

Supporting Information

Can a molecular switch exist in both superalkali electrider and superalkalide forms?

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Optimized Cartesian coordinates at the MP2/6-311+G(d,p) level.

Parallel Li₃-PHY

C	-2.42916897	-0.44412401	-0.17850895
C	-1.35563762	0.49414222	-0.21265174
C	-1.57485904	1.90299566	-0.17917239
C	-2.17151969	-1.82096088	-0.19015021
C	-0.00037922	0.00083333	-0.30079319
C	0.25005068	-1.41977223	-0.21460187
C	-0.86043908	-2.31403515	-0.18318108
C	1.59937182	-1.88039642	-0.18296193
H	1.78984114	-2.95079479	-0.16581931
C	2.66284203	-0.96876477	-0.19075683
C	2.43421064	0.41317884	-0.17950756
C	1.10458126	0.92783713	-0.21317695
C	0.82889533	2.32674498	-0.18038672
C	-0.49234646	2.79197469	-0.18842945
H	-0.68132248	3.86393865	-0.18539674
H	1.66063764	3.02682451	-0.16106744
H	-3.00545574	-2.52055005	-0.18797181
H	-0.67342568	-3.38504000	-0.16610554
H	3.68572349	-1.34106477	-0.18888638
H	3.26819059	1.11060408	-0.15993409
H	-2.59582715	2.27648003	-0.15900954
H	-3.45132523	-0.07388601	-0.15814020
Li	-1.31198763	-1.10957575	1.90115063
Li	1.61638814	-0.59387421	1.90362927
Li	-0.29461605	1.68197261	1.89455489

T-shaped Li₃-PHY

C	1.25205490	-2.02957823	-0.43214982
C	-0.00030333	-1.34603733	-0.39582445
C	-1.25300045	-2.02897239	-0.43211859
C	2.46089990	-1.31324783	-0.39190519
C	0.00004610	0.09669429	-0.25863650
C	1.25177439	0.81907382	-0.19131772
C	2.47902766	0.07626583	-0.23651858
C	1.21624946	2.22716391	-0.06043030
H	2.15654167	2.77276740	-0.02013482
C	0.00073314	2.91025998	-0.01273918
C	-1.21511575	2.22775471	-0.06046628
C	-1.25132660	0.81968662	-0.19133371
C	-2.47894477	0.07748991	-0.23661851
C	-2.46148698	-1.31203540	-0.39200569
H	-3.40310577	-1.85530435	-0.44716612

H	-3.42175694	0.61779884	-0.20040119
H	3.40225070	-1.85698471	-0.44698751
H	3.42210028	0.61610975	-0.20017235
H	0.00099527	3.99444553	0.07782798
H	-2.15514380	2.77381505	-0.02018818
H	-1.25838315	-3.11110690	-0.53311481
H	1.25690787	-3.11171580	-0.53313482
Li	1.43320577	-0.86824835	1.58189353
Li	-1.43441560	-0.86766236	1.58226902
Li	-0.00014090	-0.99306659	4.19445719

TS between Parallel and T-shaped Li₃-PHY

C	1.25138819	-2.13408833	-0.13896202
C	0.00003700	-1.44906822	-0.18458302
C	-1.25127720	-2.13415832	-0.13895402
C	2.45942538	-1.41934822	-0.19125702
C	-0.00000300	-0.00523400	-0.28799104
C	1.24952520	0.71852811	-0.24529304
C	2.47504238	-0.02109100	-0.22254804
C	1.21755618	2.13668832	-0.24446804
H	2.15841232	2.68291741	-0.23871204
C	-0.00008100	2.82273842	-0.23585504
C	-1.21767918	2.13662232	-0.24446804
C	-1.24957018	0.71846111	-0.24528904
C	-2.47504638	-0.02122600	-0.22253704
C	-2.45935438	-1.41948322	-0.19124102
H	-3.40127552	-1.96508130	-0.18747202
H	-3.41754152	0.52068108	-0.23852404
H	3.40137552	-1.96489630	-0.18750002
H	3.41750752	0.52086708	-0.23854204
H	-0.00010900	3.91127560	-0.24856604
H	-2.15856532	2.68279942	-0.23871104
H	-1.25530718	-3.22048350	-0.09457702
H	1.25547620	-3.22041349	-0.09459202
Li	1.47424922	-0.75555712	1.77927727
Li	-1.47415222	-0.75562212	1.77925927
Li	-0.00001600	1.66994326	2.61742140

