Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ESI of

External Electric Field to Control the Diels-Alder Reactions of Endohedral Fullerene

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Table S1: Component and Magnitude of dipole moment in field-free reaction.

Complex	Component of dipole moment			Magnitude
	x	y	z	
C_6H_8	0.3287	-0.0572	0.1772	0.3778
$Li^+@C_{60}$	5.9839	-13.8184	3.3582	15.4283
RC-$Li^+@C_{60}(C_6H_8)$	7.8078	-16.6970	8.0277	20.1054
TS-$Li^+@C_{60}(C_6H_8)$	5.0101	-16.1075	-5.5879	17.7701
P-$Li^+@C_{60}(C_6H_8)$	9.1255	-15.9763	10.2295	21.0514

Table S2: Component and Magnitude of dipole moment in the presence of electric field (-0.002 a.u.).

Complex	Component of dipole moment			Magnitude
	x	y	z	
C_6H_8	0.6807	-0.0806	0.1785	0.7083
$Li^+@C_{60}$	6.0799	-11.4038	3.2758	13.3320
RC-$Li^+@C_{60}(C_6H_8)$	7.4519	-16.0243	10.9409	20.7849
TS-$Li^+@C_{60}(C_6H_8)$	5.0763	-15.8536	-9.3938	19.1141
P-$Li^+@C_{60}(C_6H_8)$	9.3861	-15.9704	13.0843	22.6793

Table S3: Component and Magnitude of dipole moment in the presence of electric field (-0.004 a.u.).

Complex	Component of dipole moment			Magnitude
	x	y	z	
C_6H_8	1.0352	-0.1011	-0.1793	1.0555
$Li^+@C_{60}$	6.1997	-8.9798	3.1835	11.3670
RC-$Li^+@C_{60}(C_6H_8)$	7.7252	-15.9569	14.5787	22.9530
TS-$Li^+@C_{60}(C_6H_8)$	5.1151	-15.5596	-13.2219	21.0496
P-$Li^+@C_{60}(C_6H_8)$	9.4047	-15.9425	16.3914	24.7243

Table S4: Component and Magnitude of dipole moment in the presence of electric field (0.002 a.u.).

Complex	Component of dipole moment			Magnitude
	x	y	z	
C_6H_8	0.3278	-0.0519	-0.1739	0.3746
$Li^+@C_{60}$	5.8493	-16.2539	3.4594	17.6174
RC-$Li^+@C_{60}(C_6H_8)$	7.1602	-16.0697	4.1450	18.0744
TS-$Li^+@C_{60}(C_6H_8)$	4.9663	-16.3327	-1.7791	17.1635
P-$Li^+@C_{60}(C_6H_8)$	9.4155	-15.9406	6.4249	19.5968

Table S5: Component and Magnitude of dipole moment for the reactant-complex (RC) in the presence of different electric field.

Complex	Electric field	Component of dipole moment			Magnitude
		x	y	z	
RC-$Li^+@C_{60}(C_6H_8)$	0.002	7.1602	-16.0697	4.1450	18.0744
RC-$Li^+@C_{60}(C_6H_8)$	0.000	7.8078	-16.6970	8.0277	20.1054
RC-$Li^+@C_{60}(C_6H_8)$	-0.002	7.4519	-16.0243	10.9409	20.7849
RC-$Li^+@C_{60}(C_6H_8)$	-0.004	7.7252	-15.9569	14.5787	22.9530

Table S6: Component and Magnitude of dipole moment in presence of various EEF in transition state.

Complex	Electric field (a.u.)	Component of dipole moment			Magnitude
		x	y	z	
TS-$Li^+@C_{60}(C_6H_8)$	0.000	5.0101	-16.1075	-5.5879	17.7701
TS-$Li^+@C_{60}(C_6H_8)$	0.002	4.9663	-16.3327	-1.7791	17.1635
TS-$Li^+@C_{60}(C_6H_8)$	-0.002	5.0763	-15.8536	-9.3938	19.1141
TS-$Li^+@C_{60}(C_6H_8)$	-0.004	5.1151	-15.5596	-13.2219	21.0496

Table S7: Optimized geometries in cartesian coordinates calculated at the M06-2X/6-31G level of theory.**

Species	Cartesian Coordinates (Å)			
C_6H_8	C	-0.05346200	0.73275500	1.25266100
	C	-0.05346200	-1.41983800	0.10959200
	C	0.31901900	0.69566300	-1.18743900
	C	-0.31901900	-0.69566300	-1.18743900
	C	0.05346200	1.41983800	0.10959200
	C	0.05346200	-0.73275500	1.25266100
	H	1.40823500	0.59986500	-1.31484200
	H	-1.40823500	-0.59986500	-1.31484200
	H	0.00886900	2.50517700	0.10751500
	H	0.20084400	-1.24560300	2.19839100
	H	-0.20084400	1.24560300	2.19839100
	H	-0.00886900	-2.50517700	0.10751500
	H	-0.04336500	1.27699700	-2.03995000
	H	0.04336500	-1.27699700	-2.03995000
C_{60}	C	0.23484800	1.91473500	2.96737600
	C	-1.14027100	1.79089100	2.83189400
	C	-1.77472200	0.49942000	3.02132900
	C	2.25503700	2.06788100	1.77970800
	C	0.98650200	2.72752200	2.02862500
	C	0.32954000	3.38040700	0.99562500
	C	-2.85422000	0.38436400	2.05786500
	C	-3.11700900	-0.83647700	1.45327000
	C	2.81094600	2.09028600	0.50858500
	C	-2.88678400	1.60481900	1.27308800

