL ENERGY = -3093.1708496553 (Ha)

2. [TTDPaLi$_2$], C_{2h} structure

Charge	X	Y	Z
3	-0.068567028	-1.007494935	0.000000000
3	0.068567028	1.007494935	0.000000000
7	0.000000000	0.000000000	-1.969635697
7	0.000000000	0.000000000	1.969635697
7	-1.975923922	-0.037914635	0.000000000
7	1.975923922	0.037914635	0.000000000
6	-1.126026695	-0.006691979	2.766386269
6	1.126026695	0.006691979	-2.766386269
6	-1.126026695	-0.006691979	-2.766386269
6	1.126026695	0.006691979	2.766386269
6	-2.771127344	-0.018533834	1.125843971
6	2.771127344	0.018533834	-1.125843971
6	-2.771127344	-0.018533834	-1.125843971
6	2.771127344	0.018533834	1.125843971
6	-0.708810514	-0.002841255	4.162079826
6	0.708810514	0.002841255	-4.162079826
6	-0.708810514	-0.002841255	-4.162079826
6	0.708810514	0.002841255	4.162079826
6	-4.166897555	0.003090814	0.708996101
6	4.166897555	-0.003090814	-0.708996101
6	-4.166897555	0.003090814	-0.708996101
6	4.166897555	-0.003090814	0.708996101
7	-5.358758590	0.022040843	1.269051403
7	5.358758590	-0.022040843	-1.269051403
7	-5.358758590	0.022040843	-1.269051403
7	5.358758590	-0.022040843	1.269051403
16	0.000000000	0.000000000	-6.415216922
16	0.000000000	0.000000000	6.415216922
16	-6.419777155	0.037950405	0.000000000
16	6.419777155	-0.037950405	0.000000000
7	-1.269026800	-0.005080652	5.354210785
7	1.269026800	0.005080652	-5.354210785
7	-1.269026800	-0.005080652	-5.354210785
7	1.269026800	0.005080652	5.354210785
7	-2.386874818	-0.013442650	2.385575604
7	2.386874818	0.013442650	-2.385575604
7	-2.386874818	-0.013442650	-2.385575604
7	2.386874818	0.013442650	2.385575604

TOTAL ENERGY = -3093.1708629450 (Ha)

3. $[TTDPaLi]^-$, D_{4h} structure

Charge	X	Y	Z
3	0.000000000	0.000000000	0.000000000
7	2.011131824	0.000000000	0.000000000
7	0.000000000	2.011131824	0.000000000
7	-2.011131824	0.000000000	0.000000000
7	0.000000000	-2.011131824	0.000000000
6	2.780811676	1.125414852	0.000000000
6	-1.125414852	2.780811676	0.000000000
6	-2.780811676	-1.125414852	0.000000000
6	1.125414852	2.780811676	0.000000000
6	-2.780811676	1.125414852	0.000000000
6	-1.125414852	-2.780811676	0.000000000
6	2.780811676	-1.125414852	0.000000000
6	1.125414852	-2.780811676	0.000000000
6	4.188085286	0.713826734	0.000000000
6	-0.713826734	4.188085286	0.000000000
6	-4.188085286	-0.713826734	0.000000000
6	0.713826734	4.188085286	0.000000000
6	-4.188085286	0.713826734	0.000000000
6	-0.713826734	-4.188085286	0.000000000
6	4.188085286	-0.713826734	0.000000000
6	0.713826734	-4.188085286	0.000000000
7	5.376487477	1.272790427	0.000000000
7	-1.272790427	5.376487477	0.000000000
7	-5.376487477	-1.272790427	0.000000000
7	1.272790427	5.376487477	0.000000000
7	-5.376487477	1.272790427	0.000000000
7	-1.272790427	-5.376487477	0.000000000
7	5.376487477	-1.272790427	0.000000000
7	1.272790427	-5.376487477	0.000000000
16	6.448054629	0.000000000	0.000000000
16	0.000000000	6.448054629	0.000000000
16	-6.448054629	0.000000000	0.000000000
16	0.000000000	-6.448054629	0.000000000
7	2.388828596	2.388828596	0.000000000
7	-2.388828596	2.388828596	0.000000000
7	-2.388828596	-2.388828596	0.000000000
7	2.388828596	-2.388828596	0.000000000

TOTAL ENERGY = -3085.7148700722 (Ha)

4. $H^+[TTDPaLi]^-$, C_{2v} structure

Charge	X	Y	Z
3	0.000000000	0.000000000	-0.019725753
7	-1.432234768	0.000000000	1.422109782
7	1.432234768	0.000000000	1.422109782
7	-1.424886681	0.000000000	-1.414966720
7	1.424886681	0.000000000	-1.414966720
6	-2.785192700	0.000000000	1.163362343
6	2.785192700	0.000000000	1.163362343
6	-1.171987534	0.000000000	-2.754124480
6	1.171987534	0.000000000	-2.754124480
6	-2.766944846	0.000000000	-1.177587535
6	2.766944846	0.000000000	-1.177587535
6	-1.222895331	0.000000000	2.741250857
6	1.222895331	0.000000000	2.741250857
6	-3.485398444	0.000000000	2.451544540
6	3.485398444	0.000000000	2.451544540
6	-2.456856757	0.000000000	-3.465804607
6	2.456856757	0.000000000	-3.465804607
6	-3.466754414	0.000000000	-2.466538123
6	3.466754414	0.000000000	-2.466538123
6	-2.479158339	0.000000000	3.459489583
6	2.479158339	0.000000000	3.459489583
7	-4.714114087	0.000000000	2.917854490
7	4.714114087	0.000000000	2.917854490
7	-2.894231145	0.000000000	-4.702606930
7	2.894231145	0.000000000	-4.702606930
7	-4.699538525	0.000000000	-2.916255009
7	4.699538525	0.000000000	-2.916255009
7	-2.908865702	0.000000000	4.700885105
7	2.908865702	0.000000000	4.700885105
16	-4.565620444	0.000000000	4.565710141
16	4.565620444	0.000000000	4.565710141
16	-4.548980866	0.000000000	-4.569907543
16	4.548980866	0.000000000	-4.569907543
7	-3.384791357	0.000000000	-0.007519446
7	3.384791357	0.000000000	-0.007519446
7	0.000000000	0.000000000	-3.364771018
7	0.000000000	0.000000000	3.322842155
1	0.000000000	0.000000000	4.335451606

TOTAL ENERGY = -3086.1986341181 (Ha)