Parallel Na₃-PHY

C	-2.44147151	-0.37050968	-0.71786984
C	-1.34306510	0.53642888	-0.68572298
C	-1.51826013	1.95017743	-0.71424190
C	-2.22423402	-1.75340526	-0.73717910
C	-0.00115034	0.00266928	-0.74485209

C	0.20753278	-1.42656872	-0.69180091
C	-0.92917594	-2.28501413	-0.72442665
C	1.54217192	-1.92421035	-0.72575133
H	1.70220922	-3.00031469	-0.75373312
C	2.63118177	-1.04455719	-0.74001396
C	2.44402664	0.34272599	-0.72094534
C	1.13223419	0.89779623	-0.68734865
C	0.89591831	2.30262106	-0.71599951
C	-0.41039122	2.80597597	-0.72941120
H	-0.56758421	3.88239493	-0.79078525
H	1.74785667	2.97935821	-0.74070248
H	-3.07786229	-2.42746202	-0.80151294
H	-0.77492041	-3.36195889	-0.75251553
H	3.64180967	-1.44646726	-0.80542557
H	3.29959187	1.01489136	-0.74523336
H	-2.52814092	2.35511592	-0.73759322
H	-3.45351861	0.02900649	-0.74092533
Na	-1.54874456	-1.23243073	1.90517164
Na	1.84035598	-0.73777849	1.90458627
Na	-0.28264280	1.94936002	1.90677007

T-shaped Na₃-PHY

C	0.02348614	-1.25087626	2.15031641
C	-0.25328258	0.00019581	1.52449460
C	0.02302997	1.25150661	2.14993116
C	-0.35213016	-2.45668119	1.53824987
C	-0.94145933	0.00005795	0.25085897
C	-1.22591101	-1.25159596	-0.41655605
C	-0.96943985	-2.47511086	0.28340956
C	-1.85043416	-1.21606795	-1.68831379
H	-2.08633775	-2.15647711	-2.18287167
C	-2.12587577	-0.00070378	-2.31673204
C	-1.85102101	1.21510152	-1.68888514
C	-1.22633025	1.25136516	-0.41719737
C	-0.97007140	2.47507914	0.28258790
C	-0.35280381	2.45702133	1.53745997
H	-0.18520875	3.39578421	2.06448663
H	-1.27172981	3.41610574	-0.17354813
H	-0.18422637	-3.39538696	2.06527806
H	-1.27103413	-3.41617923	-0.17269615
H	-2.60267642	-0.00096508	-3.29506436
H	-2.08729378	2.15529561	-2.18368405
H	0.49249263	1.25663803	3.13129506
H	0.49314542	-1.25567019	3.13157508

Na	1.56148336	-1.69552147	-0.18300190
Na	1.56149388	1.69582428	-0.18278825
Na	4.25305260	0.00016136	-1.59080210

TS between Parallel and T-shaped Na₃-PHY

C	1.24296642	-2.29634600	0.05204025
C	-0.00608851	-1.64607731	-0.17306497
C	-1.25919299	-2.28787484	0.05405189
C	2.45044891	-1.66128061	-0.27943965
C	-0.00179305	-0.32409512	-0.76348410
C	1.25091231	0.36084441	-0.98953697
C	2.47084144	-0.36256237	-0.79716975
C	1.22025575	1.68327151	-1.49984208
H	2.16256953	2.19033716	-1.69954898
C	0.00603182	2.33563629	-1.72376329
C	-1.21211564	1.69134587	-1.49781542
C	-1.25032610	0.36910756	-0.98751831
C	-2.47505736	-0.34586689	-0.79315545
C	-2.46296188	-1.64463004	-0.27539334
H	-3.40346358	-2.18148969	-0.15469744
H	-3.41472880	0.13787961	-1.05321963
H	3.38742453	-2.20463913	-0.16033849
H	3.41349732	0.11448527	-1.05881667
H	0.00911010	3.34871245	-2.12284038
H	-2.15142117	2.20453937	-1.69598059
H	-1.26738526	-3.30557001	0.43925397
H	1.24490215	-3.31407814	0.43722633
Na	1.72293233	-0.13426732	1.80905153
Na	-1.71857723	-0.12237073	1.81092105
Na	0.01164203	2.78218245	2.29943731