C	-2.28754300	-0.84739500	-2.56446000
C	-2.87474300	0.29687000	-2.04395300
C	-2.24035900	1.58845200	-2.23334300
C	-1.04666500	1.67871300	-2.93482200
C	-0.43262300	0.48178500	-3.47956200
C	-2.25502600	-2.06785700	-1.77959800
C	-2.81104600	-2.09039000	-0.50868000
C	-3.42494300	-0.89319200	0.03606500
C	-3.45599200	0.27350400	-0.71413200
C	-2.42949800	2.36322300	-1.02055200
C	-1.41691200	3.19433700	-0.56330400
C	-0.16835200	3.28896000	-1.29755800
C	0.01258400	2.54801000	-2.45637100
C	1.28121000	1.88846700	-2.70546600
C	1.00605300	0.61137200	-3.33779700
C	2.31311600	1.99860700	-1.78459900
C	2.12375500	2.77341000	-0.57190600
C	0.91102100	3.40417400	-0.33389800
C	-3.18083300	1.55053300	-0.08185600
C	-1.10910600	3.25080800	0.85382300
C	-1.03908100	-0.75286200	-3.29859700
C	-1.82764500	2.47422600	1.75136100
C	1.03895500	0.75285100	3.29854700
C	0.43253500	-0.48169400	3.47954900
C	-1.00600000	-0.61127900	3.33779000
C	2.28762700	0.84748000	2.56451900

	C	2.87448600	-0.29681000	2.04372600
	C	-1.28120400	-1.88853600	2.70555400
	C	-2.31288300	-1.99845400	1.78443100
	C	-0.01258500	-2.54799400	2.45649600
	C	-0.98641500	-2.72746600	-2.02856900
	C	-0.32952700	-3.38073200	-0.99574000
	C	1.10917300	-3.25112300	-0.85394200
	C	1.82752800	-2.47419000	-1.75132100
	C	1.14032300	-1.79100800	-2.83187500
	C	-2.12376700	-2.77351200	0.57203200
	C	-0.91094000	-3.40406500	0.33398300
	C	1.41678900	-3.19426000	0.56340400
	C	2.42949400	-2.36331600	1.02070800
	C	3.18098600	-1.55060400	0.08178600
	C	2.88675900	-1.60478400	-1.27297100
	C	2.85411000	-0.38429600	-2.05779800
	C	1.77483400	-0.49939900	-3.02133500
	C	3.11730300	0.83658300	-1.45343500
	C	3.42481100	0.89326000	-0.03597700
	C	3.45611000	-0.27342800	0.71424500
	C	0.16836900	-3.28880300	1.29741200
	C	2.24015100	-1.58836200	2.23312700
	C	-0.23489100	-1.91486000	-2.96739500
	C	1.04663200	-1.67879900	2.93488200
$Li^+@C_{60}$	C	3.22213400	-0.62855100	-1.32594400
	C	3.24274600	0.76220600	-1.20129000

C	3.26158000	1.37577100	0.12165500
C	1.83100000	-2.48210400	-1.74199100
C	2.36105100	-1.25821700	-2.31757200
C	1.55898100	-0.47094600	-3.13495600
C	2.43176500	2.57198400	0.07128000
C	1.63695600	2.90749000	1.16093600
C	0.52279300	-2.86211200	-2.01270200
C	1.90573300	2.69898500	-1.27712700
C	-2.37840900	2.60342500	0.38959500
C	-1.58047800	3.11601400	-0.62253800
C	-1.59835200	2.50547000	-1.93921300
C	-2.41355100	1.41038700	-2.18459700
C	-3.25202800	0.87657700	-1.12653300
C	-1.85198300	2.47495400	1.73693400
C	-0.55087200	2.86611900	2.01547300
C	0.28611400	3.39866000	0.95521900
C	-0.21575000	3.51902600	-0.33301900
C	-0.24487400	2.53120100	-2.46448200
C	0.22936300	1.46527500	-3.21637000
C	-0.62566300	0.32099300	-3.47653700
C	-1.91585200	0.29390800	-2.96860600
C	-2.44717600	-0.92955600	-2.39457500
C	-3.27268900	-0.56915700	-1.25610400
C	-1.66427700	-2.07373800	-2.35048900
C	-0.31080200	-2.04382600	-2.87524000
C	0.19551100	-0.87516400	-3.42666500

C	0.60952400	3.15846800	-1.47212700
C	1.57982100	0.97664000	-3.00501000
C	-3.23483800	1.45987100	0.13173800
C	2.40208200	1.58261100	-2.06259700
C	3.21908200	-1.46762200	-0.13328000
C	3.23728500	-0.88049500	1.13354500
C	3.25891800	0.57203200	1.26396800
C	2.35649000	-2.61196900	-0.39390100
C	1.55015600	-3.11385400	0.62056600
C	2.42586700	0.93025000	2.40394400
C	1.63403900	2.07124100	2.34984800
C	1.89517400	-0.29466000	2.97726300
C	-2.38299900	1.25139900	2.31086100
C	-1.58939000	0.46988600	3.13757900
C	-1.61022900	-0.97564500	3.00805300
C	-2.42361400	-1.57444200	2.05743900
C	-3.25743100	-0.75680200	1.19505100
C	0.28146100	2.04619400	2.87727200
C	-0.22499000	0.87529600	3.42371500
C	-0.25867000	-1.46440100	3.21379200
C	0.21561600	-2.53333600	2.46620700
C	-0.63763000	-3.16250900	1.47418500
C	-1.92628100	-2.69084400	1.27346000
C	-2.45273900	-2.56240300	-0.07398600
C	-3.27556200	-1.36731500	-0.12180400
C	-1.66713700	-2.90884500	-1.16329900