5. [TTDPaHLi], C_S structure

Charge	X	Y	Z
1	-1.257922567	-0.792665280	0.000000000
3	0.190566062	0.551071505	0.000000000
7	-0.021997936	0.053803128	1.961368319
7	-0.021997936	0.053803128	-1.961368319
7	-2.100962487	-0.238805880	0.000000000
7	2.050028767	0.317362383	0.000000000
6	-1.126556605	-0.103375899	2.765470138
6	-1.126556605	-0.103375899	-2.765470138
6	-2.839473982	-0.078377842	1.175438144
6	-2.839473982	-0.078377842	-1.175438144
6	1.117616630	0.070629235	2.732318770
6	1.117616630	0.070629235	-2.732318770
6	2.812971488	0.268306232	1.123911259
6	2.812971488	0.268306232	-1.123911259
6	-0.687870332	-0.197386246	4.153401709
6	-0.687870332	-0.197386246	-4.153401709
6	-4.178363338	0.199063706	0.715322000
6	-4.178363338	0.199063706	-0.715322000
6	0.724954402	-0.088266681	4.133141568
6	0.724954402	-0.088266681	-4.133141568
6	4.221944234	0.257820861	0.711969824
6	4.221944234	0.257820861	-0.711969824
7	-1.222975430	-0.350309854	5.344809003
7	-1.222975430	-0.350309854	-5.344809003
7	-5.346318866	0.482565205	1.266460847
7	-5.346318866	0.482565205	-1.266460847
7	1.307150837	-0.149239451	5.309994638
7	1.307150837	-0.149239451	-5.309994638
7	5.409369412	0.232387372	1.269444305
7	5.409369412	0.232387372	-1.269444305
16	0.064669670	-0.344163035	6.387953800
16	0.064669670	-0.344163035	-6.387953800
16	-6.367819898	0.713968708	0.000000000
16	6.477709612	0.215108684	0.000000000
7	-2.400085834	-0.110316916	2.405186611
7	-2.400085834	-0.110316916	-2.405186611
7	2.384531948	0.184830997	2.367646651
7	2.384531948	0.184830997	-2.367646651

TOTAL ENERGY = -3086.1729795300 (Ha)

6. [TTDPaH$_2$], D_{2h} structure

Charge	X	Y	Z
7	2.057275462	0.000000000	0.000000000
7	-2.057275462	0.000000000	0.000000000
7	0.000000000	-1.991978537	0.000000000
7	0.000000000	1.991978537	0.000000000
6	2.802117689	-1.164454947	0.000000000
6	-2.802117689	-1.164454947	0.000000000
6	2.802117689	1.164454947	0.000000000
6	-2.802117689	1.164454947	0.000000000
6	1.114796604	-2.780000051	0.000000000
6	-1.114796604	-2.780000051	0.000000000
6	1.114796604	2.780000051	0.000000000
6	-1.114796604	2.780000051	0.000000000
6	4.181928644	-0.712624171	0.000000000
6	-4.181928644	-0.712624171	0.000000000
6	4.181928644	0.712624171	0.000000000
6	-4.181928644	0.712624171	0.000000000
6	0.708605737	-4.186685996	0.000000000
6	-0.708605737	-4.186685996	0.000000000
6	0.708605737	4.186685996	0.000000000
6	-0.708605737	4.186685996	0.000000000
7	5.377315252	-1.267213294	0.000000000
7	-5.377315252	-1.267213294	0.000000000
7	5.377315252	1.267213294	0.000000000
7	-5.377315252	1.267213294	0.000000000
7	1.269732958	-5.373859070	0.000000000
7	-1.269732958	-5.373859070	0.000000000
7	1.269732958	5.373859070	0.000000000
7	-1.269732958	5.373859070	0.000000000
16	6.432549748	0.000000000	0.000000000
16	-6.432549748	0.000000000	0.000000000
16	0.000000000	-6.442330953	0.000000000
16	0.000000000	6.442330953	0.000000000
7	2.384557245	-2.401235982	0.000000000
7	-2.384557245	-2.401235982	0.000000000
7	2.384557245	2.401235982	0.000000000
7	-2.384557245	2.401235982	0.000000000
1	1.046618324	0.000000000	0.000000000
1	-1.046618324	0.000000000	0.000000000

TOTAL ENERGY = -3079.1691980653 (Ha)

7. $[TTDPa]^{2-}$, D_{4h} structure

Charge	X	Y	Z
7	2.020945579	0.000000000	0.000000000
7	0.000000000	2.020945579	0.000000000
7	-2.020945579	0.000000000	0.000000000
7	0.000000000	-2.020945579	0.000000000
6	2.778942988	1.119165590	0.000000000
6	-1.119165590	2.778942988	0.000000000
6	-2.778942988	-1.119165590	0.000000000
6	1.119165590	2.778942988	0.000000000
6	-2.778942988	1.119165590	0.000000000
6	-1.119165590	-2.778942988	0.000000000
6	2.778942988	-1.119165590	0.000000000
6	1.119165590	-2.778942988	0.000000000
6	4.198802090	0.719183150	0.000000000
6	-0.719183150	4.198802090	0.000000000
6	-4.198802090	-0.719183150	0.000000000
6	0.719183150	4.198802090	0.000000000
6	-4.198802090	0.719183150	0.000000000
6	-0.719183150	-4.198802090	0.000000000
6	4.198802090	-0.719183150	0.000000000
6	0.719183150	-4.198802090	0.000000000
7	5.384573341	1.278255297	0.000000000
7	-1.278255297	5.384573341	0.000000000
7	-5.384573341	-1.278255297	0.000000000
7	1.278255297	5.384573341	0.000000000
7	-5.384573341	1.278255297	0.000000000
7	-1.278255297	-5.384573341	0.000000000
7	5.384573341	-1.278255297	0.000000000
7	1.278255297	-5.384573341	0.000000000
16	6.468418231	0.000000000	0.000000000
16	0.000000000	6.468418231	0.000000000
16	-6.468418231	0.000000000	0.000000000
16	0.000000000	-6.468418231	0.000000000
7	2.389641236	2.389641236	0.000000000
7	-2.389641236	2.389641236	0.000000000
7	-2.389641236	-2.389641236	0.000000000
7	2.389641236	-2.389641236	0.000000000

TOTAL ENERGY = -3078.0230506409 (Ha)

