Supporting Information

Impact of Ether Coordination on the Solid-State Luminescence of a Lithium β-Diketiminate Complex

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Measurements

^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (100 MHz) NMR spectra were recorded on JEOL JNM-AL400 spectrometer. In ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, residual solvent peaks were used as an internal standard. High-resolution mass (HRMS) spectrometry was performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the HRMS spectra were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer for direct analysis in real time (DART). The HRMS(DART) measurements were carried out using solid samples of compounds immediately after a vial containing them was unsealed. All photophysical measurements were carried out under nitrogen atmosphere. All solution and solid samples for those measurements were prepared in a glovebox and sealed with a PTFE tape. UV−vis absorption spectra were recorded on a SHIMADZU UV–3600 spectrophotometer. Fluorescence and phosphorescence emission spectra and phosphorescence decay were measured with a HORIBA JOBIN YVON Fluorolog–3 spectrofluorometer and an Oxford Optistat DN for temperature and control. Absolute photoluminescence quantum yields were measured with a Hamamatsu Photonics Quantaurus-QY Plus C13534-01 and a sample holder for low temperature, A11238-05, was used for the measurements at 77 K. Photoluminescence lifetimes were measured by a Horiba DeltaFlex system with a UV diode laser (DeltaDiode 375 nm). Single-crystal X-ray diffraction data were collected using a Rigaku R-AXIS RAPID-F or a Rigaku Varimax Mo optics diffractometer (graphite-monochromated Mo-Kα radiation) equipped with a MicroMax-007 HF X-ray generator and a Saturn 724+ CCD detector. Equivalent reflections were merged and a symmetry related absorption correction was carried out with the program ABSCOR.[1] The structures were solved with SHELXT 2014[2] and refined on F^2 with SHELXL[3] on Yadokari-XG[4] or Shelxle.[5] The program ORTEP-3[6] was used to generate the X-ray structural diagram. Powder X-ray diffraction patterns were taken by using CuKα radiation with a Rigaku SmartLab diffractometer equipped with a gas-tight sample holder.

Materials

All reactions were performed under argon atmosphere using modified Schlenk line techniques and an MBRAUN glovebox system UNIlab, unless otherwise noted. Analytical thin layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. *n*-BuLi (1.55 M in hexane, Kanto Chemical Co., Inc.), deoxygenated toluene (Wako Pure Chemical Industries, Ltd.; Wako), and deoxygenated hexane (Wako) were purchased from commercial sources and used as received. LH was synthesized according to the literature.[7]

Synthesis of LLi: To a slurry of **LH** (0.50 g, 0.91 mmol) and hexane (9 mL) was added *n*-BuLi (1.55 M in hexane, 0.65 mL, 1.0 mmol) dropwise at –78 °C. The mixture was stirred for 10 min at –78 °C, then allowed to slowly warm to r.t. and stirred for 5 h. The yellow slurry was concentrated under reduced pressure. The yellow powder was washed with hexane to give a pure product as a yellow powder (0.50 g, 99% yield). X-ray quality crystals were obtained from hexane/toluene mixed solution by slow evaporation method at 10 °C. ^{1}H NMR (C_6D_6): δ = 7.59–7.57 (m, 4H), 7.25–6.96 (m, 12H), 5.54 (s, 1H), 3.46 (sept, 4H, $^{3}J_{H–H}$ = 6.8 Hz), 1.18 (d, 12H, $^{3}J_{H–H}$ = 6.8 Hz), 1.12 (d, 12H, $^{3}J_{H–H}$ = 6.8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 166.2, 148.3, 143.1, 140.4, 129.2, 127.5, 127.4, 123.6, 123.5, 98.1, 28.4, 25.2, 23.7. HRMS (DART) $[M+H]^+$; Found: 549.3798. Calcd.: 549.3816.

Synthesis of LLi·OEt$_2$: On the diethyl ether solution of **LLi** was carefully added hexane to form a bilayer solution. X-ray quality crystals were obtained from the solution by slow evaporation method at 10 °C. After drying in vacuo, an analytically pure yellow solid was obtained. All characterization data agreed with the previous report.[7] ^{1}H NMR (C_6D_6) δ = 7.49 (m, 4H), 7.02–6.87 (m, 12H), 5.44 (s, 1H), 3.58 (sept, $^{3}J_{H–H}$ = 6.9 Hz, 4H), 2.66 (q, $^{3}J_{H–H}$ = 7.0 Hz, 4H), 1.22 (d, $^{3}J_{H–H}$ = 6.8 Hz, 12H), 1.10 (d, $^{3}J_{H–H}$ = 6.9 Hz, 12H), 0.43 (t, $^{3}J_{H–H}$ = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (C_6D_6) δ = 166.2, 149.1, 143.6, 140.6, 129.1, 127.4,

127.2, 123.4, 123.2, 97.7, 62.7, 28.3, 25.2, 23.3, 13.1. HRMS (DART) $[M+H]^+$; Found: 622.4472. Calcd.: 622.4474.

Synthesis of LLi·THF: On the tetrahydrofuran solution of **LLi** was carefully added hexane to form a bilayer solution. X-ray quality crystals were obtained from the solution by slow evaporation method at 10 °C. After drying in vacuo, an analytically pure yellow solid was obtained. ^{1}H NMR (400 MHz) δ = 7.54–7.51 (m, 5H), 7.03–6.88 (m, 14H), 5.46 (s, 1H), 3.65 (7, $^3J_{H–H}$ = 6.9 Hz, 4H), 2.61 (m, 4H), 1.21 (d, $^3J_{H–H}$ = 6.9 Hz, 12H), 1.14 (d, $^3J_{H–H}$ = 6.9 Hz, 12H), 0.90–0.86 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz) δ = 166.2, 148.8, 143.5, 140.6, 129.0, 127.4, 127.2, 123.2, 123.1, 97.1, 67.8, 28.2, 25.2, 24.7, 23.1. HRMS (DART) $[M+H]^+$; Found: 620.4323. Calcd.: 620.4318.

Synthesis of LLi·DOX: On the 1,4-dioxane solution of **LLi** was carefully added hexane to form a bilayer solution. X-ray quality crystals were obtained from the solution by slow evaporation method at 10 °C. After drying in vacuo, an analytically pure yellow solid was obtained. ^{1}H NMR (C_6D_6) δ = 7.51 (m, 4H), 7.00–6.83 (m, 14H), 5.44 (s, 1H), 3.57 (sept, $^3J_{H–H}$ = 6.8 Hz, 4H), 2.76 (br, 8H), 1.17 (d, $^3J_{H–H}$ = 6.8 Hz, 12H), 1.09 (d, $^3J_{H–H}$ = 6.9 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz) δ = 166.2, 148.6, 143.2, 140.5, 128.9, 127.5, 127.4, 123.3, 123.1, 66.8, 28.1, 25.5, 23.0. HRMS (DART) $[M+H]^+$; Found: 634.4470. Calcd.: 634.4474.