	C	-0.31535700	-3.39585300	-0.95380000
	C	0.18638400	-3.52165700	0.33401700
	C	0.59742500	-0.32039900	3.47176600
	C	1.56816000	-2.50251800	1.93930300
	C	-3.23763700	0.62457700	1.31886600
	C	2.39190100	-1.41241200	2.19382700
	Li	1.44429500	-0.01111100	-0.00200100
RC-Li^+@C_{60}(C_6H_8)	C	-1.78897300	0.90087400	3.26299400
	C	-0.62816300	0.07489400	3.54248200
	C	0.55854600	0.83787400	3.19619900
	C	0.13088700	2.13333500	2.70220900
	C	-1.31991700	2.17239300	2.74328200
	C	0.76122400	3.15320500	-0.65878800
	C	0.07692400	3.40637000	0.59659100
	C	0.81303300	2.73669500	1.65399200
	C	1.95289900	2.06965300	1.05336300
	C	1.92193100	2.32764300	-0.37847000
	C	-1.87815900	-1.89580200	2.76449800
	C	-1.48322800	-2.93419400	1.82971500
	C	-0.03245000	-2.97205300	1.78830100
	C	0.46874400	-1.95545200	2.69636800
	C	-0.67260000	-1.29075400	3.30090300
	C	1.53758100	1.12040300	-2.48927000
	C	2.30360500	1.33539700	-1.27390100
	C	2.74184300	0.03790700	-0.77918700
	C	2.23505900	-0.98141100	-1.69023500

C	1.49135300	-0.30892900	-2.74616300
C	0.42310200	1.90623700	-2.75239700
C	-0.78364900	1.30250700	-3.29023200
C	-1.92402600	1.97041700	-2.68953200
C	-1.42229600	2.98537100	-1.78106300
C	0.02838500	2.94605100	-1.81981400
C	-2.93981800	0.32325100	2.74712100
C	-3.67779900	0.99147800	1.69071100
C	-4.17878400	-0.02361900	0.78215500
C	-3.75057100	-1.31954200	1.27664400
C	-2.98494600	-1.10551600	2.49164100
C	1.65408100	0.20155400	2.62599700
C	1.60809700	-1.22810700	2.37111800
C	2.30005100	-1.48547500	1.11641200
C	2.77702400	-0.20919200	0.59478700
C	2.36844900	0.83210400	1.53010200
C	-2.02298400	2.80905800	1.73116400
C	-1.30920200	3.43845900	0.63398000
C	-2.07542700	3.22451700	-0.58083100
C	-3.26170300	2.46319800	-0.23427200
C	-3.22933300	2.20660700	1.19404500
C	-3.05552100	1.24022600	-2.35657200
C	-3.10077000	-0.18841300	-2.61240000
C	-3.81400300	-0.81799500	-1.51539000
C	-4.20980700	0.22160200	-0.58272000
C	-3.74098900	1.49324200	-1.10235900

C	-0.13989800	-3.43499200	-0.62761600
C	0.57303600	-2.80655600	-1.72650900
C	1.78782300	-2.20658800	-1.19285300
C	1.82014900	-2.46456300	0.24480100
C	0.62550300	-3.22160100	0.58890700
C	-3.40816000	-2.05748300	-1.04324600
C	-2.26593800	-2.72179800	-1.64493100
C	-1.52764100	-3.38905000	-0.58772100
C	-2.21367400	-3.13708200	0.66706700
C	-3.37578900	-2.31407900	0.38510400
C	0.33346900	-0.88660100	-3.25327700
C	-0.13513000	-2.15961600	-2.73341000
C	-1.58585000	-2.12117200	-2.69525800
C	-2.01371200	-0.82566100	-3.19212700
C	-0.82820000	-0.06226700	-3.53737700
C	5.91061900	-0.80531800	1.15908900
C	5.66283100	-1.45178000	0.00980300
C	5.73760600	-0.74562200	-1.27219700
C	5.79720400	0.59508600	-1.31333200
H	5.88872900	-1.33766900	2.10639100
H	5.42151700	-2.51142000	0.01102200
H	5.72878900	-1.32616500	-2.19016700
H	5.82668700	1.11559900	-2.26681500
Li	0.62304100	-0.55237100	-0.11865100
C	5.79278800	1.41293300	-0.04678800
H	4.75915100	1.73460400	0.16379500