8. $[TTDPaH]^-$, C_{2v} structure

Charge	X	Y	Z
7	2.024606944	0.000000000	-0.037117703
7	-2.024606944	0.000000000	-0.037117703
7	0.000000000	0.000000000	-2.016820145
7	0.000000000	0.000000000	1.984913813
6	2.770589290	0.000000000	1.098899306
6	-2.770589290	0.000000000	1.098899306
6	1.166848838	0.000000000	-2.771890074
6	-1.166848838	0.000000000	-2.771890074
6	1.112848329	0.000000000	2.752385105
6	-1.112848329	0.000000000	2.752385105
6	2.820358573	0.000000000	-1.130570947
6	-2.820358573	0.000000000	-1.130570947
6	4.194204162	0.000000000	0.717429165
6	-4.194204162	0.000000000	0.717429165
6	0.714017402	0.000000000	-4.147476078
6	-0.714017402	0.000000000	-4.147476078
6	0.713378705	0.000000000	4.173196920
6	-0.713378705	0.000000000	4.173196920
6	4.224990426	0.000000000	-0.709214574
6	-4.224990426	0.000000000	-0.709214574
7	5.369037984	0.000000000	1.300287758
7	-5.369037984	0.000000000	1.300287758
7	1.270167535	0.000000000	-5.344408845
7	-1.270167535	0.000000000	-5.344408845
7	1.273952328	0.000000000	5.357224041
7	-1.273952328	0.000000000	5.357224041
7	5.421871592	0.000000000	-1.246218405
7	-5.421871592	0.000000000	-1.246218405
16	6.470792433	0.000000000	0.050015140
16	-6.470792433	0.000000000	0.050015140
16	0.000000000	0.000000000	-6.401351383
16	0.000000000	0.000000000	6.436178263
7	2.377546845	0.000000000	2.361888182
7	-2.377546845	0.000000000	2.361888182
7	2.422666813	0.000000000	-2.395489072
7	-2.422666813	0.000000000	-2.395489072
1	0.000000000	0.000000000	-0.993932614

TOTAL ENERGY = -3078.6621634009 (Ha)

9. H[TTDPa]$^-$, C_{2v} structure

Charge	X	Y	Z
7	1.448359490	0.000000000	1.415590459
7	-1.448359490	0.000000000	1.415590459
7	1.437863599	0.000000000	-1.414302865
7	-1.437863599	0.000000000	-1.414302865
6	2.792274360	0.000000000	1.158870397
6	-2.792274360	0.000000000	1.158870397
6	1.175729157	0.000000000	-2.741065887
6	-1.175729157	0.000000000	-2.741065887
6	2.766491899	0.000000000	-1.182818769
6	-2.766491899	0.000000000	-1.182818769
6	1.230161355	0.000000000	2.717770436
6	-1.230161355	0.000000000	2.717770436
6	3.501466815	0.000000000	2.452289567
6	-3.501466815	0.000000000	2.452289567
6	2.458121658	0.000000000	-3.475697902
6	-2.458121658	0.000000000	-3.475697902
6	3.478422934	0.000000000	-2.474760694
6	-3.478422934	0.000000000	-2.474760694
6	2.482271304	0.000000000	3.460140063
6	-2.482271304	0.000000000	3.460140063
7	4.725015300	0.000000000	2.924883756
7	-4.725015300	0.000000000	2.924883756
7	2.888712920	0.000000000	-4.712471293
7	-2.888712920	0.000000000	-4.712471293
7	4.707692160	0.000000000	-2.927006081
7	-4.707692160	0.000000000	-2.927006081
7	2.901191141	0.000000000	4.702258920
7	-2.901191141	0.000000000	4.702258920
16	4.569416298	0.000000000	4.582546201
16	-4.569416298	0.000000000	4.582546201
16	4.554668809	0.000000000	-4.590881369
16	-4.554668809	0.000000000	-4.590881369
7	3.397804638	0.000000000	-0.010554767
7	-3.397804638	0.000000000	-0.010554767
7	0.000000000	0.000000000	-3.353301773
7	0.000000000	0.000000000	3.301061314
1	0.000000000	0.000000000	4.311226480

TOTAL ENERGY = -3078.6222830322 (Ha)

Table S7. Wavelength (λ, nm) and oscillator strength (in parenthesis), corresponding to the energies of the electronic transitions [a)] from the ground[b)] to the excited singlet states.