NMR Spectra

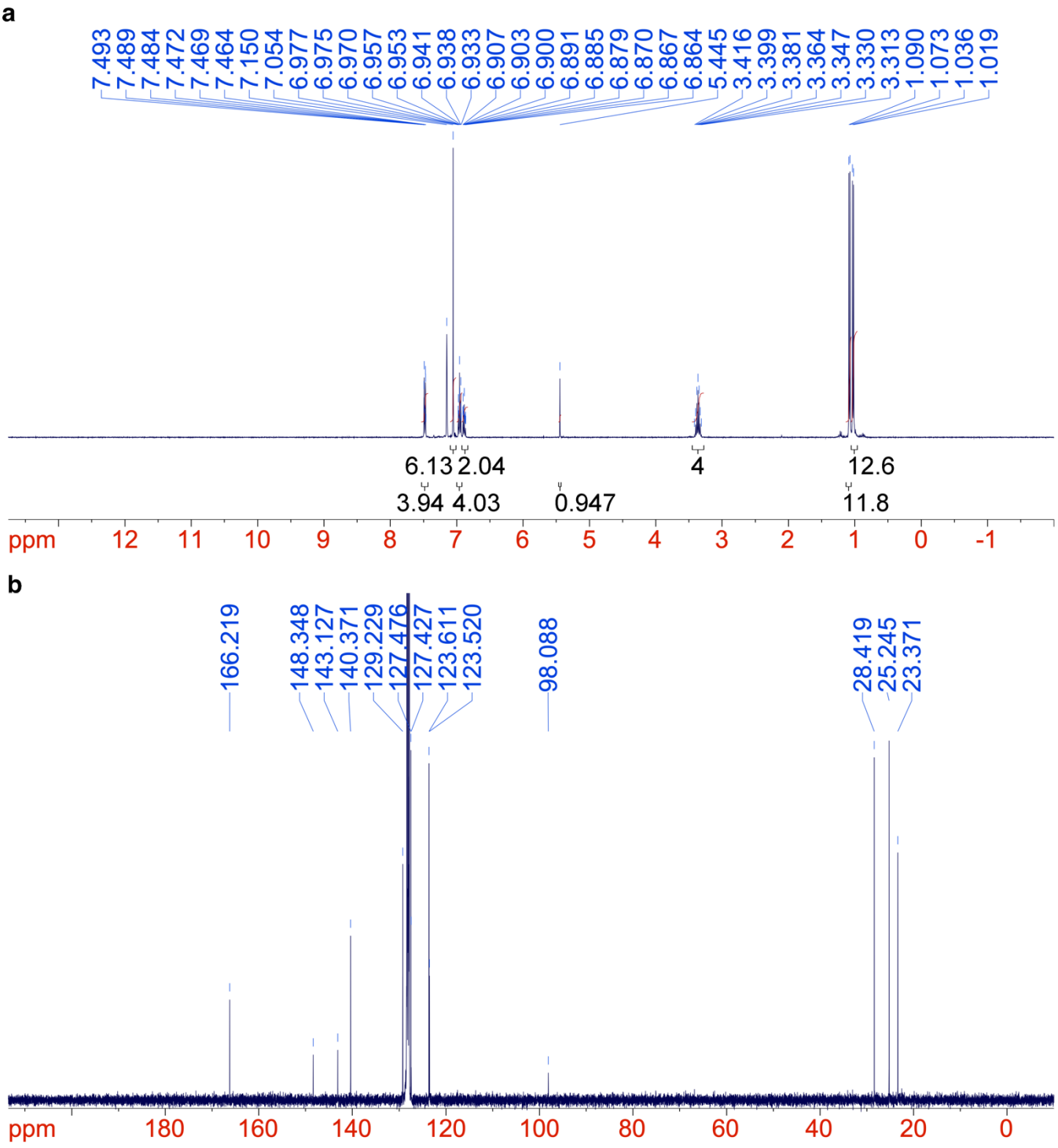

Chart S1. (a) ^{1}H and (b) $^{13}C\{^{1}H\}$ NMR spectra of **LLi** in C_6D_6.

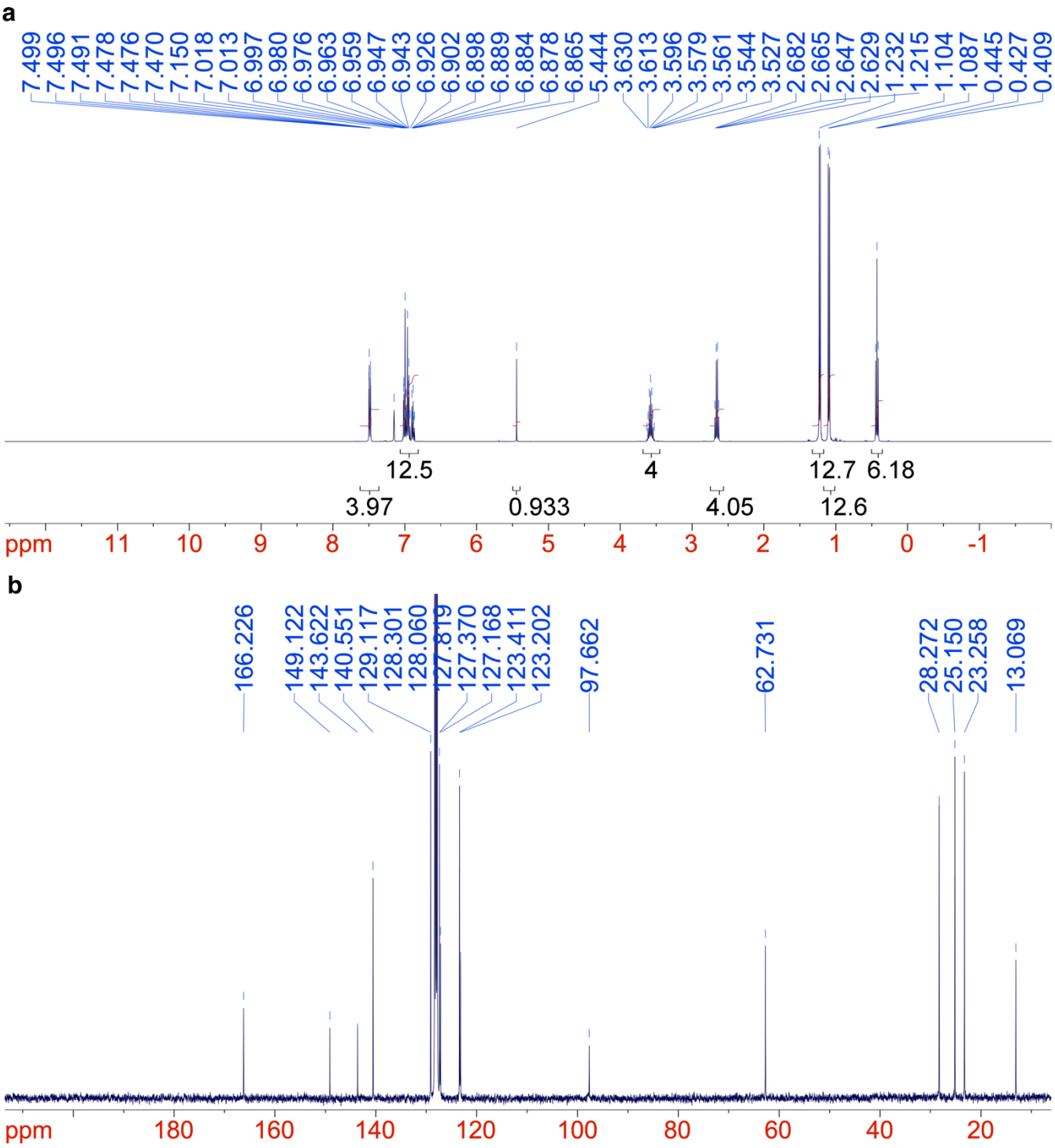

Chart S2. (a) ^{1}H and (b) $^{13}C\{^{1}H\}$ NMR spectra of **LLi·OEt$_2$** in C_6D_6.