	H	6.36067200	2.33606300	-0.19019000
	C	6.35405300	0.63569600	1.14998600
	H	7.45278600	0.64408700	1.11030700
	H	6.07981400	1.13430800	2.08383300
TS-Li^+@C_{60}(C_6H_8)	C	-0.13197200	2.75499500	-2.08488800
	C	1.31871600	2.79680600	-2.08032600
	C	1.80296000	1.69926100	-2.89831500
	C	0.65106800	0.97687200	-3.40548800
	C	-0.54317600	1.63177700	-2.89715500
	C	0.69196600	-0.40466000	-3.52139500
	C	2.94270700	1.00335300	-2.52099100
	C	1.99715000	3.14820200	-0.92215500
	C	-0.84185900	3.06382000	-0.92979200
	C	-1.64550800	0.87148200	-2.52184300
	C	-0.46056200	-1.19951400	-3.13040000
	C	-1.60364700	-0.57299300	-2.64155100
	C	-1.99501000	2.27453000	-0.54920700
	C	-2.39355300	1.19813300	-1.32540200
	C	-0.13090100	3.43582400	0.28021000
	C	1.25584800	3.47479700	0.28355100
	C	3.19129800	2.42414100	-0.53063400
	C	3.65382400	1.37491200	-1.31188300
	C	1.88519000	-1.13280300	-3.13174600
	C	2.98421700	-0.44358400	-2.63931100
	C	3.72045100	-0.96515200	-1.50239400
	C	4.13509000	0.15839700	-0.68261700

C	-1.99519900	2.15551600	0.91002800
C	-0.84214100	2.87265500	1.41375200
C	1.99695800	2.95712900	1.42054400
C	3.19111100	2.30599300	0.91704900
C	-2.33186100	-1.13416800	-1.52100600
C	-2.94682400	-0.03842600	-0.73265300
C	0.01715400	-2.41405500	-2.50851700
C	1.46791900	-2.37391300	-2.50324500
C	-1.87287600	-2.30179500	-0.92763600
C	-0.67126300	-2.94736200	-1.42155300
C	-2.94701100	-0.15662000	0.71595000
C	-2.39385300	0.96752800	1.50138500
C	-0.13248100	2.38063800	2.50364000
C	1.31820000	2.42261200	2.50624100
C	3.65344700	1.14402200	1.51803000
C	4.13489700	0.04560100	0.70003700
C	2.17039700	-2.86950500	-1.41356000
C	3.32353700	-2.15270900	-0.90389300
C	3.32334100	-2.27075500	0.54360200
C	3.72016700	-1.19596500	1.32679200
C	2.94208600	0.58142300	2.65078500
C	1.80227900	1.20701700	3.13570000
C	-0.54383100	1.14062700	3.12299100
C	-1.64608700	0.45124900	2.62920200
C	-2.33209100	-1.36564900	1.31637500
C	-1.87302000	-2.42171000	0.54174300

C	0.06596900	-3.46744400	-0.28296000
C	1.45383600	-3.42695600	-0.27950300
C	2.98362300	-0.86556500	2.53304300
C	0.65029500	0.41197200	3.51877400
C	-1.60418700	-0.99351400	2.51321000
C	-0.67147200	-3.13882500	0.92474900
C	2.17009500	-3.06065700	0.93007300
C	-0.46121900	-1.69102500	2.89433900
C	0.01665200	-2.78872700	2.08394100
C	0.69121400	-0.97008500	3.40926700
C	1.88455600	-1.62550000	2.90707400
C	1.46741100	-2.74829600	2.08555500
H	-4.96680900	0.05884500	-2.44934100
C	-5.11737400	-0.00093600	-1.37328000
C	-5.43106300	-1.33659500	0.59609700
C	-5.47459900	1.15828200	0.87234300
C	-5.11675300	-0.22434000	1.35478700
C	-5.47391200	1.28502600	-0.67213100
C	-5.43147100	-1.22175800	-0.80548500
H	-6.47854100	1.36676000	1.25688900
H	-4.96570300	-0.34037800	2.42617500
H	-4.81700900	2.09299800	-1.00518000
H	-5.46212100	-2.11728200	-1.41850000
H	-5.46130800	-2.31995400	1.05520400
H	-4.81917100	1.90205600	1.33329000
H	-6.47713600	1.55512700	-1.01827300

	Li	-0.75510600	-0.43878800	-0.03597700
P-Li^+@C_{60}(C_6H_8)	C	1.81778900	3.03411000	1.43000300
	C	0.65281700	3.48108800	0.68991100
	C	-0.52836700	3.02700600	1.40613300
	C	-0.09659200	2.30964300	2.57879100
	C	1.35401200	2.30810200	2.59858800
	C	-0.80090600	-1.17253700	2.98561600
	C	-0.08261000	0.00379900	3.43872000
	C	-0.80087700	1.17920000	2.98309800
	C	-1.96841000	0.74518400	2.24987800
	C	-1.96843200	-0.74006800	2.25146400
	C	1.84530000	3.03117400	-1.41277300
	C	1.40366900	2.30240200	-2.58832900
	C	-0.04707400	2.30411300	-2.59651300
	C	-0.50061500	3.02408700	-1.43395400
	C	0.66637600	3.47981100	-0.69608600
	C	-1.64616900	-2.58262300	0.70806400
	C	-2.40151800	-1.43502900	1.14598200
	C	-3.16311100	-0.80911900	-0.03529100
	C	-2.37568300	-1.43655300	-1.19934700
	C	-1.63110000	-2.58354200	-0.74453200
	C	-0.52848400	-3.02382000	1.41276800
	C	0.65266600	-3.47952100	0.69753500
	C	1.81765800	-3.03096700	1.43662500
	C	1.35393100	-2.30236400	2.60363100
	C	-0.09664200	-2.30386600	2.58382800