Parallel K₃-PHY

C	-2.42916808	-0.43710778	-1.15782622
C	-1.35962176	0.50034128	-1.07450721
C	-1.57323340	1.90677356	-1.15206122
C	-2.17095127	-1.81077602	-1.21155422
C	-0.00222457	0.00474112	-1.11985821
C	0.24766395	-1.41861858	-1.08344421
C	-0.86361807	-2.30639586	-1.16721122
C	1.59439173	-1.87537202	-1.16914922
H	1.78320869	-2.94541464	-1.23731822
C	2.65511526	-0.96474638	-1.21547022
C	2.43033184	0.41480564	-1.16189721
C	1.10560709	0.93219964	-1.07666521

C	0.82826471	2.32743416	-1.15435321
C	-0.49059160	2.79123075	-1.19947522
H	-0.67768572	3.85904125	-1.31433223
H	1.66077316	3.02615593	-1.21750222
H	-3.00195150	-2.50620890	-1.33087123
H	-0.67751614	-3.37690230	-1.23546022
H	3.67295569	-1.33601399	-1.33625123
H	3.26407219	1.11206134	-1.22471122
H	-2.59379565	2.28080935	-1.21358522
H	-3.45059848	-0.06535693	-1.21907122
K	-1.80798918	-1.52369610	1.76975400
K	2.22266902	-0.81720566	1.76689599
K	-0.40474601	2.31799501	1.77860999

T-shaped K₃-PHY

C	-1.22057809	1.25158409	-2.11633515
C	-1.27920209	0.00053800	-1.43504411
C	-1.21815509	-1.24927109	-2.11829615
C	-1.47655811	2.44917017	-1.43489010
C	-1.59215612	-0.00037300	-0.02337100
C	-1.67805812	1.25100109	0.69598505
C	-1.72357313	2.46417518	-0.05951000
C	-1.85972914	1.21367909	2.10277515
H	-1.94240014	2.15309215	2.64680119
C	-1.90137714	-0.00300800	2.78683820
C	-1.85741013	-1.21842409	2.10070315
C	-1.67644712	-1.25327009	0.69409705
C	-1.72102612	-2.46533218	-0.06348000
C	-1.47364111	-2.44808718	-1.43879510
H	-1.51580111	-3.37976325	-2.00266114
H	-1.92226114	-3.40292924	0.45264603
H	-1.51993411	3.38156324	-1.99748414
H	-1.92532314	3.40080124	0.45813003
H	-2.03364914	-0.00411700	3.86727128
H	-1.93869814	-2.15877116	2.64340219
H	-1.04797907	-1.25268909	-3.19313523
H	-1.05073208	1.25700909	-3.19124423
K	1.18092009	1.97628814	-0.14021201
K	1.18250208	-1.97428814	-0.14036601
K	4.95048535	0.00071100	0.39490503

TS between Parallel and T-shaped K₃-PHY

C	-2.44455002	1.25034080	-1.00218909
C	-1.98157779	0.00003019	-0.49702004

C	-2.44478690	-1.25038237	-1.00211965
C	-2.11908455	2.44875501	-0.35091375
C	-1.15653984	-0.00008433	0.69076537
C	-0.68848821	1.25162784	1.24199043
C	-1.27454808	2.46440343	0.76175731
C	0.21142519	1.21628252	2.33795681
H	0.54999456	2.15658566	2.76980477
C	0.67877769	0.00021423	2.84090755
C	0.21153941	-1.21588611	2.33789083
C	-0.68856248	-1.25150632	1.24217758
C	-1.27471687	-2.46436047	0.76204704
C	-2.11933170	-2.44882661	-0.35067070
H	-2.56566497	-3.38059224	-0.69802359
H	-1.03118604	-3.40114418	1.26097591
H	-2.56530332	3.38048503	-0.69851508
H	-1.03108887	3.40125931	1.26058826
H	1.36957550	0.00020787	3.68256592
H	0.55021596	-2.15613866	2.76976035
H	-3.12780407	-1.25420901	-1.84966400
H	-3.12751461	1.25421005	-1.84978491
K	0.61829772	2.00265461	-1.46112851
K	0.61776734	-2.00243561	-1.46122314
K	4.10716867	-0.00044587	-0.27360550