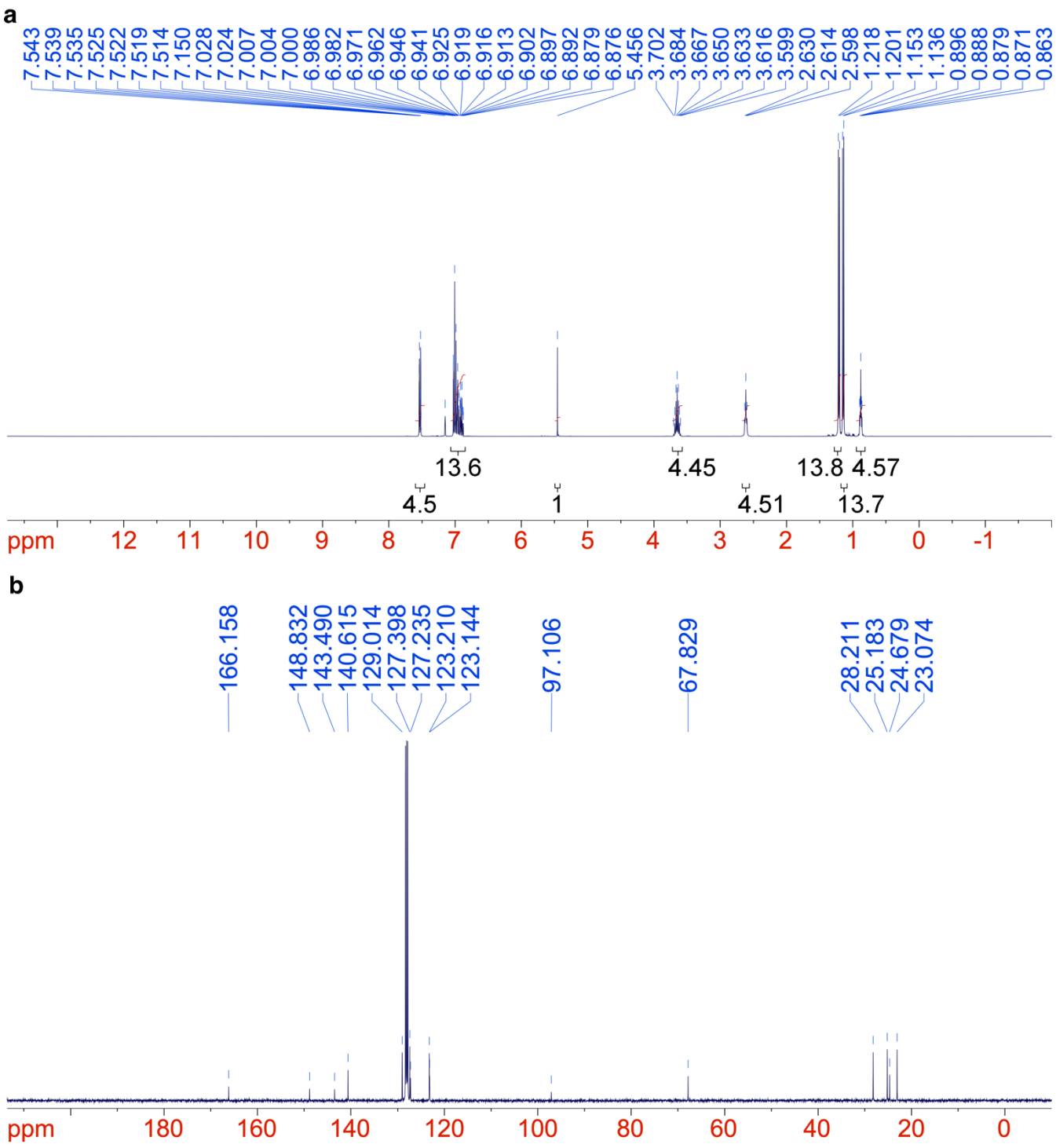

Chart S3. (a) ^{1}H and (b) $^{13}C\{^{1}H\}$ NMR spectra of **LLi·THF** in C_6D_6.

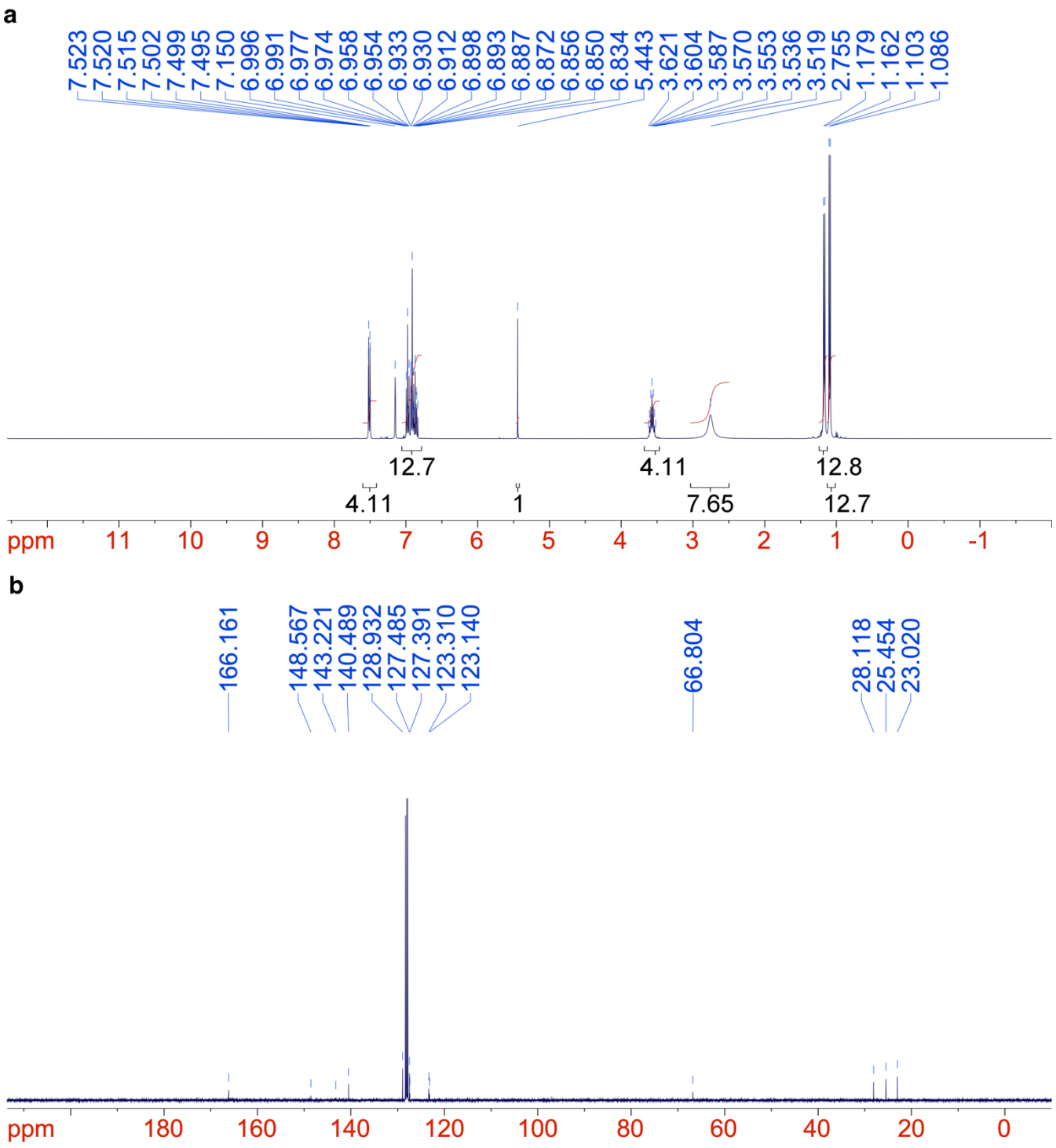

Chart S4. (a) ^{1}H and (b) $^{13}C\{^{1}H\}$ NMR spectra of **LLi·DOX** in C_6D_6.