	electronic transition	λ	Терм	electronic transition	λ
[μ-(TTDPa) Li_2]					
1^1E_u	$2a_{1u} \rightarrow 7e_g(90)$	615(0.481)	8^1E_u	$6a_{2u} \rightarrow 8e_g(76)$; $6e_g \rightarrow 7a_{2u}(14)$	255(0.671)
2^1E_u	$2a_{1u} \rightarrow 8e_g(85)$; $6a_{2u} \rightarrow 7e_g(12)$	398(0.019)	9^1E_u	$6e_g \rightarrow 7a_{2u}(25)$; $4b_{2u} \rightarrow 8e_g(24)$; $2b_{1u} \rightarrow 7e_g(20)$; $1a_{1u} \rightarrow 7e_g(14)$;	250(0.515)
3^1E_u	$4b_{2u} \rightarrow 7e_g(82)$; $5a_{2u} \rightarrow 7e_g(14)$	363(0.092)			
5^1E_u	$6a_{2u} \rightarrow 7e_g(75)$; $2a_{1u} \rightarrow 8e_g(10)$	325(2.122)	12^1E_u	$1a_{1u} \rightarrow 7e_g(58)$; $5a_{2u} \rightarrow 8e_g(24)$	231(0.160)
$[TTDPaLi]^-$					
1^1E_u	$2a_{1u} \rightarrow 7e_g(88)$	588(0.454)	5^1E_u	$4a_{2u} \rightarrow 7e_g(82)$; $5a_{2u} \rightarrow 8e_g(12)$	305(0.451)
2^1E_u	$2a_{1u} \rightarrow 8e_g(86)$; $5a_{2u} \rightarrow 7e_g(13)$	428(0.082)	6^1E_u	$5a_{2u} \rightarrow 8e_g(83)$; $4a_{2u} \rightarrow 7e_g(10)$	285(1.026)
3^1E_u	$5a_{2u} \rightarrow 7e_g(44)$; $4b_{2u} \rightarrow 7e_g(33)$	344(1.006)	8^1E_u	$6e_g \rightarrow 6a_{2u}(48)$; $6e_g \rightarrow 5b_{2u}(37)$	261(0.466)
4^1E_u	$4b_{2u} \rightarrow 7e_g(61)$; $5a_{2u} \rightarrow 7e_g(29)$	324(0.362)	11^1E_u	$2b_{1u} \rightarrow 7e_g(69)$; $4a_{2u} \rightarrow 8e_g(24)$	234(0.252)
$[TTDPa]^{2-}$					
1^1E_u	$2a_{1u} \rightarrow 7e_g(85)$	596(0.288)	6^1E_u	$6e_g \rightarrow 6a_{2u}(44)$; $4a_{2u} \rightarrow 7e_g(33)$; $6e_g \rightarrow 5b_{2u}(22)$	276(0.118)
2^1E_u	$2a_{1u} \rightarrow 8e_g(78)$; $5a_{2u} \rightarrow 7e_g(20)$	473(0.138)			
1^1A_{2u}	$16b_{1g} \rightarrow 5b_{2u}(74)$;$28e_u \rightarrow 7e_g(24)$	402(0.001)	7^1E_u	$4a_{2u} \rightarrow 7e_g(62)$; $6e_g \rightarrow 5b_{2u}(18)$; $6e_g \rightarrow 6a_{2u}(16)$	275(0.699)
3^1E_u	$5a_{2u} \rightarrow 7e_g(53)$; $5a_{2u} \rightarrow 8e_g(28)$	371(0.653)			
4^1E_u	$5a_{2u} \rightarrow 8e_g(65)$; $5a_{2u} \rightarrow 7e_g(13)$	333(1.522)	8^1E_u	$6e_g \rightarrow 5b_{2u}(58)$; $6e_g \rightarrow 6a_{2u}(35)$	269(0.470)
5^1E_u	$4b_{2u} \rightarrow 7e_g(88)$	303(0.086)			
$[TTDPaH_2]$					
1^1B_{2u}	$4a_u \rightarrow 7b_{2g}(91)$	609(0.286)	4^1B_{2u}	$7b_{1u} \rightarrow 7b_{3g}(60)$;$8b_{1u} \rightarrow 7b_{3g}(38)$;	325(0.148)
1^1B_{3u}	$4a_u \rightarrow 7b_{3g}(86)$	570(0.252)	5^1B_{3u}	$7b_{1u} \rightarrow 7b_{2g}(74)$; $8b_{1u} \rightarrow 7b_{2g}(12)$	312(0.260)
2^1B_{3u}	$9b_{1u} \rightarrow 7b_{2g}(90)$	414(0.058)	5^1B_{2u}	$8b_{1u} \rightarrow 7b_{3g}(42)$; $7b_{1u} \rightarrow 7b_{3g}(34)$	305(0.967)
2^1B_{2u}	$4a_u \rightarrow 8b_{2g}(59)$	391(0.058)	8^1B_{2u}	$6b_{3g} \rightarrow 11b_{1u}(44)$;$9b_{1u} \rightarrow 8b_{3g}(23)$; $3a_u \rightarrow 7b_{2g}(16)$; $2a_u \rightarrow 7b_{2g}(13)$	253(0.575)
4^1B_{3u}	$8b_{1u} \rightarrow 7b_{2g}(90)$; $7b_{1u} \rightarrow 7b_{2g}(20)$	330(1.039)	8^1B_{3u}	$6b_{2g} \rightarrow 10b_{1u}(76)$	249(0.363)
[TTDPzLiH], C_s (protonated N_p)					
$1^1A''$	$60a'' \rightarrow 79a'(91)$	649(0.208)	$12^1A''$	$76a' \rightarrow 61a''(39)$; $77a' \rightarrow 61a''(23)$	320(0.866)
$1^1A'$	$60a'' \rightarrow 61a''(88)$	590(0.249)	$28^1A''$	$78a' \rightarrow 62a''(60)$; $77a' \rightarrow 62a''(28)$	258(0.085)
$2^1A''$	$60a'' \rightarrow 80a'(91)$	460(0.048)	$29^1A'$	$60a'' \rightarrow 64a''(20)$; $69a' \rightarrow 79a'(19)$; $52a'' \rightarrow 61a''(16)$; $68a' \rightarrow 79a'(10)$	256(0.096)
$3^1A''$	$60a'' \rightarrow 81a'(91)$	418(0.004)			
$2^1A'$	$77a' \rightarrow 79a'(55)$;$60a'' \rightarrow 62a''(24)$; $78a' \rightarrow 79a'(14)$	399(0.023)	$31^1A'$	$77a' \rightarrow 82a'(50)$; $68a' \rightarrow 79a'(15)$; $78a' \rightarrow 82a'(15)$	255(0.106)
$8^1A'$	$74a' \rightarrow 79a'(33)$;$76a' \rightarrow 79a'(23)$; $77a' \rightarrow 79a'(12)$	342(0.362)	$30^1A''$	$59a'' \rightarrow 81a'(41)$; $53a'' \rightarrow 79a'(12)$	254(0.319)
			$32^1A''$	$77a' \rightarrow 62a''(52)$; $78a' \rightarrow 62a''(29)$	252(0.123)
$9^1A'$	$74a' \rightarrow 79a'(45)$;$57a'' \rightarrow 61a''(24)$; $76a' \rightarrow 79a'(11)$	333(0.266)	$33^1A'$	$74a' \rightarrow 80a'(30)$; $76a' \rightarrow 81a'(28)$; $77a' \rightarrow 82a'(10)$	252(0.128)
$10^1A'$	$57a'' \rightarrow 61a''(64)$;$76a' \rightarrow 79a'(13)$	326(0.449)			
H[TTDPzLi], C_{2v} (protonated N_m)					
1^1B_1	$12a_2 \rightarrow 14b_2(89)$	590(0.362)	13^1B_1	$12b_2 \rightarrow 14a_2(50)$; $10b_2 \rightarrow 13a_2(39)$	268(0.145)
1^1A_1	$12a_2 \rightarrow 13a_2(89)$	576(0.225)	15^1B_1	$10a_2 \rightarrow 15b_2(90)$	263(0.170)
7^1A_1	$12b_2 \rightarrow 14b_2(59)$	322(1.013)	14^1A_1	$11b_2 \rightarrow 15b_2(64)$; $13b_2 \rightarrow 16b_2(20)$	259(0.233)
7^1B_1	$12b_2 \rightarrow 13a_2(74)$	317(0.692)	16^1A_1	$10a_2 \rightarrow 14a_2(73)$; $11a_2 \rightarrow 15a_2(13)$	256(0.110)
11^1A_1	$10b_2 \rightarrow 14b_2(79)$	280(0.115)	17^1B_1	$11a_2 \rightarrow 16b_2(54)$; $10b_2 \rightarrow 13a_2(18)$	253(0.215)
Терм	Электронный переход	λ	Терм	Электронный переход	λ
$[TTDPaH]^-$, C_{2v} (protonated N_p)					
1^1B_1	$10a_2 \rightarrow 16b_2(89)$	634(0.162)	9^1B_1	$15b_2 \rightarrow 12a_2(75)$; $13b_2 \rightarrow 11a_2(17)$	290(0.547)
1^1A_1	$10a_2 \rightarrow 11a_2(84)$; $15b_2 \rightarrow 16b_2(11)$	569(0.210)	10^1A_1	$15b_2 \rightarrow 19b_2(88)$	289(0.279)
2^1B_1	$10a_2 \rightarrow 17b_2(89)$	480(0.089)	14^1A_1	$13b_2 \rightarrow 17b_2(51)$; $14b_2 \rightarrow 18b_2(17)$; $11b_2 \rightarrow 16b_2(14)$	264(0.095)
3^1A_1	$15b_2 \rightarrow 16b_2(52)$;$10a_2 \rightarrow 12a_2(17)$; $13b_2 \rightarrow 16b_2(10)$	368(0.548)	15^1A_1	$13b_2 \rightarrow 17b_2(40)$; $11b_2 \rightarrow 16b_2(30)$	262(0.116)
5^1B_1	$9a_2 \rightarrow 16b_2(40)$;$15b_2 \rightarrow 11a_2(25)$; $14b_2 \rightarrow 11a_2(20)$	362(0.220)	13^1B_1	$8a_2 \rightarrow 16b_2(78)$; $11b_2 \rightarrow 11a_2(15)$	262(0.198)
7^1B_1	$14b_2 \rightarrow 11a_2(52)$; $15b_2 \rightarrow 11a_2(30)$	329(0.216)	19^1A_1	$8a_2 \rightarrow 11a_2(46)$; $13b_2 \rightarrow 18b_2(17)$; $14b_2 \rightarrow 19b_2(13)$	248(0.098)
5^1A_1	$13b_2 \rightarrow 16b_2(51)$;$15b_2 \rightarrow 17b_2(37)$	326(0.101)	18^1B_1	$7a_2 \rightarrow 16b_2(53)$; $13b_2 \rightarrow 12a_2(34)$	238(0.129)