C	2.94446200	2.59811800	0.74602900
C	3.66096300	1.42208000	1.20177900
C	4.11920200	0.69366300	0.03301100
C	3.68351100	1.41941900	-1.14576300
C	2.95844800	2.59646800	-0.70635000
C	-1.64604600	2.58427600	0.70235200
C	-1.63100300	2.58196000	-0.75023100
C	-2.37562800	1.43396100	-1.20246700
C	-3.16305200	0.80914900	-0.03705800
C	-2.40136600	1.43769800	1.14280400
C	2.03854800	1.17973500	3.02937200
C	1.30361000	0.00379200	3.46377500
C	2.03848200	-1.17309200	3.03194500
C	3.21838800	-0.72444300	2.32198800
C	3.21840500	0.72948200	2.32038600
C	2.94433000	-2.59655600	0.75172400
C	2.95836900	-2.59811500	-0.70065100
C	3.68345500	-1.42206600	-1.14262100
C	4.11918300	-0.69371700	0.03456000
C	3.66090400	-1.41951900	1.20491500
C	-0.01707900	-0.00379500	-3.45063600
C	-0.74425300	-1.17934900	-3.00911000
C	-1.92680000	-0.74545500	-2.29969000
C	-1.92676000	0.74045100	-2.30127700
C	-0.74422400	1.17277100	-3.01166400
C	3.26207100	-0.72946100	-2.26954300

	C	2.09609900	-1.17980300	-3.00108100
	C	1.36945700	-0.00381500	-3.44930600
	C	2.09616100	1.17315400	-3.00365700
	C	3.26209700	0.72436000	-2.27114200
	C	-0.50073200	-3.02723500	-1.42732500
	C	-0.04714700	-2.30982900	-2.59144600
	C	1.40358300	-2.30815900	-2.58327100
	C	1.84519200	-3.03436900	-1.40613200
	C	0.66626200	-3.48136700	-0.68846100
	C	-4.66244500	1.28577600	-0.07922000
	C	-5.30511900	0.66594900	-1.29177000
	C	-5.30513100	-0.66858600	-1.29037600
	C	-4.66246100	-1.28588100	-0.07657300
	H	-4.66288700	2.37830500	-0.11515400
	H	-5.72848800	1.27457200	-2.08305700
	H	-5.72848900	-1.27887700	-2.08038900
	H	-4.66283000	-2.37848200	-0.11023600
	Li	-0.87198300	-0.00055900	-0.04806100
	C	-5.37919400	-0.77166800	1.18843000
	H	-4.88658700	-1.16805100	2.08111500
	H	-6.39893700	-1.16118500	1.18649300
	C	-5.37894900	0.77417800	1.18694100
	H	-6.39853300	1.16406600	1.18473800
	H	-4.88582500	1.17210300	2.07864900

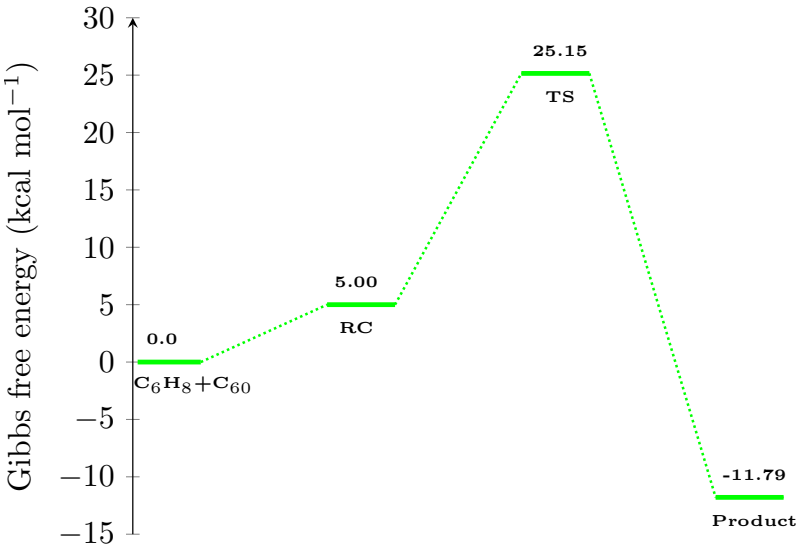

Figure S1: Gibbs free energy (kcal mol^{-1}) for the Diels-Alder reaction of C_{60} with C_6H_8 (reaction A) calculated at M06-2X/6-31G** level of theory.