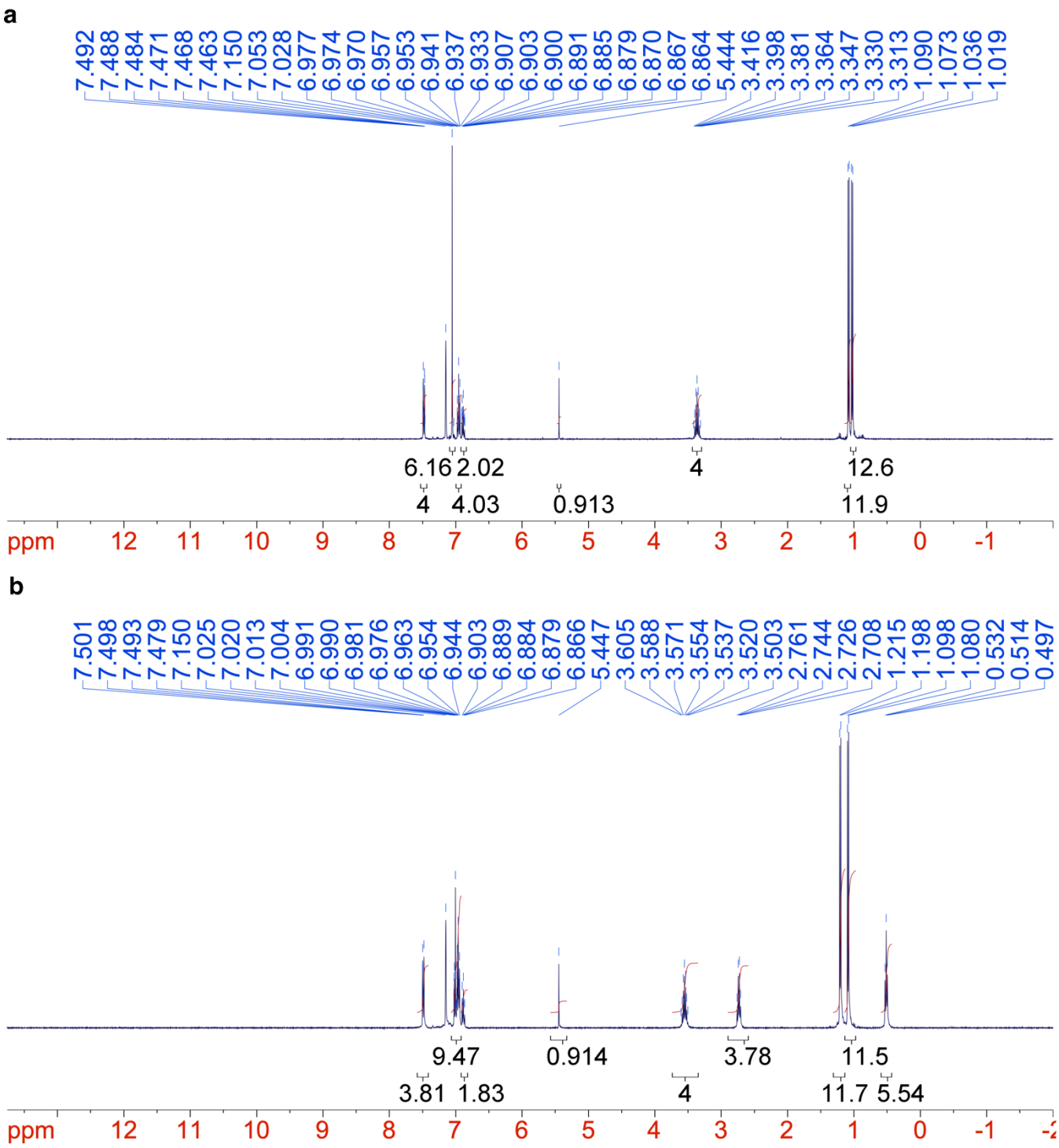

Chart S5. ^{1}H NMR spectra of **LLi** (a) before and (b) after EtO_2 vapor treatment. Both powder samples were dried under vacuum over 3 h before dissolved in C_6D_6.

Single Crystal X-ray Analysis

The low data quality (completeness = 96%) resulted from the instability and poor quality of the **LLi·THF** crystals, which prevented us from improving the quality of the analysis.

Table S1. Selected X-ray data collection and refinement parameters for **LLi**

	LLi	**LLi·OEt$_2$**	**LLi·THF**	**LLi·DOX** · $C_4H_8O_2$
CCDC Deposition Number	2391300	2391301	2440658	2440659
Chemical formula	$C_{39}H_{45}LiN_2$	$C_{43}H_{55}LiN_2O$	$C_{43}H_{53}LiN_2O$	$C_{43}H_{53}LiN_2O_2$ · $C_4H_8O_2$
F_w (g mol^{-1})	548.71	622.83	620.81	724.91
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, P–1	Triclinic, P–1	Tetragonal, P 42/n
a (Å)	13.0332 (10)	8.6715 (3)	8.625(3)	26.271(6)
b (Å)	15.6288 (10)	12.0089 (3)	12.085(5)	26.271(6)
c (Å)	17.0389 (12)	18.3158 (6)	18.367(7)	12.344(3)
α, β, γ (°)	90 112.015 (8) 90	87.453 (6) 84.286 (6) 81.445 (6)	84.102(18) 82.022(13) 81.110(15)	90 90 90
V (Å^3)	3217.6 (4)	1875.88 (11)	1866.6(12)	8519(4)
Z	4	2	2	8
μ (mm^{-1})	0.06	0.06	0.06	0.070
Crystal size (mm)	0.50 × 0.15 × 0.15	0.39 × 0.36 × 0.23	0.25 × 0.18 × 0.16	0.400 × 0.220 × 0.160
T_{min}, T_{max}	0.4572, 1.000	0.7550, 1.1337	0.702, 1.000	0.972, 0.989
Reflections collected	29904	41334	14433	67767
Independent reflections	7345	8575	4489	9750
Observed [$I > 2\sigma(I)$] reflections	4886	6778	8063	8610
No. of parameters	396	434	432	480
R_{int}	0.075	0.109	0.0383	0.0523
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.114, 1.01	0.068, 0.205, 1.11	0.0539, 0.1222, 0.932	0.0847, 0.1940, 1.113

DFT Calculations

All calculations were carried out using Gaussian 16 Revision C.03 at the (TD-)CAM-B3LYP/6-31G(d,p) level of theory for geometry optimizations and time-dependent single-point calculations. All optimized structures were confirmed to be at local minimum using frequency calculations. The crystal structures were employed as the initial geometries of the optimizations at S_0 states. The optimized geometries, calculated low frequencies, and the results of TD-DFT are listed in Tables S2–S5 and S8.

Single-point TD-DFT calculations were also performed for the monomeric (Table S6) and dimeric (Table S7) structures in the crystal of **LLi** (Table S9 and Figure S3). As a result of the interaction between the lithium atom and the phenyl group within the dimer, the vacant lithium orbital of one of the complexes was removed from the unoccupied frontier orbitals, while the other remained. Since the vacant lithium orbital was not involved in the low-lying excited states, the calculated S_1 and S_2 energies of the dimer were not significantly differred from the S1 of the monomer. Although the out-of-phase (S_1) and in-phase (S_2) exciton interactions were observed between the transition dipole moments of the two complexes, the splitting energy was quite small (0.062 eV). Therefore, the Li–π interactions in the crystal of **LLi** should not result in significant effects on the excitation and emission energy.

Unfortunately, we were not able to obtain optimized structures of all complexes in the S_1 states using the same calculation conditions.