7^1A_1	$15b_2 \rightarrow 17b_2(44); 13b_2 \rightarrow 16b_2(27)$	309(0.419)	22^1A_1	$7a_2 \rightarrow 11a_2(70); 12b_2 \rightarrow 18b_2(20)$	231(0.085)
8^1B_1	$13b_2 \rightarrow 11a_2(67); 15b_2 \rightarrow 12a_2(21)$	307(0.327)			
{H[TTDPaLi]}$^-$, C_{2v} (protonated N_m)					
1^1A_1	$12a_2 \rightarrow 13a_2(85)$	588(0.133)	8^1A_1	$11b_2 \rightarrow 14b_2(66); 12b_2 \rightarrow 14b_2(10)$	307(0.543)
1^1B_1	$12a_2 \rightarrow 14b_2(81)$	585(0.323)	9^1B_1	$12a_2 \rightarrow 17b_2(49); 13b_2 \rightarrow 14a_2(14); 12b_2 \rightarrow 13a_2(13)$	303(0.190)
4^1B_1	$11a_2 \rightarrow 14b_2(69); 13b_2 \rightarrow 13a_2(20)$	377(0.152)	10^1A_1	$13b_2 \rightarrow 16b_2(64); 11a_2 \rightarrow 14a_2(19)$	292(0.226)
4^1A_1	$13b_2 \rightarrow 14b_2(40); 12b_2 \rightarrow 14b_2(26); 12a_2 \rightarrow 15a_2(12)$	371(0.283)	12^1B_1	$11b_2 \rightarrow 13a_2(70); 13b_2 \rightarrow 15a_2(11)$	286(0.313)
5^1B_1	$13b_2 \rightarrow 13a_2(56); 11a_2 \rightarrow 14b_2(27)$	359(0.155)	13^1B_1	$12b_2 \rightarrow 14a_2(93)$	275(0.165)
6^1A_1	$13b_2 \rightarrow 15b_2(44); 12b_2 \rightarrow 14b_2(31); 11b_2 \rightarrow 14b_2(13)$	343(0.233)	14^1B_1	$10a_2 \rightarrow 15b_2(68); 9a_2 \rightarrow 14b_2(21)$	267(0.184)
7^1A_1	$13b_2 \rightarrow 15b_2(47); 12b_2 \rightarrow 14b_2(20)$	338(0.189)	15^1B_1	$11a_2 \rightarrow 16b_2(47); 9a_2 \rightarrow 14b_2(28); 10a_2 \rightarrow 15b_2(16)$	263(0.092)
8^1B_1	$12b_2 \rightarrow 13a_2(45); 12a_2 \rightarrow 17b_2(27); 10a_2 \rightarrow 14b_2(10)$	311(0.183)	15^1A_1	$10a_2 \rightarrow 14a_2(35); 11a_2 \rightarrow 15a_2(32); 10b_2 \rightarrow 14b_2(14)$	258(0.301)

[a] one-electron transitions between filled and unoccupied MO and their contributions (>10%) to the corresponding electronic configurations of the excited states

[b] Electronic configurations of the groud:

$[TTDPzLi_2]$ …$(19a_{1g})^2(10a_{2g})^2(2a_{1u})^2(6a_{2u})^2(16b_{1g})^2(12b_{2g})^2(2b_{1u})^2(4b_{2u})^2(6e_g)^2(28e_u)^2$;

$[TTDPaLi]^-$ …$(19a_{1g})^2(10a_{2g})^2(2a_{1u})^2(5a_{2u})^2(16b_{1g})^2(12b_{2g})^2(2b_{1u})^2(4b_{2u})^2(6e_g)^2(28e_u)^2$;

$[TTDPa]^{2-}$ …$(18a_{1g})^2(10a_{2g})^2(2a_{1u})^2(5a_{2u})^2(16b_{1g})^2(12b_{2g})^2(2b_{1u})^2(4b_{2u})^2(6e_g)^2(28e_u)^2$;

$[TTDPaH]_2$ …$(34a_g)^2(4a_u)^2(22b_{1g})^2(9b_{1u})^2(6b_{2g})^2(28b_{2u})^2(6b_{3g})^2(28b_{3u})^2$;

[TTDPaLiH] - C_s - ... $(78a')^2(60a'')^2$; C_{2v} – …$(59a_1)^2(12a^2)^2(54b_1)^2(13b_2)^2$

$[TTDPaH]^-$ …$(62a_1)^2(10a_2)^2(50b_1)^2(15b_2)^2$;

$\{H[TTDPaH]\}^-$ …$(58a_1)^2(12a_2)^2(54b_1)^2(13b_2)^2$

Table S8. Calculated frequencies of normal vibrations (cm^{-1}) for D_{4h} and C_{2h} geometric configurations of [μ-TTDPa)Li_2].