Table S1. Differences of mainly absorption wavelengths between M06-2X and B3YP results for both parallel and T-shaped Li₃-PHY.

	parallel		T-shaped	
	M06-2X	B3YP	M06-2X	B3YP
			551	596
			529	514
E ₁	667	663	506	508
	665	662		
E ₂	503	507	453	462
E ₃	380	401	385	405

Table S2. NBO charges of the parallel and T-shaped M-PHY (in Å) at the MP2/6-311+G (2d, p) level

	H-shaped			T-shaped		
	M: Li	Na	K	Li	Na	K
M1	0.328	0.330	0.288	0.545	0.580	0.449
M2	0.328	0.332	0.288	0.545	0.580	0.449
M3	0.331	0.329	0.288	-0.172	-0.223	-0.044
				<u>-0.110</u>	<u>-0.149</u>	<u>-0.208</u>
				<i>(-0.089)</i>	<i>(-0.150)</i>	<i>(-0.228)</i>
M ₃ ring	0.987	0.991	0.864	0.918	0.937	0.946
	<u>1.014^a</u>	<u>0.969^a</u>	<u>1.011^a</u>	<u>0.914</u>	<u>0.931</u>	<u>0.951</u>
	<i>(1.005)^b</i>	<i>(0.981)^b</i>	<i>(1.008)^b</i>	<i>(0.917)</i>	<i>(0.936)</i>	<i>(1.008)</i>
C4	-0.109	-0.089	-0.066	-0.125	-0.094	-0.078
C5	-0.005	0.001	0.010	0.009	0.002	0.013
C6	-0.005	0.001	0.010	-0.010	-0.013	-0.013
C7	-0.374	-0.371	-0.362	-0.411	-0.394	-0.376
C8	-0.158	-0.148	-0.139	-0.147	-0.141	-0.132
C9	-0.375	-0.371	-0.362	-0.395	-0.391	-0.383
C10	-0.375	-0.371	-0.362	-0.295	-0.310	-0.315
C11	-0.158	-0.148	-0.139	-0.085	-0.095	-0.097
PHY ring	-0.987	-0.991	-0.864	-0.918	-0.937	-0.854

^a Underlined and italic values are at the B3LYP/6-311+G (2d, p) level. ^b italic values in brackets are at the M06-2X/6-311+G (2d, p) level.

Table S3. Relative energies of different excited states (in kcal/mol) of the $e^- \cdots M_3^+$ -PHY and $M^{\delta-} M_2^{(1-\delta)+}$ -PHY as well as the corresponding transition states at the TD-M06-2X/6-311++G(2d, p) level

	$e^- \cdots M_3^+$ -PHY	ETS	$M^{\delta-} M_2^{(1-\delta)+}$ -PHY
M = Li			
	0.00	10.13	21.40
		10.49	23.82
E ₁	17.27	21.28	30.39
	17.35	23.93	32.37
E ₂	31.23	36.63	26.04
E ₃	49.68	47.86	73.91
M = Na			
E ₁	0.00	7.72	9.98
	0.00	8.90	15.54
E ₂	23.92	28.31	20.50
		34.50	34.04
E ₃	36.24	36.29	35.69
M = K			
E ₁	0.00	9.35	11.53
	0.00	10.56	13.95
	15.81	25.09	
		27.12	
E ₂	21.57	21.66	18.48
E ₃	46.15	46.16	45.84
	46.16	48.53	47.37