Table S2. Optimized geometry of **LLi** at S_0 state

	Coordinates (Angstroms)		
Atomic Number	x	y	z
7	1.485234	-0.338589	0.112661
7	-1.485228	-0.33859	-0.112682
6	-1.276028	0.96948	-0.0913
6	2.41474	1.946553	0.184243
6	-2.776909	-0.928902	-0.105993
6	0.000001	1.566251	0.000062
1	-0.000005	2.646789	0.000108
6	2.776904	-0.92892	0.10592
6	-3.575326	-0.942873	1.055381
6	-2.414737	1.946555	-0.184087
6	3.353847	1.866343	1.214339
1	3.275655	1.07567	1.951022
6	1.276035	0.969481	0.091377
6	2.528255	2.983475	-0.744474
1	1.802995	3.055837	-1.548147
6	3.575337	-0.942788	-1.055445
6	-3.353808	1.866464	-1.214225
1	-3.275581	1.075884	-1.951003
6	-2.528291	2.98336	0.744755
1	-1.803056	3.055633	1.548459
6	3.188402	-1.639295	1.255792
6	-3.561271	3.908616	0.655312
1	-3.638203	4.702227	1.391621
6	-4.379662	2.797303	-1.311243
1	-5.096194	2.723746	-2.122973
6	-3.188443	-1.639135	-1.255938
6	4.490309	3.81857	0.37466
1	5.295824	4.542018	0.448571
6	-3.125943	-0.291944	2.354751
1	-2.261367	0.336981	2.138823
6	4.783426	-1.639411	-1.027111
1	5.40404	-1.656002	-1.917578
6	4.401938	-2.320165	1.235319
1	4.728091	-2.860128	2.118138
6	3.561229	3.90873	-0.654949
1	3.63813	4.702432	-1.391163
6	4.379694	2.797179	1.31144
1	5.096253	2.723527	2.123137
6	-4.490317	3.818575	-0.374338
1	-5.295837	4.542024	-0.448184
6	5.204342	-2.319561	0.103607
1	6.149128	-2.853394	0.10194
6	2.29566	-1.686052	2.486798
1	1.640807	-0.811285	2.446169
6	3.126003	-0.291702	-2.354753
1	2.261371	0.337135	-2.138796
6	-4.783435	-1.639459	1.02699
1	-5.404038	-1.656126	1.917463
6	-4.401997	-2.319976	-1.23552
1	-4.728178	-2.859829	-2.118395
6	-2.66799	-1.360567	3.356832
1	-3.489773	-2.035367	3.616071
1	-2.307856	-0.898109	4.281201
1	-1.857592	-1.969766	2.944741
6	-4.202073	0.606632	2.972405
1	-4.534955	1.368739	2.264441
1	-3.807936	1.114017	3.858255
1	-5.077578	0.032851	3.290733
6	-5.204383	-2.319475	-0.103796
1	-6.149184	-2.853282	-0.102176
6	1.400354	-2.93342	2.460978
1	0.813906	-3.004764	1.536114
1	0.698195	-2.93799	3.300111
1	2.003299	-3.845122	2.513231
6	-2.295731	-1.685757	-2.486972
1	-1.640905	-0.810973	-2.446281
6	2.668194	-1.360204	-3.357029
1	3.49004	-2.034907	-3.616317
1	2.308095	-0.897626	-4.281353
1	1.857808	-1.969522	-2.945093
6	-1.400386	-2.933099	-2.461297
1	-0.813895	-3.004505	-1.536467
1	-0.69826	-2.937569	-3.30046
1	-2.003305	-3.844814	-2.513611
6	4.202126	0.607031	-2.972192
1	4.534911	1.36905	-2.264089
1	3.808026	1.114527	-3.857995
1	5.077687	0.033347	-3.290541
6	3.064929	-1.624375	3.809418
1	2.368106	-1.537951	4.648042
1	3.739151	-0.764301	3.839466
1	3.664468	-2.523474	3.97906
6	-3.065039	-1.623983	-3.809565
1	-3.66454	-2.523093	-3.97928
1	-2.368243	-1.537442	-4.648199
1	-3.739303	-0.763938	-3.839508
3	0.000003	-1.452704	-0.000021

Table S3. Low frequencies for the optimized geometry of **LLi** at S_0 state

Low Frequencies / cm^{-1}:

-2.1713	-1.0438	-1.0314	-0.0006	0.0001	0.0005
14.0265	19.2006	21.8823			

Table S4. Optimized geometry of **LLi·OEt$_2$** at S_0 state

	Coordinates (Angstroms)		
Atomic Number	x	y	z
3	-0.022023	-1.032345	0.031331
7	-1.488795	0.181395	0.267666
7	1.486641	0.127511	0.274097
6	-1.253646	1.478409	0.368467
6	0.031598	2.048108	0.487033
1	0.045964	3.113504	0.669775
6	1.296256	1.427039	0.44111
6	-2.373832	2.483567	0.352413
6	-3.408752	2.452516	1.287639
1	-3.417509	1.686089	2.052262
6	-4.416078	3.408451	1.261973
1	-5.208398	3.373274	2.002927
6	-4.411291	4.406422	0.294283
1	-5.202187	5.149227	0.272041
6	-3.383895	4.449821	-0.640514
1	-3.367747	5.22747	-1.397563
6	-2.369742	3.500111	-0.605058
1	-1.562546	3.538019	-1.32917
6	2.454071	2.374481	0.601839
6	3.421942	2.171418	1.586313
1	3.345632	1.31082	2.239009
6	4.466995	3.070973	1.750694
1	5.205645	2.900192	2.527387
6	4.567616	4.185913	0.926342
1	5.387717	4.885562	1.051625
6	3.607996	4.401023	-0.055648
1	3.675007	5.270085	-0.702438
6	2.55633	3.50576	-0.210391
1	1.804926	3.677377	-0.974012
6	-2.788908	-0.350438	0.066012
6	-3.358678	-0.388271	-1.223733
6	-4.560705	-1.070651	-1.408166
1	-5.000721	-1.108405	-2.40007
6	-5.201357	-1.707339	-0.357353
1	-6.135647	-2.234206	-0.522849
6	-4.639937	-1.658155	0.910446
1	-5.146479	-2.14931	1.735166
6	-3.44166	-0.98767	1.145056
6	2.770294	-0.440228	0.065736
6	3.427289	-0.308803	-1.178287
6	4.604387	-1.024223	-1.396124
1	5.108703	-0.932355	-2.353107
6	5.141413	-1.854473	-0.424921
1	6.058262	-2.402444	-0.617123
6	4.495999	-1.972266	0.796496
1	4.91715	-2.617655	1.561375
6	3.317812	-1.27879	1.06261
6	-2.669626	0.243073	-2.424109
1	-1.845952	0.85516	-2.053357
6	-2.060238	-0.834801	-3.330669
1	-1.349988	-1.45725	-2.778872
1	-1.529604	-0.380357	-4.17335
1	-2.836264	-1.491362	-3.737729
6	-3.600854	1.162862	-3.22045
1	-4.425499	0.609316	-3.679631
1	-3.04881	1.65225	-4.02887
1	-4.028215	1.939157	-2.58178
6	-2.840224	-0.96575	2.543437
1	-2.124047	-0.140693	2.575426
6	-2.055258	-2.251519	2.83057
1	-2.710369	-3.127652	2.77984
1	-1.608004	-2.222001	3.829169
1	-1.247114	-2.394786	2.108899
6	-3.880464	-0.727935	3.643324
1	-4.49182	0.155346	3.439506
1	-3.383946	-0.582351	4.607038
1	-4.558513	-1.579201	3.755192
6	2.860076	0.539059	-2.308442
1	2.063342	1.160577	-1.899232
6	2.22568	-0.345092	-3.389656
1	2.963213	-1.025938	-3.827021
1	1.811379	0.265696	-4.198024
1	1.4129	-0.948938	-2.976818
6	3.903257	1.480174	-2.919834
1	4.361197	2.111715	-2.155448
1	3.433644	2.131812	-3.663156
1	4.700563	0.930796	-3.429378
6	2.633079	-1.451554	2.410853
1	1.867566	-0.674717	2.486981
6	1.924871	-2.809734	2.502887
1	1.197473	-2.938548	1.697081
1	1.395971	-2.910963	3.455886
1	2.647251	-3.629654	2.431134
6	3.594825	-1.281648	3.592852
1	4.33629	-2.085216	3.630972
1	3.043008	-1.303509	4.537258
1	4.139587	-0.33533	3.541289
8	-0.076314	-2.851975	-0.659778
6	-1.2833	-3.629852	-0.675145
1	-1.554798	-3.852773	-1.712174
1	-2.049947	-2.965699	-0.274048
6	-1.197102	-4.901801	0.147881
1	-0.502414	-5.63018	-0.277656
1	-2.184378	-5.369903	0.183167
1	-0.887472	-4.684898	1.173028
6	1.103119	-3.497291	-1.165908
1	1.378888	-4.320331	-0.497773
1	1.887027	-2.741885	-1.094928
6	0.967487	-3.986998	-2.595851
1	0.269701	-4.822641	-2.689659
1	1.944091	-4.332371	-2.944921
1	0.636881	-3.182808	-3.257428

Table S5. Low frequencies for the optimized geometry of **LLi·OEt$_2$** at S_0 state

Low Frequencies / cm^{-1}:

-2.6168	-2.185	-0.0009	-0.0006	0.001	0.7694
18.9317	19.7445	28.0719			

Table S6. Optimized geometry of **LLi·THF** at S_0 state

	Coordinates (Angstroms)		
Atomic Number	x	y	z
8	0.081254	-2.830549	-0.484879
7	1.480729	0.199423	0.323716
7	-1.483332	0.149578	0.29619
6	2.768049	-0.355952	0.111996
6	-2.462596	2.402766	0.532433
6	2.375053	2.497544	0.32483
6	-1.300538	1.454042	0.423225
6	1.250184	1.499677	0.3762
6	-0.034939	2.075149	0.472435
1	-0.048543	3.144945	0.627289
6	3.430488	-0.979968	1.19232
6	-2.746882	-0.449941	0.065198
6	3.310497	-0.436366	-1.187959
6	-3.381179	-0.355442	-1.1936
6	4.499623	-1.14019	-1.378608
1	4.919522	-1.208822	-2.37764
6	-2.5282	3.535947	-0.281384
1	-1.74471	3.707444	-1.011903
6	3.420347	2.477291	1.248863
1	3.430899	1.726558	2.028998
6	2.601194	0.165798	-2.391729
1	1.790592	0.795848	-2.022538
6	-3.290763	-1.292968	1.061511
6	2.369	3.492845	-0.654673
1	1.554748	3.521189	-1.371257
6	-2.826866	0.500918	-2.323853
1	-2.022144	1.11655	-1.921075
6	-3.475439	2.197311	1.470306
1	-3.430308	1.334124	2.122395
6	5.152233	-1.759196	-0.32417
1	6.076332	-2.302421	-0.49399
6	4.435149	3.423822	1.19182
1	5.235436	3.397821	1.924551
6	2.852527	-0.922496	2.599268
1	2.136096	-0.097294	2.621696
6	-4.53145	-1.10883	-1.42547
1	-5.017743	-1.04377	-2.394135
6	4.614505	-1.672419	0.951807
1	5.128299	-2.152878	1.778435
6	-2.633872	-1.424826	2.428556
1	-1.876925	-0.639273	2.500527
6	-3.584966	4.431602	-0.17205
1	-3.622518	5.301839	-0.819628
6	4.427744	4.400826	0.202896
1	5.224513	5.136183	0.15596
6	-4.44149	-2.02594	0.780469
1	-4.859732	-2.672757	1.545984
6	-5.06416	-1.943461	-0.455974
1	-5.96	-2.521047	-0.660174
6	-4.526781	3.096772	1.588928
1	-5.300668	2.923772	2.329983
6	-4.588649	4.214479	0.76451
1	-5.41333	4.914248	0.854045
6	1.962767	-0.934499	-3.250648
1	2.72448	-1.609233	-3.655407
1	1.415135	-0.502619	-4.094171
1	1.260461	-1.533983	-2.663313
6	-2.213879	-0.368607	-3.429153
1	-1.388838	-0.974422	-3.044085
1	-1.819956	0.254404	-4.238434
1	-2.958344	-1.045579	-3.860503
6	3.911135	-0.655355	3.674691
1	4.595266	-1.500887	3.792987
1	3.431768	-0.49004	4.64393
1	4.51449	0.22569	3.439711
6	3.390676	4.432758	-0.721652
1	3.373085	5.193775	-1.495399
6	2.074622	-2.201826	2.932205
1	1.258803	-2.36916	2.224266
1	1.639467	-2.14517	3.935005
1	2.73244	-3.076831	2.899459
6	3.521862	1.052472	-3.236199
1	3.967104	1.845635	-2.631282
1	2.956804	1.519909	-4.048601
1	4.333544	0.478715	-3.693693
6	-3.882081	1.448672	-2.905165
1	-4.689003	0.901556	-3.402058
1	-3.428939	2.108012	-3.652009
1	-4.325322	2.072274	-2.125986
6	1.258881	-3.670031	-0.517339
1	1.439177	-4.05183	0.492922
1	2.109533	-3.057353	-0.819862
6	-1.91827	-2.774627	2.574997
1	-2.633788	-3.601654	2.515277
1	-1.407762	-2.8435	3.540747
1	-1.173606	-2.923176	1.787879
6	-3.623997	-1.229238	3.582977
1	-4.167084	-0.284451	3.497043
1	-3.095591	-1.229273	4.540963
1	-4.366334	-2.032095	3.620193
6	-1.034632	-3.505503	-1.111761
1	-1.225349	-3.032502	-2.079924
1	-1.915016	-3.375083	-0.480485
6	0.920019	-4.792999	-1.48605
1	1.48713	-5.702394	-1.278303
1	1.131505	-4.485578	-2.514845
6	-0.586424	-4.950485	-1.27448
1	-1.093434	-5.448132	-2.103332
1	-0.786549	-5.519013	-0.360974
3	0.020697	-1.014679	0.150435

Table S7. Low frequencies for the optimized geometry of **LLi·THF** at S_0 state

Low Frequencies / cm^{-1}:

-1.7149	-0.0006	0.0005	0.0006	0.717	2.1073
15.7073	21.5244	26.062			

Table S8. Optimized geometry of **LLi·DOX** at S_0 state

	Coordinates (Angstroms)		
Atomic Number	x	y	z
3	-0.000003	-0.896258	0.270116
7	-1.485224	0.303331	0.331892
7	1.485226	0.303322	0.331889
6	-1.275837	1.608532	0.279566
6	0.000007	2.21013	0.280175
1	0.00001	3.290728	0.311625
6	1.275847	1.608524	0.279568
6	-2.419784	2.582785	0.208345
6	-3.432262	2.589563	1.168469
1	-3.401026	1.876671	1.982858
6	-4.465889	3.514732	1.10252
1	-5.240068	3.510298	1.863183
6	-4.510011	4.443448	0.068971
1	-5.321256	5.16228	0.015136
6	-3.50561	4.448672	-0.891537
1	-3.528448	5.171965	-1.70048
6	-2.465331	3.530131	-0.816573
1	-1.677822	3.538043	-1.562891
6	2.4198	2.582771	0.208358
6	3.432271	2.589541	1.168489
1	3.401027	1.876645	1.982873
6	4.465899	3.514709	1.102554
1	5.240073	3.510269	1.863222
6	4.51003	4.443432	0.069011
1	5.321276	5.162264	0.015188
6	3.505636	4.448664	-0.891504
1	3.528481	5.171962	-1.700443
6	2.465355	3.530123	-0.816554
1	1.677852	3.538042	-1.562877
6	-2.769234	-0.28343	0.192242
6	-3.365983	-0.419925	-1.080104
6	-4.541291	-1.161907	-1.195854
1	-5.000111	-1.275949	-2.173246
6	-5.132574	-1.762311	-0.095422
1	-6.04652	-2.336473	-0.208619
6	-4.546758	-1.614948	1.153163
1	-5.012466	-2.078394	2.017365
6	-3.373251	-0.883412	1.320107
6	-2.734633	0.166723	-2.334275
1	-1.933468	0.839254	-2.0256
6	-2.092578	-0.93471	-3.187723
1	-1.327446	-1.474511	-2.622413
1	-1.615552	-0.511041	-4.077011
1	-2.840651	-1.660974	-3.522695
6	-3.727372	0.988685	-3.162768
1	-4.530468	0.367782	-3.571002
1	-3.21645	1.4561	-4.010207
1	-4.182176	1.779355	-2.561956
6	-2.749232	-0.760108	2.70285
1	-2.010954	0.04454	2.65428
6	-2.001755	-2.042323	3.090379
1	-1.525702	-1.937114	4.070212
1	-1.221388	-2.286594	2.364887
1	-2.688594	-2.893788	3.13943
6	-3.768978	-0.398948	3.788934
1	-4.478703	-1.212144	3.967461
1	-4.347864	0.489477	3.522991
1	-3.258949	-0.20042	4.736077
6	2.769235	-0.283443	0.192234
6	3.365982	-0.419928	-1.080114
6	4.541291	-1.161908	-1.19587
1	5.000111	-1.275943	-2.173263
6	5.132574	-1.762321	-0.095443
1	6.046521	-2.336481	-0.208644
6	4.546758	-1.614968	1.153144
1	5.012467	-2.078421	2.017342
6	3.373251	-0.883434	1.320094
6	2.73463	0.166728	-2.334281
1	1.933461	0.839253	-2.0256
6	2.092583	-0.9347	-3.187739
1	2.84066	-1.660957	-3.522716
1	1.615556	-0.511026	-4.077024
1	1.327453	-1.474511	-2.622436
6	3.727367	0.988702	-3.162766
1	4.182168	1.779368	-2.561948
1	3.216443	1.456121	-4.010201
1	4.530465	0.367805	-3.571004
6	2.749232	-0.760141	2.702837
1	2.01096	0.044513	2.654275
6	2.001744	-2.042354	3.090351
1	2.688577	-2.893825	3.139396
1	1.221378	-2.286613	2.364853
1	1.525687	-1.937151	4.070183
6	3.768978	-0.399	3.788927
1	3.258949	-0.200478	4.736071
1	4.34787	0.489424	3.522994
1	4.478696	-1.212203	3.967447
8	-0.000008	-2.784701	-0.190895
8	-0.000021	-5.305391	-1.443826
6	-1.18639	-3.594193	-0.226168
1	-2.037461	-2.911858	-0.248885
1	-1.228266	-4.196885	0.689825
6	-1.162136	-4.498769	-1.441719
1	-2.023415	-5.170962	-1.426649
1	-1.207499	-3.891812	-2.357964
6	1.162089	-4.498762	-1.441758
1	1.207417	-3.891804	-2.358005
1	2.023373	-5.170949	-1.426716
6	1.186378	-3.594186	-0.226207
1	1.228288	-4.196878	0.689784
1	2.037443	-2.911845	-0.248952