D_{4h}	C_{2h}	D_{4h}	C_{2h}	D_{4h}	C_{2h}
40*i*(e_g)	21(b_g)	527(a_{2u}, 62.8)	527(b_u,62.8)	853(a_{1g})	853(a_g)
	33(a_g)	542(a_{1u})	542(a_u,0.0)	876(e_u, 45.9)	876(a_u,22.9)
15(b_{2u})	15(b_u,0.0)	542(a_{1g})	542(a_g)		877(b_u,22.6)
42(a_{2u},0.2)	42(b_u,0.2)	582(b_{1g})	583(a_g)	927(b_{2g})	927(b_g)
55(b_{1u})	55(a_u,0.0)	590(a_{1g})	591(a_g)	1030(b_{2g})	1029(b_g)
86(e_g)	98(a_g)	608(e_u, 33.2)	608(a_u,16.2)	1079(e_u, 3.3)	1077(b_u,3.4)
	103(b_g)		609(b_u,16.2)		1080(a_u,1.3)
117(b_{2g})	117(b_g)	617(e_g)	617(a_g)	1109(e_u, 452.4)	1109(b_u,226.9)
121(b_{1g})	137(a_g)		617(b_g)		1109(a_u,227.4)
128(e_u, 3.8)	128(b_u,1.5)	622(a_{2g})	622(b_g)	1135(a_{2g})	1135(b_g)
	128(a_u,2.0)	685(b_{1u})	684(a_u,19.6)	1181(a_{2g})	1181(b_g)
133(b_{2u})	133(b_u,0.8)	687(a_{2g})	688(b_g)	1199(b_{2g})	1199(b_g)
143(e_g)	145(b_g)	691(e_u, 289.1)	692(b_u,145.2)	1248(b_{1g})	1248(a_g)
	155(a_g)		692(a_u,125.2)	1272(a_{1g})	1272(a_g)
148(a_{1u})	148(a_u,0.0)	714(a_{1g})	714(a_g)	1279(e_u, 526.4)	1278(a_u,265.1)
215(a_{2u}, 55.3)	210(b_u,60.1)	731(b_{1g})	732(a_g)		1280(b_u,269.9)
228(b_{2g})	228(b_g)	732(b_{2u})	732(b_u,0.3)	1325(e_u, 43.5)	1325(b_u,19.8)
232(a_{1g})	233(a_g)	761(e_g)	761(a_g)		1326(a_u,23.2)
236(a_{2g})	236(b_g)		761(b_g)	1346(a_{1g})	1346(a_g)
265(e_g)	266(a_g)	763(e_u, 37.6)	762(a_u,19.4)	1364(b_{1g})	1364(a_g)
	266(b_g)		763(b_u,19.6)	1432(e_u, 0.2)	1431(b_u,0.2)
266(b_{2u})	260(b_u,4.8)	771(b_{2g})	772(b_g)		1432(a_u,0.1)
267(e_u, 32.0)	273(a_u,7.1)	777(a_{2u}, 30.6)	777(b_u,30.5)	1458(b_{1g})	1458(a_g)
	275(b_u,10.4)	785(e_u, 80.3)	785(b_u,41.3)	1470(b_{2g})	1470(b_g)
274(b_{1u})	275(a_u,1.2)		785(a_u,40.4)	1473(a_{1g})	1473(a_g)
295(a_{2u}, 54.7)	294(b_u,25.1)	787(b_{1g})	787(a_g)	1505(e_u, 0.7)	1505(a_u,0.5)
303(e_u, 60.6)	306(a_u,31.7)	788(a_{1g})	788(a_g)		1505(b_u,0.7)
	323(b_u,44.4)	800(a_{2g})	800(b_g)	1525(a_{2g})	1525(b_g)
312(e_g)	312(a_g)	820(b_{1u})	820(a_u,0.0)	1537(e_u, 13.0)	1537(a_u,6.5)
	312(b_g)	823(e_g)	823(b_g)		1537(b_u,6.6)
352(a_{2u}, 2.1)	354(b_u,5.3)		823(a_g)	1562(a_{2g})	1562(b_g)
512(b_{2g})	512(b_g)	823(a_{1u})	823(a_u,0.0)	1562(a_{1g})	1562(a_g)
518(b_{2u})	518(b_u,0.0)	833(e_u, 27.4)	833(a_u,13.2)	1572(e_u, 64.8)	1572(b_u,32.4)
519(e_g)	519(a_g)		833(b_u,13.0)		1572(a_u,31.9)
	519(b_g)	843(b_{1g})	844(a_g)	1574(b_{2g})	1575(b_g)
524(e_u, 5.7)	524(a_u,2.4)			1604(b_{1g})	1604(a_g)
	524(b_u,2.6)				

Symmetry and intensity (km/mol) of IR active vibrations.

D_{4h} - $\Gamma_{vib} = 10a_{1g}+8a_{2g}+9b_{1g}+9b_{2g}+9e_g+3a_{1u}+6a_{2u}+4b_{1u}+5b_{2u}+18e_u$;

C_{2h} - $\Gamma_{vib} = 28a_g+26b_g+25a_u+29b_u$.

Table S9. Calculated frequencies of normal vibrations infrared active vibrational modes for anion $[TTDPaLi]^{-}$ and $[\mu\text{-}(TTDPa)Li]_2$.