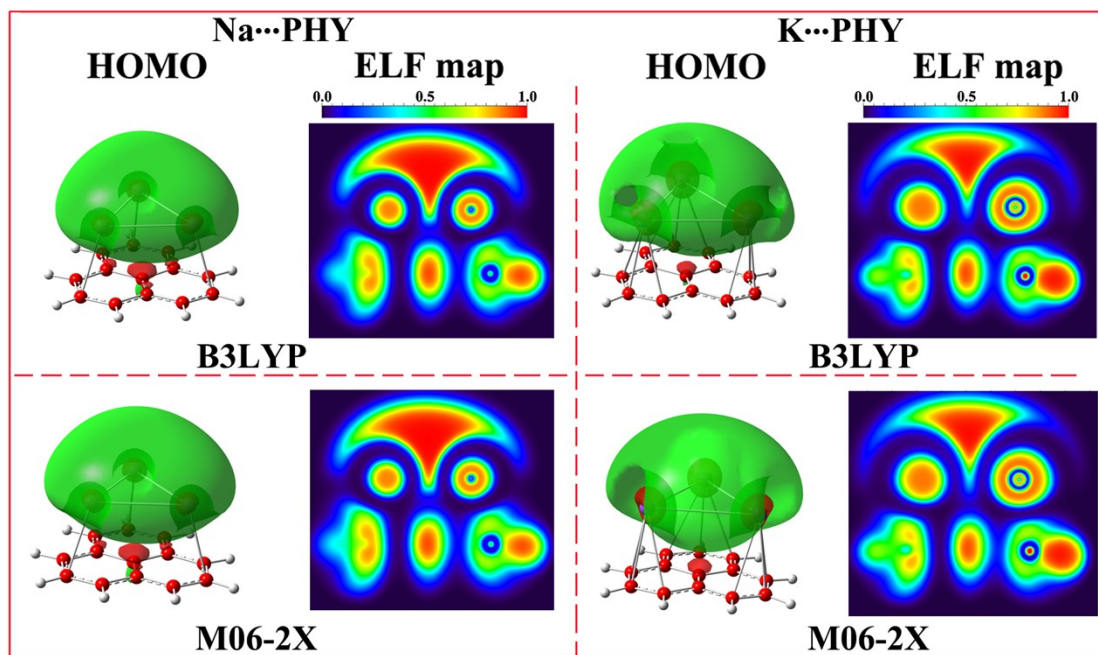


Fig. S1. HOMO (isovalue of 0.02 au) and ELF maps of $e^-\cdots\text{M}_3^+\text{-PHY}$ at different methods with 6-311++G(2d, p) basis set.

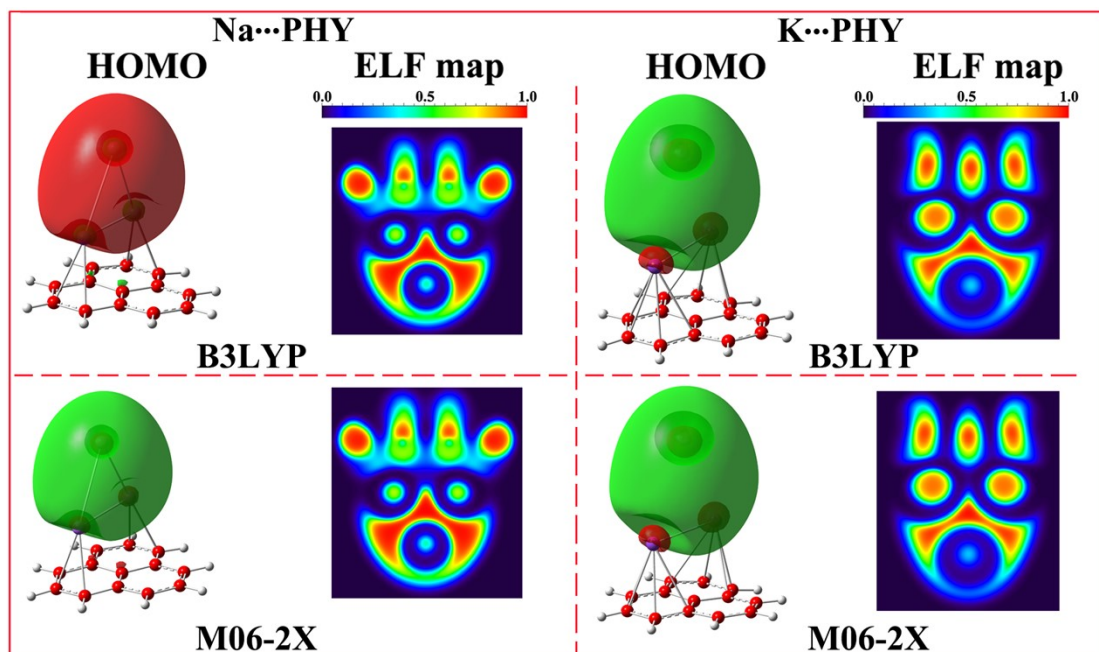


Fig. S2. HOMO (isovalue of 0.02 au) and ELF maps of $\text{Li}^{\delta-}-\text{Li}_2^{(1-\delta)+}-\text{PHY}$ at different methods with 6-311++G(2d, p) basis set.