Table S9. Low frequencies for the optimized geometry of **LLi·DOX** at S_0 state

Low Frequencies / cm^{-1}:

-1.037	-0.0005	0.0002	0.0006	2.3777	3.0722
10.1556	22.7695	23.3173			

Table S10. Geometry of monomeric **LLi** obtained from its crystal structure

	Coordinates (Angstroms)		
Atomic Number	x	y	z
7	1.427174	-0.176586	0.425708
7	-1.424183	-0.339127	0.022637
6	-1.277369	0.950833	-0.258579
6	2.432964	1.864334	-0.504351
6	-2.680787	-1.008662	0.005098
6	-0.018948	1.582138	-0.345639
1	-0.029328	2.498612	-0.59393
6	2.721824	-0.767509	0.561882
6	-3.657813	-0.812978	0.997763
6	-2.460187	1.867894	-0.491094
6	3.472869	2.142439	0.382682
1	3.435474	1.804748	1.268546
6	1.255859	1.020835	-0.111104
6	2.514574	2.371484	-1.794796
1	1.815455	2.194325	-2.415146
6	3.422694	-1.256528	-0.550242
6	-3.530862	1.544743	-1.32627
1	-3.518282	0.727409	-1.810218
6	-2.500118	3.082358	0.191869
1	-1.765675	3.337657	0.739033
6	3.213956	-0.963339	1.86501
6	-3.601226	3.92978	0.084649
1	-3.623182	4.743444	0.574308
6	-4.615519	2.406079	-1.459351
1	-5.32589	2.183386	-2.050223
6	-2.857054	-2.032449	-0.955098
6	4.625832	3.402536	-1.299255
1	5.371874	3.926776	-1.569355
6	-3.441776	0.142768	2.156387
1	-2.604947	0.658321	1.975131
6	4.619026	-1.941533	-0.327776
1	5.115135	-2.261228	-1.072026
6	4.396896	-1.673923	2.029078
1	4.729793	-1.826358	2.905319
6	3.608032	3.136194	-2.190413
1	3.653886	3.475565	-3.077069
6	4.557921	2.907429	-0.015
1	5.25764	3.090892	0.599882
6	-4.66665	3.58928	-0.735022
1	-5.423505	4.158864	-0.798844
6	5.09787	-2.162778	0.943674
1	5.904059	-2.649193	1.073147
6	2.478684	-0.379848	3.065086
1	1.96333	0.417196	2.747238
6	2.904034	-1.098115	-1.96984
1	2.138844	-0.4557	-1.946764
6	-4.825661	-1.568722	0.954957
1	-5.497599	-1.424235	1.610104
6	-4.040811	-2.757228	-0.953159
1	-4.175259	-3.430488	-1.608487
6	-3.232022	-0.647899	3.452448
1	-4.026023	-1.191714	3.634721
1	-3.086336	-0.025658	4.194124
1	-2.45189	-1.232236	3.356054
6	-4.591152	1.144913	2.292304
1	-4.716721	1.613781	1.441564
1	-4.37786	1.794032	2.994852
1	-5.414475	0.667223	2.52638
6	-5.025526	-2.518753	-0.018811
1	-5.838639	-3.008799	-0.047871
6	1.483715	-1.365136	3.671141
1	0.864398	-1.67361	2.976922
1	0.97836	-0.923	4.384361
1	1.967694	-2.132655	4.042262
6	-1.779773	-2.340358	-1.983656
1	-0.919042	-1.94671	-1.659242
6	2.377098	-2.436842	-2.509776
1	3.103133	-3.095172	-2.515085
1	2.044255	-2.311177	-3.423277
1	1.648841	-2.755731	-1.93749
6	-1.562055	-3.82902	-2.212824
1	-1.386096	-4.268884	-1.354563
1	-0.793397	-3.95817	-2.808751
1	-2.361922	-4.218591	-2.622231
6	3.95888	-0.533637	-2.91587
1	4.309359	0.305437	-2.552413
1	3.555258	-0.367607	-3.793901
1	4.691424	-1.179385	-3.011851
6	3.430331	0.090313	4.165506
1	2.927223	0.592129	4.839877
1	4.119866	0.666624	3.776033
1	3.853097	-0.686667	4.585015
6	-2.12454	-1.686217	-3.301628
1	-3.035052	-1.939295	-3.564173
1	-1.493488	-1.985174	-3.989947
1	-2.070837	-0.713071	-3.207406
3	-0.011048	-1.318391	0.835695