$[TTDPzLi]^{-}$		$[\mu\text{-}TTDPaLi_2]$	
$\omega_i(A_i)$	Assignment	$\omega_i(A_i)$	Assignment
Symmetry A_{2u}			
37 (0)	dom	42 (0)	dom
208 (6)	fold(C_β-C_β)	215 (55)	fold(C_β-C_β)
328 (12)	fold(C_β-C_β), OPB(Li)	295 (55)	fold(C_β-C_β), OPB(Li)
364 (1)	OPB(N_m), OPB(N_p), OPB(Li)	352 (2)	OPB(N_m), OPB(N_p), OPB(Li_2)
520 (64)	fold($N_t\cdots N_t$)	527 (63)	fold($N_t\cdots N_t$)
771 (22)	fold($C_\alpha\cdots C_\alpha$)	777 (31)	fold($C_\alpha\cdots C_\alpha$)
Symmetry E_u			
129 (7)	IPR(Py+TD)	128 (4)	IPR(Py+TD)
285 (12)	r(M-N_p),φ($C_\alpha N_m C_\alpha$), φ($N_m C_\alpha C_\beta$)	267 (32)	r(M-N_p),φ($C_\alpha N_m C_\alpha$), φ($N_m C_\alpha C_\beta$)
467 (2)	r(M-N_p), IPR(TD)	303 (61)	r(M-N_p),φ($C_\alpha N_m C_\alpha$), φ($N_m C_\alpha C_\beta$)
526 (3)	IPB(Py)	524 (6)	IPB(Py)
614 (11)	φ($C_\alpha N_m C_\alpha$), φ($N_m C_\alpha C_\beta$)	608 (33)	φ($C_\alpha N_m C_\alpha$), φ($N_m C_\alpha C_\beta$)
690 (421)	φ($N_p C_\alpha C_\beta$), φ($N_m C_\alpha C_\beta$)	691 (289)	φ($N_p C_\alpha C_\beta$), φ($N_m C_\alpha C_\beta$)
748 (83)	r(S-N_t),φ($C_\alpha N_m C_\alpha$)	763 (38)	r(S-N_t),φ($C_\alpha N_m C_\alpha$)
764 (124)	r(S-N_t),φ($C_\alpha N_m C_\alpha$), φ($C_\alpha C_\beta N_t$)	785 (80)	r(S-N_t),φ($C_\alpha N_m C_\alpha$), φ($C_\alpha C_\beta N_t$)
830 (17)	IPB(Py+TD)	833 (27)	IPB(Py+TD)
881 (21)	bre(Py+TD), IPR(Py)	876 (46)	bre(Py+TD), IPR(Py)
1083 (175)	r(N_p-C_α), φ($N_p C_\alpha C_\beta$)	1079 (3)	r(N_p-C_α), φ($N_p C_\alpha C_\beta$)
1115 (390)	r(C_α-C_β), r(C_α-N_m), φ($N_p C_\alpha C_\beta$), r(C_β-N_t)	1109 (452)	r(C_α-C_β), r(C_α-N_m), φ($N_p C_\alpha C_\beta$), r(C_β-N_t)
1278 (726)	φ($N_m C_\alpha C_\beta$), φ($C_\alpha N_m C_\alpha$)	1279 (526)	φ($N_m C_\alpha C_\beta$), φ($C_\alpha N_m C_\alpha$)
1315 (4)	r(N_p-C_α),φ($C_\alpha N_m C_\alpha$),φ($N_m C_\alpha C_\beta$)	1325 (44)	r(N_p-C_α),φ($C_\alpha N_m C_\alpha$),φ($N_m C_\alpha C_\beta$), r(C_α-C_β), φ($N_p C_\alpha C_\beta$)
1415 (4)	φ($N_m C_\alpha C_\beta$), r(C_β-N_t), r(C_α-N_m), φ($N_p C_\alpha C_\beta$)	1432 (0)	φ($N_m C_\alpha C_\beta$), r(C_β-N_t), r(C_α-N_m), φ($N_p C_\alpha C_\beta$)
1496 (51)	r(C_β-N_t), r(C_α-N_m), r(C_α-C_β), φ($N_p C_\alpha C_\beta$)	1505 (1)	r(C_β-N_t), r(C_α-N_m), r(C_α-C_β), φ($N_p C_\alpha C_\beta$)
1530 (59)	r(C_α-N_m), φ($N_p C_\alpha C_\beta$)	1537 (13)	r(C_α-N_m), φ($N_p C_\alpha C_\beta$)
1575 (83)	r(C_β-N_t), r(C_α-C_β)	1572 (65)	r(C_β-N_t), r(C_α-C_β)

dom. – doming; fold (X-Y) – folding along X-Y line; OPB - out-of-plane bending, IPR – in-plane rocking; Py – pyrrole ring; TD – thiadiazole ring; r – bond stretching; φ - angle bending; IPB – in-plane bending; bre – breathing

Table S10. Calculated frequencies of normal vibrations infrared inactive vibrational modes for anion $[TTDPaLi]^{-}$ and $[\mu\text{-}(TTDPa)Li]_2$.

$TTDPzLi^{-}$	$TTDPzLi_2$	$TTDPzLi^{-}$	$TTDPzLi_2$	$TTDPzLi^{-}$	$TTDPzLi_2$
Symmetry A_{1g}		Symmetry B_{1g}		Symmetry A_{2g}	
230	232	142	121	234	236
586	542	582	582	615	622
713	590	733	731	680	687
769	714	768	787	787	800
855	788	844	843	1147	1135
1255	853	1271	1248	1201	1181
1346	1272	1337	1364	1496	1525
1472	1346	1460	1458	1569	1562
1542	1473	1588	1604		
	1562				
Symmetry B_{2g}		Symmetry E_g		Symmetry B_{2u}	
111	117	59	$40i$[a]	16	15
210	228	145	86	142	133
507	512	259	143	273	266
757	771	317	265	508	518
922	927	509	312	726	732
1029	1030	616	519		
1217	1199	755	617		
1460	1470	822	761		
1578	1574		823		
Symmetry A_{1u}		Symmetry B_{1u}			
152	148	61	55		
540	542	275	274		
823	823	686	685		
		819	820		

[a] imaginary value

Table S11. Total energies (in Hartree) and frontier MO levels (in eV) for the optimized structures of TTDPa macrocycle its Li complex and their anionic forms.

	Total energy, Ha	HOMO, eV	LUMO, eV
[TTDPaLi$_2$] (D_{4h})	-3093.1708496553	-5.867	-3.679
(C_{2h})	-3093.1708629450		
[TTDPaLi]$^-$	-3085,5706669461	-2.865	-0.514
H[TTDPaLi]	-3086,1986341181	-5.965	-3.831/ -3.570
[TTDPaHLi]	-3086,1729795300	-6.038	-3.946/ -3.761
[TTDPa]$^{2-}$	-3078,0230506409	0.302	2.746
[TTDPaH]$^-$	-3078,6621584073	-2.912	-0.688/ -0.473
{H[TTDPa]}$^-$	-3078,6222830330	-2.767	-0.558/ -0.294
[TTDPaH$_2$]	-3079,1691980653	-6.144	-4.006/ -3.780