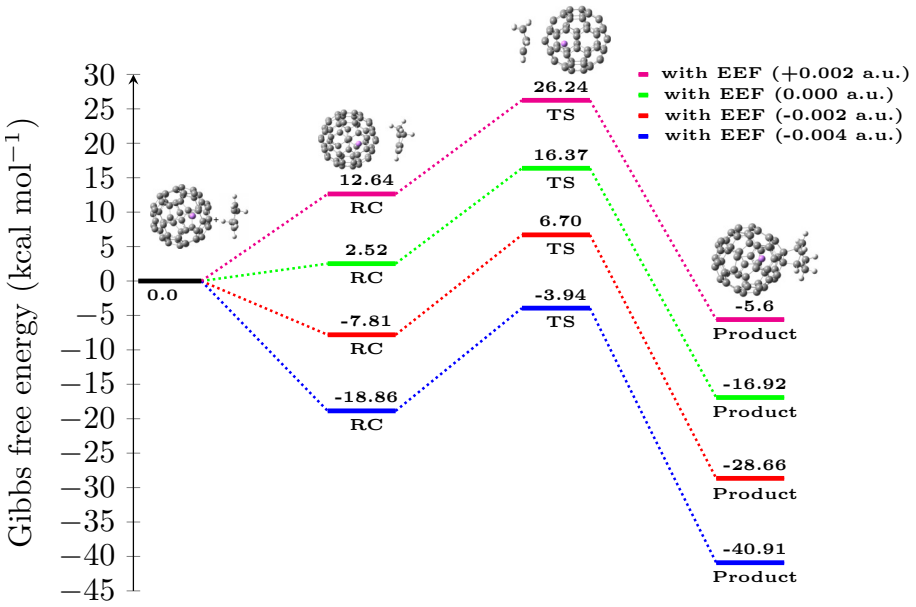

Figure S2: Gibbs free energy (kcal mol^{-1}) at 298 K for the Diels-Alder reaction of $Li^+@C_{60}$ with C_6H_8 calculated at M06-2X/6-31G** level of theory. Gibbs free energy in absence of EEF is shown in green colour (reaction B), at an EEF of -0.002 a.u. in red (reaction C), at -0.004 a.u. in blue (reaction D) and at 0.002 a.u. in magenta (reaction E).

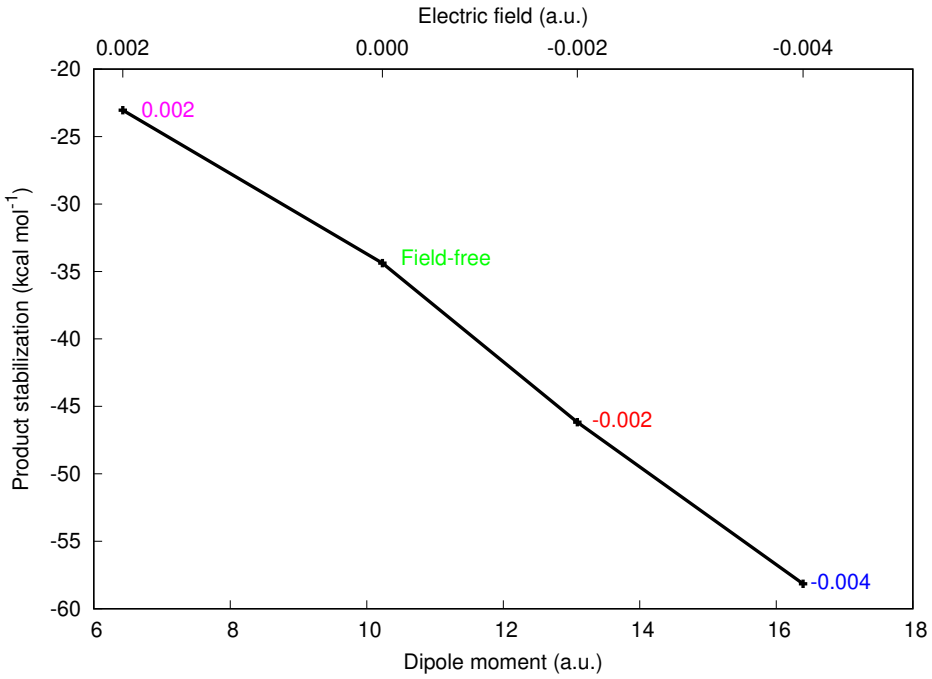

Figure S3: External electric field vs. Dipole moment of product at various external electric field (+0.002 a.u., 0.000 a.u., -0.002 a.u., -0.004 a.u.)