Table S11. Geometry of dimeric **LLi** obtained from its crystal structure

	Coordinates (Angstroms)		
Atomic Number	x	y	z
3	-2.973143	-0.099333	-0.032019
7	-4.821538	-0.544256	0.019051
7	-3.111246	1.774176	-0.118413
6	-5.737277	0.329472	-0.384255
6	-5.482125	1.711042	-0.504001
1	-6.22113	2.250132	-0.761893
6	-4.265588	2.395664	-0.288289
6	-7.137931	-0.08854	-0.772813
6	-7.926248	-0.94612	-0.004723
1	-7.597601	-1.266969	0.826967
6	-9.188017	-1.337906	-0.441863
1	-9.721105	-1.903347	0.104314
6	-9.672277	-0.909959	-1.66709
1	-10.518032	-1.206608	-1.980184
6	-8.907318	-0.041292	-2.432839
1	-9.237294	0.268574	-3.267628
6	-7.658945	0.375414	-1.982114
1	-7.15437	0.986724	-2.505029
6	-4.346048	3.895673	-0.263788
6	-3.523264	4.691627	-1.058642
1	-2.900098	4.282341	-1.647415
6	-3.603116	6.073113	-0.998982
1	-3.037331	6.603597	-1.547578
6	-4.501305	6.681926	-0.146275
1	-4.553261	7.629976	-0.106149
6	-5.320804	5.910012	0.646512
1	-5.938309	6.325741	1.236485
6	-5.246571	4.521216	0.58677
1	-5.818368	3.995507	1.133929
6	-5.097784	-1.922328	0.247093
6	-5.321368	-2.83137	-0.798017
6	-5.501114	-4.176664	-0.494535
1	-5.674547	-4.792676	-1.195993
6	-5.433871	-4.632789	0.802811
1	-5.582493	-5.551998	0.994275
6	-5.151107	-3.750854	1.819232
1	-5.08333	-4.0746	2.709774
6	-4.961652	-2.398889	1.572488
6	-1.909714	2.481924	0.197309
6	-0.883995	2.484588	-0.764277
6	0.345786	3.031994	-0.420947
1	1.051005	3.027664	-1.057717
6	0.565596	3.581284	0.826895
1	1.414628	3.947897	1.04551
6	-0.454687	3.595115	1.750925
1	-0.304812	3.993331	2.601273
6	-1.703059	3.0383	1.470856
6	-5.295901	-2.403134	-2.253106
1	-5.250533	-1.404265	-2.276693
6	-4.034801	-2.94683	-2.935857
1	-3.240919	-2.604306	-2.475921
1	-4.019864	-2.658102	-3.871985
1	-4.038181	-3.925762	-2.895733
6	-6.5631	-2.832151	-2.99741
1	-6.600975	-3.810984	-3.040946
1	-6.548259	-2.464579	-3.906379
1	-7.351532	-2.49621	-2.52186
6	-4.622105	-1.456148	2.716284
1	-4.33123	-0.563434	2.372517
6	-3.605699	-2.023703	3.694458
1	-3.996388	-2.789398	4.163921
1	-3.356908	-1.333959	4.343667
1	-2.807871	-2.313479	3.204223
6	-5.993887	-1.327224	3.611549
1	-5.83376	-0.726659	4.369588
1	-6.71406	-0.965461	3.055043
1	-6.250898	-2.2126	3.944481
6	-1.133122	1.931603	-2.160709
1	-2.113116	2.009376	-2.347319
6	-0.755537	0.458718	-2.277701
1	0.209757	0.358112	-2.145851
1	-0.999654	0.128744	-3.168168
1	-1.234639	-0.056717	-1.596303
6	-0.39142	2.714628	-3.245429
1	0.571322	2.551983	-3.164309
1	-0.570764	3.672145	-3.138422
1	-0.699215	2.421339	-4.128255
6	-2.772589	3.01602	2.547853
1	-3.632219	2.73199	2.12241
6	-2.425739	1.99255	3.638621
1	-2.356555	1.100304	3.23908
1	-3.129466	1.991113	4.321004
1	-1.570454	2.232858	4.051794
6	-2.99117	4.390458	3.175999
1	-2.181598	4.66449	3.653818
1	-3.74261	4.347238	3.803622
1	-3.191054	5.042802	2.472113
3	5.425548	-1.619494	0.59296
7	3.663932	-2.124701	0.087978
7	5.327681	0.226041	0.245118
6	2.697005	-1.216269	0.010863
6	2.948634	0.168586	-0.087394
1	2.183957	0.724687	-0.177079
6	4.196587	0.831415	-0.067998
6	1.231264	-1.588194	0.043827
6	0.680322	-2.611643	-0.72911
1	1.231024	-3.086874	-1.340293
6	-0.666003	-2.944643	-0.616818
1	-1.030281	-3.627447	-1.167539
6	-1.478183	-2.286991	0.293754
1	-2.388395	-2.540549	0.394461
6	-0.948911	-1.256187	1.054429
1	-1.502497	-0.790021	1.671226
6	0.389421	-0.901187	0.919222
1	0.736031	-0.180005	1.430562
6	4.174624	2.291592	-0.42499
6	4.748925	3.259464	0.396151
1	5.154512	3.000562	1.21474
6	4.733255	4.59628	0.030944
1	5.126902	5.24644	0.60087

6	4.150058	4.986982	-1.156688
1	4.141798	5.902932	-1.405522
6	3.57943	4.041207	-1.979628
1	3.177673	4.30689	-2.79937
6	3.588318	2.697842	-1.614764
1	3.188464	2.053427	-2.18626
6	3.423128	-3.527462	0.077901
6	2.870287	-4.208428	1.173645
6	2.746012	-5.59145	1.115293
1	2.353351	-6.054999	1.846156
6	3.181625	-6.304518	0.020434
1	3.068265	-7.246521	-0.012207
6	3.782556	-5.6429	-1.024125
1	4.100721	-6.140774	-1.768379
6	3.932791	-4.262831	-1.017419
6	6.591639	0.890437	0.163033
6	7.283609	1.124251	1.363664
6	8.576619	1.627698	1.296149
1	9.059891	1.778511	2.100152
6	9.174846	1.914734	0.0837
1	10.061694	2.255056	0.056594
6	8.476646	1.703803	-1.083712
1	8.88503	1.922294	-1.913112
6	7.184256	1.177591	-1.077763
6	2.475545	-3.488046	2.449006
1	2.543451	-2.504847	2.27897
6	3.458428	-3.837478	3.572661
1	4.364609	-3.572144	3.309322
1	3.203511	-3.361137	4.389998
1	3.436032	-4.804026	3.737746
6	1.031217	-3.793915	2.855659
1	0.950793	-4.742331	3.087197
1	0.786943	-3.246196	3.63037
1	0.431882	-3.587721	2.107512
6	4.626124	-3.567778	-2.177494
1	4.830023	-2.614595	-1.956103
6	5.868821	-4.292659	-2.669714
1	5.611394	-5.151004	-3.066172
1	6.321169	-3.7436	-3.344583
1	6.476269	-4.449192	-1.916474
6	3.587425	-3.670426	-3.446538
1	3.984884	-3.234864	-4.230644
1	2.746198	-3.223666	-3.217854
1	3.412961	-4.612355	-3.651377
6	6.612868	0.865226	2.705412
1	5.62587	0.947917	2.572138
6	6.891527	-0.538883	3.231225
1	7.849968	-0.634675	3.415429
1	6.384425	-0.685134	4.056017
1	6.620715	-1.199128	2.559192
6	7.023346	1.877694	3.774323
1	7.961797	1.732822	4.019711
1	6.914492	2.786205	3.423306
1	6.457453	1.764681	4.56718
6	6.48316	0.899998	-2.396187
1	5.528146	0.683169	-2.195406
6	7.105915	-0.315292	-3.098198
1	7.024743	-1.103004	-2.520753
1	6.6371	-0.480049	-3.942233
1	8.052563	-0.138503	-3.278686
6	6.504938	2.107329	-3.329842
1	7.429574	2.301412	-3.591874
1	5.973132	1.911411	-4.129366
1	6.125654	2.884398	-2.868029

Table S12. Calculated parameters of S_0–S_n transition of monomeric and dimeric structures of **LLi** in its crystal packing[a]

	State	E / eV, λ / nm[b]	f[c]	Composition, CI Coefficient[d]
monomer	S_1	3.6651, 338.28	0.6010	HOMO → LUMO, 0.66240
dimer	S_1	3.5942, 344.96	0.0750	HOMO-1 → LUMO, 0.59244 HOMO → LUMO+2, 0.32942
	S_2	3.6560, 339.13	0.9538	HOMO-1 → LUMO, -0.33504 HOMO → LUMO+2, 0.59253

[a]Calculated at the TD-CAM-B3LYP/6-31G(d,p) level of theory. [b]Excitation energy between S_0 and S_n states. [c]Oscillator strengths. [d]Configuration interaction expansion coefficient of each component.

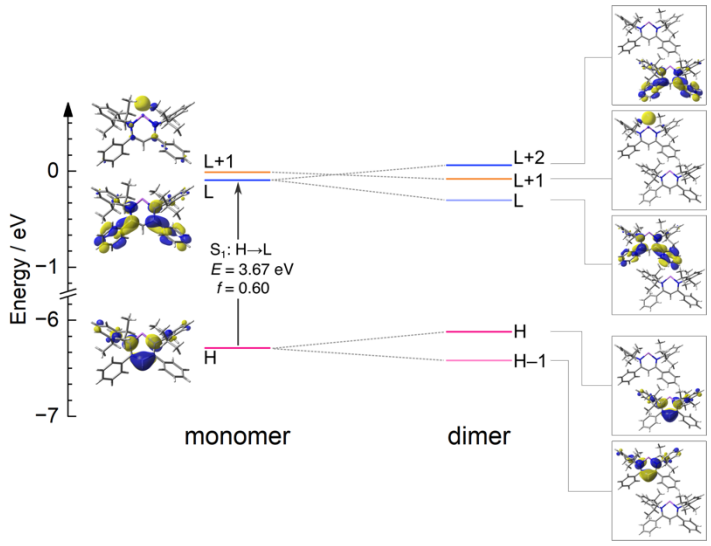

Figure S1. Molecular orbital energy diagram of monomeric and dimeric structures of **LLi** in its crystal packing.

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