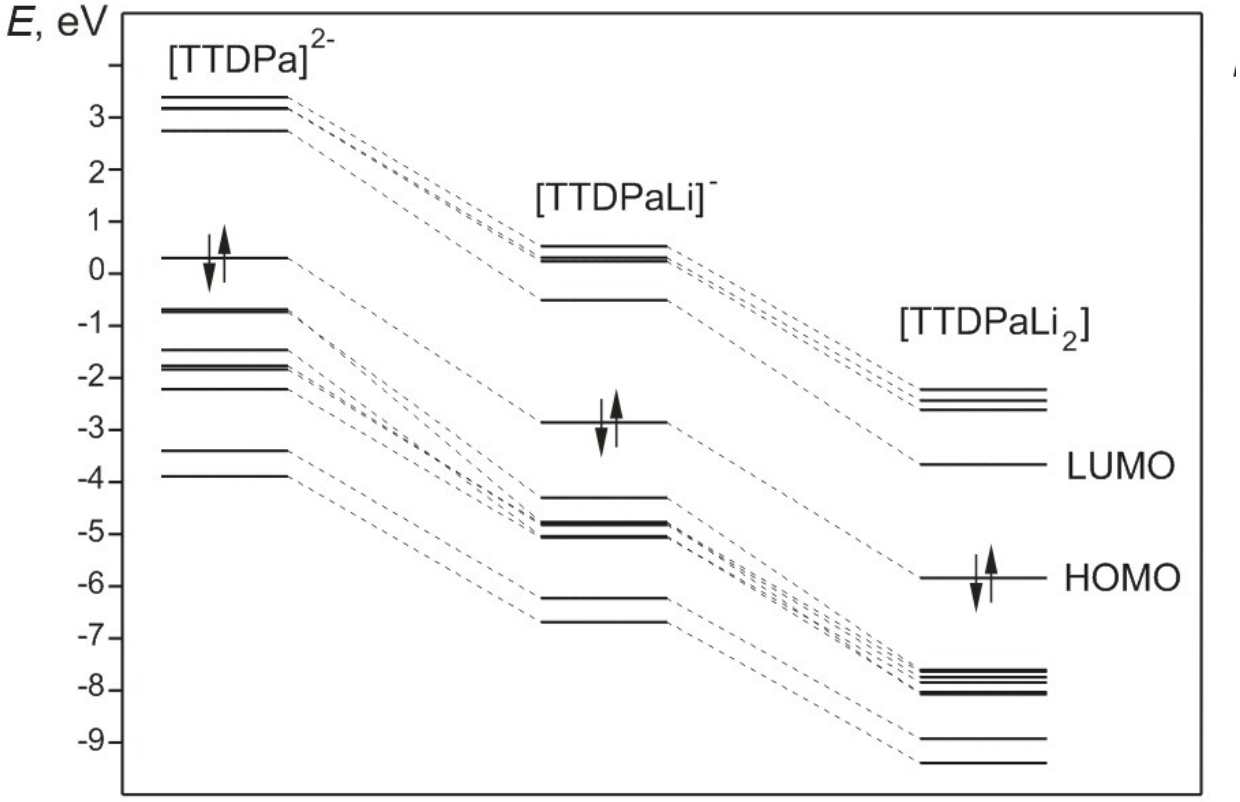


Figure S1. MO level diagram for the optimized structures of [TTDPa]$^{2-}$ and its mono- and dilithium complexes

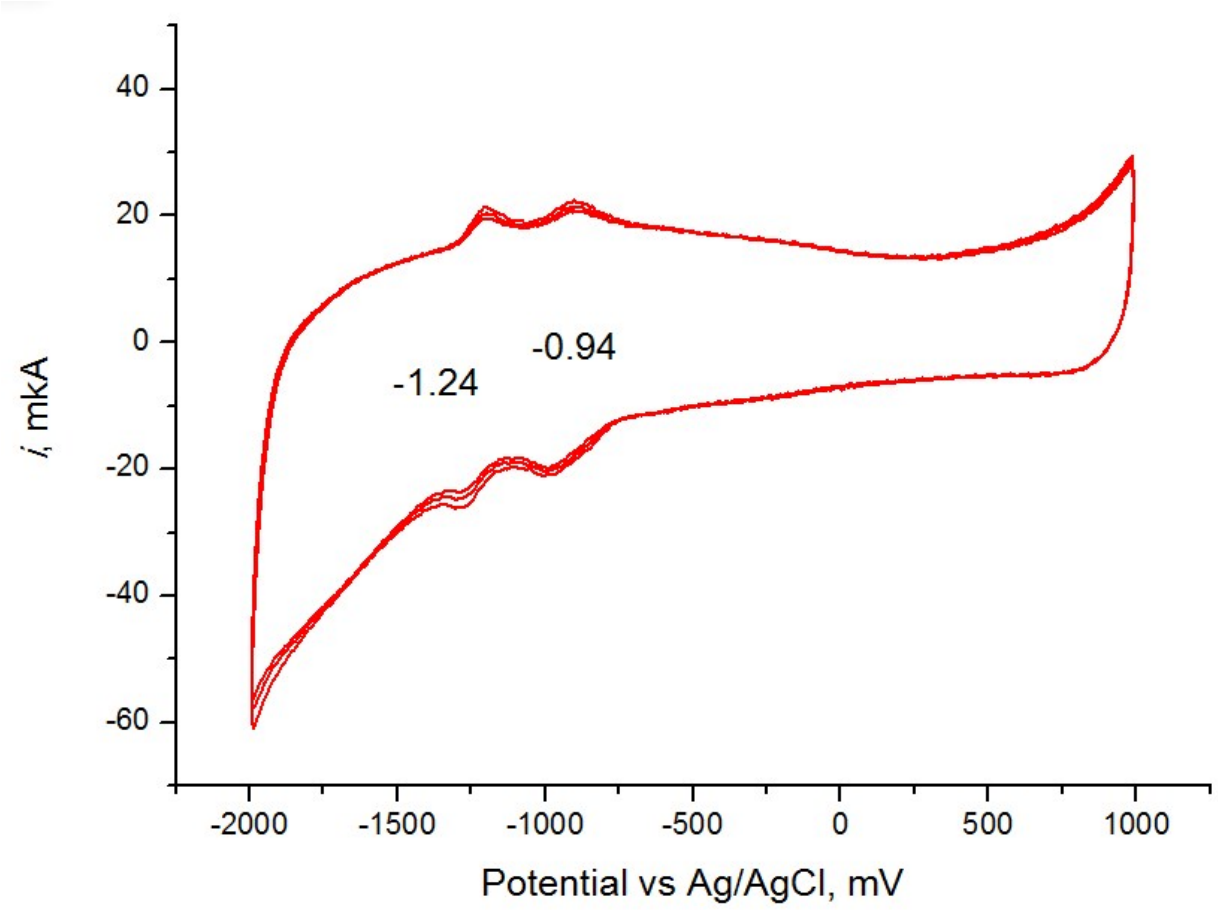


Figure S2. Cyclovoltammogramm of $[TTDPaLi]^-(Li^+)$ in DMSO in the presence of 0.1 M $tbaClO_4$. Scan rate 100 mV/s.