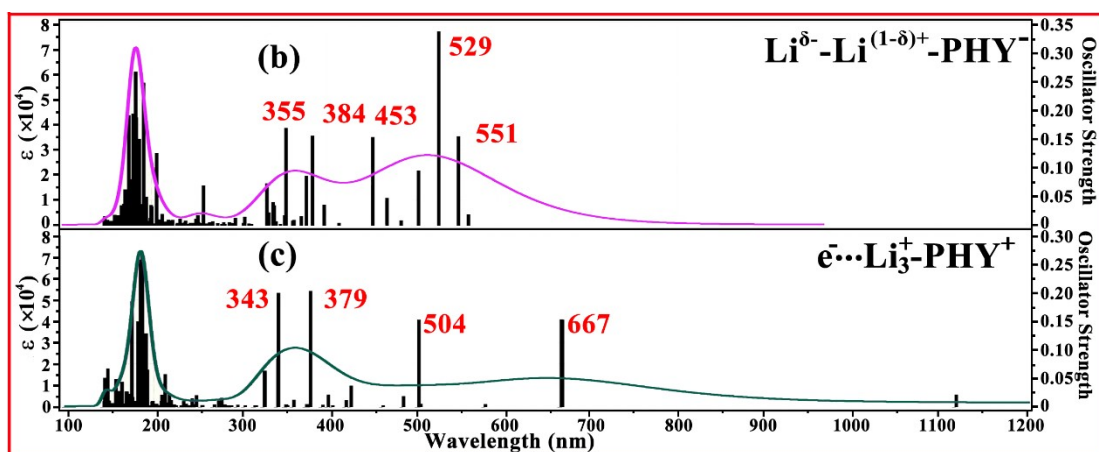


Fig. S3. Electronic absorption spectra and crucial excited states of both parallel and T-shaped Li-PHY (isovalue of 0.02 au). a) for $e^- \cdots \text{Li}_3^+-\text{PHY}^+$ and b) for $\text{Li}^{\delta^-}-\text{Li}_2^{(1-\delta)^+}-\text{PHY}^-$.