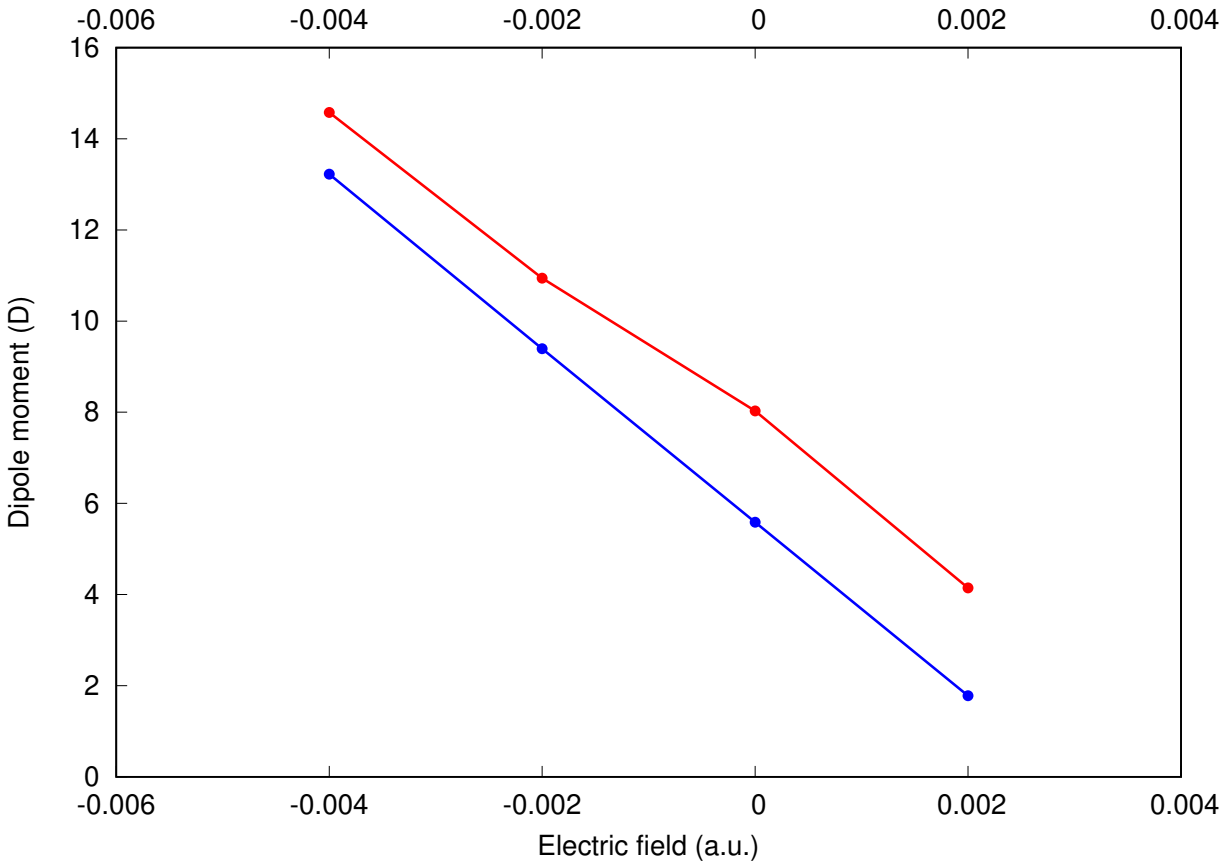

Figure S4: Dipole moment vs Electric field of RC (in red) and TS (in blue) at M06-2X/6-31G** level of theory.

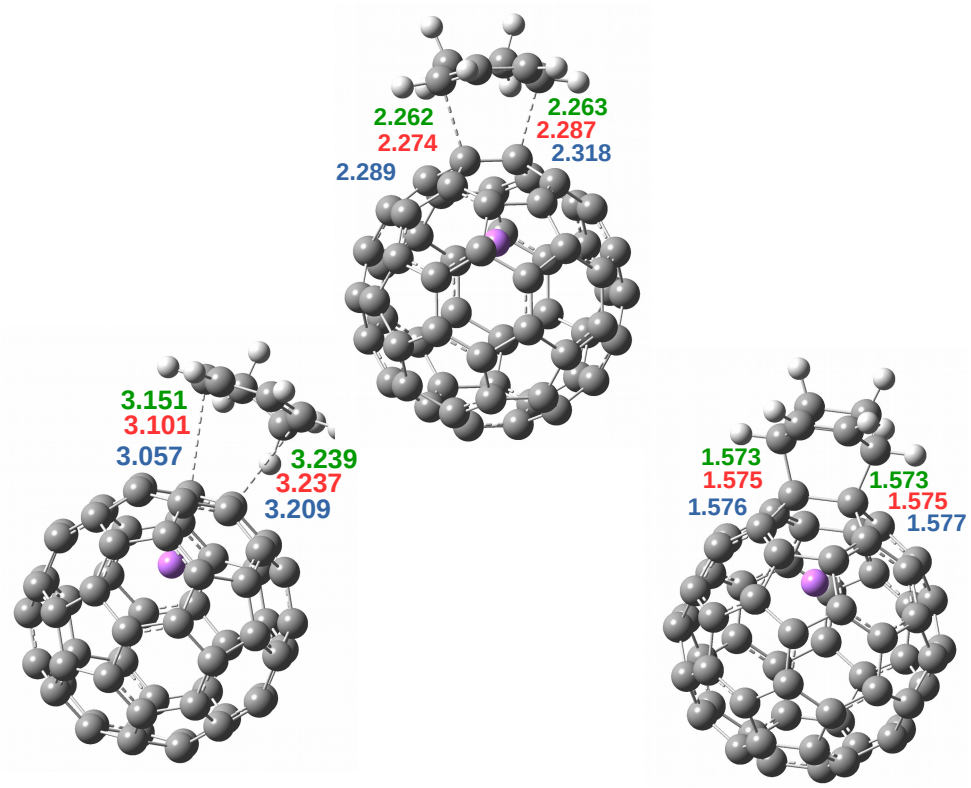

Figure S5: The bond length (Å) of reactant-complex, transition state, and product at different EEF at the level of theory M06-2X/6-31G**. The bond lengths in field free are denoted in green colour, at -0.002 a.u. EEF in red and at -0.004 a.u. EEF in blue colour.

13. A detailed discussion on kinetics of the title reaction

Gibbs free energy profile often helps in choosing a method for the estimation of the rate of a reaction. The Gibbs free energy profiles at 298 K for the reaction of C_{60} with C_6H_8 as well as for the title reaction at different EEF, are shown in figure S1 and S2, respectively. It can be clearly seen from figure S1 and S2 that for the reaction of A (C_{60} + C_6H_8), B ($Li^+@C_{60}$ + C_6H_8) and E ($Li^+@C_{60}$ + C_6H_8 (0.002 a.u. EEF)), the Gibbs free energy barrier for the formation of reactants from RC (bimolecular dissociation) is very low compared to the same for RC to product. It suggests that the time scale associated with bimolecular dissociation is much lower than the same for the unimolecular transformation. It also suggests that we can think of these reactions in two steps; first, equilibration process between reactants and RC followed by a slow unimolecular transformation. Therefore, we have applied pre-equilibrium approximation for these three reaction pathways using KISTHELP software package[1]. It is also evident from figure S2 that the RC is $\sim$ -7.81 and $\sim$ -18.86 kcal mol^{-1} stable than the reactants for the reaction C ($Li^+@C_{60}$ + C_6H_8 (-0.002 a.u. EEF)) and D ($Li^+@C_{60}$ + C_6H_8 (-0.004 a.u. EEF)), respectively. For this kind of GES, pre-equilibrium approximation is not valid. Thus, we have used master equation for these two reaction channels as implemented in MESMER software package[2].