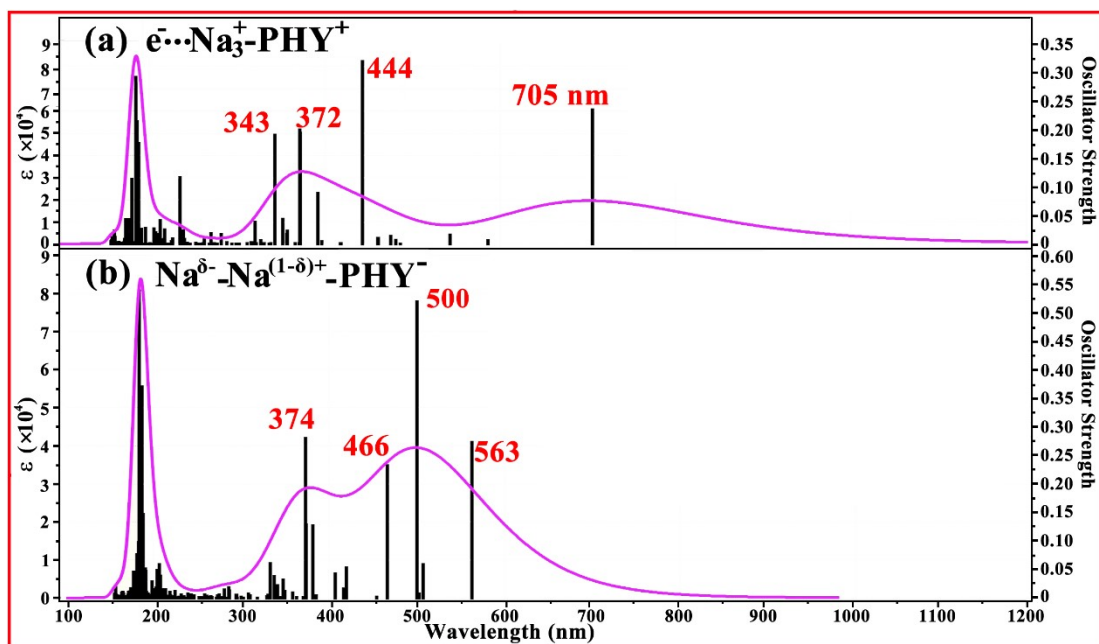


Fig. S4. Electronic absorption spectra and crucial excited states of both parallel and T-shaped Li-PHY (isovalue of 0.02 au). a) for $e^- \cdots Na_3^+ - PHY^+$ and b) for $Na^{\delta-} - Na^{(1-\delta)+} - PHY^-$.

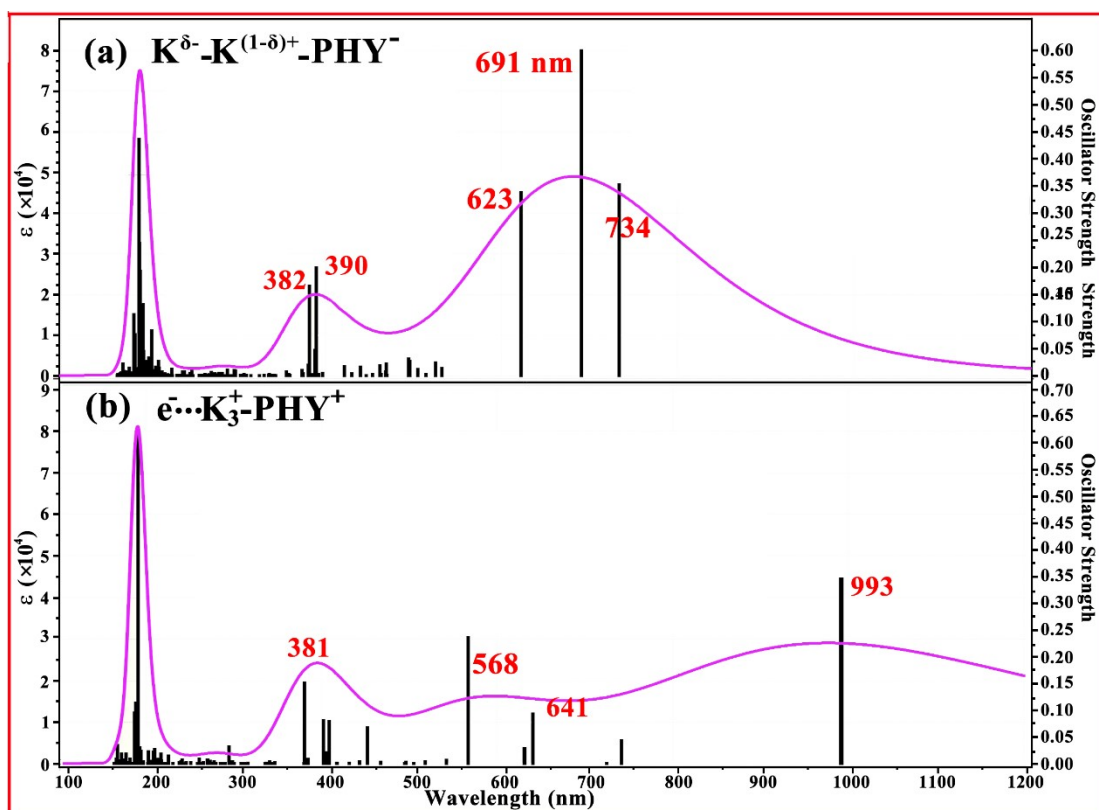


Fig. S5. Electronic absorption spectra and crucial excited states of both parallel and T-shaped Li-PHY (isovalue of 0.02 au).a)for $e^{-}\cdots K_3^{+}-PHY$ and b) for $K^{\delta-}-K_2^{(1-\delta)+}-PHY$.