Pre-equilibrium approximation

The reaction mechanism for the reactions can be represented as:

$$C_6H_8 + Li^+@C_{60} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RC \xrightarrow[TS]{k_{uni}} Product$$

Here, above equation suggests that the reaction proceeds via two steps; first, a reactant-complex (RC) is formed with barrierless association process of the reactants and in second step, RC dissociates to form product through a corresponding transition state. In the first step, k_{eq} has been obtained using following formula:

$$k_{eq} = \sigma \frac{Q_{RC}}{Q_{C_6H_8} Q_{Li^+@C_{60}}} exp[\frac{-(E_{RC} - E_R)}{RT}] \quad (1)$$

where σ is the symmetry number, variable Q denote the overall partition functions for the subscripted species C_6H_8, $Li^+@C_{60}$ and RC. E_{RC} and E_R represent energies of reactant-complex and isolated reactants respectively. In the second step, k_{uni} has been obtained using following equation:

$$k_{uni} = \frac{k_B T}{h} \frac{Q_{TS}}{Q_{RC}} exp[\frac{-(E_{TS} - E_{RC})}{RT}] \tag{2}$$

Here, k_B; Boltzmann constant, h; Planck's constant, T; Temperature, E_{TS} and E_{RC} denote the relative energies of TS and RC respectively. The overall rate constant, k_{bi} can thus be obtained as

$$k_{bi} = k_{eq} * k_{uni} \tag{3}$$

Master equation

To determine the rate constants using a master equation approach, we have used MESMER suite of programs. As a input, we need two rate constants; First, the rate constant for the barrierless association process and second, rate constant for the unimolecular dissociation process. For the unimolecular transformation, we have used Rice-Ramsperger-Kessel-Marcus (RRKM) theory to compute the rate while for the bimolecular association process, MESMER uses the Inverse Laplace Transformation method (ILT). The ILT method requires a pre-exponential factor as a input to compute the rate constants. The methodology used in determining the pre-equilibrium constant for a bimolecular association process is described in the next section. Air is taken as a bath gas to mimic the atmospheric environment with the L-J parameters, σ=3.68 and ϵ=86.2 K. The L-J parameters of C_6H_8, C_{60} and RC were not known. Therefore, we have considered the L-J parameters of C_6H_6 in place of C_6H_8 as these two are almost similar in size. The L-J parameters of the C_{60} were calculated by the fitting of the L-J equation and the L-J parameters of the RC were deduced from the

combining rule[3] which uses following equations:

$$(\epsilon/k_B)_{AB} = [(\epsilon/k_B)_A(\epsilon/k_B)_B]^{1/2} \tag{4}$$

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) \tag{5}$$

The collisional parameters for RC using equation 4 and 5 are estimated to be, σ=5.23 $\mathring{A}$ and ϵ=77.94 K. A single exponential down model is used for describing collisional energy transfer probabilities with an energy grain size of 100 cm^{-1} and ΔE_{down}= 130 cm^{-1}.

Pre-exponential factor estimation

An equilibrium constant for the reaction is the ratio of forward rate constant and the reverse rate constant which can be expressed using Arrhenius equation as follows:

$$k_{eq} = \frac{k_f}{k_r} = \frac{A_f e^{-\beta E_f}}{A_r e^{-\beta E_r}} \tag{6}$$

Where k_f is the forward rate constant and k_r denotes the reverse rate constant. Correspondingally, A_f denotes the pre-exponential factor for the forward rate constant expression and A_r represents the pre-exponential factor for the reverse rate constant expression. Similarly, E_f and E_r represent the activation energies for the forward and reverse rate constant, respectively. Interestingly, the forward reactions at an EEF of -0.002 a.u. and -0.004 a.u., i.e., reaction C and D (see figure S2) are barrierless association reactions, hence one can assume the activation energy for these two reactions to be zero. In addition, the equilibrium constant (k_{eq}) can be recasted in the form of $A_{eq}e^{-\beta E_{eq}}$ which suggests the equation 6 can be written in the following form. The value of A_{eq} and E_{eq} can be obtained from the THERMO program using MULTIWELL suite of codes.

$$A_{eq}e^{-\beta E_{eq}} = \frac{A_f}{A_r e^{-\beta E_r}} \tag{7}$$

Equation 7 suggests that A_f=A_{eq}*A_r and E_{eq}=-E_r. To estimate A_r, we have calculated the

reverse rate constants k_r for the different temperatures assuming the TS to be close to the reactants using the following equation:

$$k_r = \frac{k_B T}{h} e^{-\triangle G^*/RT} \tag{8}$$

Where ΔG^* is the relative Gibbs free energy barrier of the reactants with respect to the RC and T is the temperature. Here, upon fitting the rate constants at different temperatures in an Arrhenius expression, one can easily obtain the value of A_r. Using this approach, the obtained values of A_r for reactions C and D were found to be 2.56×10^{-8} and 2.94×10^{-8} cm^3 $molecule^{-1}$ sec^{-1}, respectively.

14. References

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