Supporting Information

Theoretical inside into double-headed superalkalide ion pair $K^{\delta-}[AE^{+}@HMHC]K^{\delta-}$ (AE = Ca&Sr) as stable and high-performance single-pole double-throw mid-far-infrared NLO molecular switch

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Contents

Optimized Cartesian coordinates at the K[M@HMHC]K (M = Ca & Sr) at the *ω*B97XD/ma-SVP/def2-ECP level

K[Ca@HMHC]K

1

Ca	-0.15466199	-0.02746123	0.07245727
N	-2.53891398	1.26851254	0.41176464
N	-2.16588707	-1.72972928	0.80485025
N	0.41850047	-2.74607213	-0.37083369
N	2.84786411	-1.05910476	0.14436021
N	2.25453923	1.50426206	-1.31838934
N	0.07742516	2.76551266	0.31944694
C	-3.17892107	1.68555007	-0.83650507
C	-2.08206676	-2.19832568	2.18872264
C	0.65647291	-2.84052833	-1.80987997
C	-1.23834621	3.37458946	0.56123650
C	-2.21179553	2.43344609	1.23930199
C	-3.43313817	0.37360047	1.15421990
C	-3.44020233	-1.03525787	0.59134602
C	-2.05673447	-2.85423226	-0.12921088
C	-0.73479978	-3.58334186	-0.01087748
C	3.18439372	-0.68083231	1.51123863
C	1.98998254	1.13251601	-2.70277095
C	0.92560723	2.96045782	1.49375396
C	1.58471951	-3.18620822	0.40328333
C	2.88100196	-2.51203843	0.00134835
C	3.74456520	-0.42720409	-0.81552456
C	3.58458875	1.07819569	-0.90104212
C	2.09720514	2.94573108	-1.14523235
C	0.66570154	3.36774767	-0.88234231
H	-2.46126441	2.15949343	-1.51885266
H	-4.02016538	2.38375550	-0.64094187
H	-3.56165105	0.81505160	-1.38189508
H	-2.78455893	-3.03929220	2.36957792
H	-2.31769902	-1.38506256	2.88498359
H	-1.06214196	-2.51162422	2.44728759
H	-0.27863699	-2.65618873	-2.35476415
H	1.04773599	-3.83919732	-2.09801525
H	1.36228366	-2.07020624	-2.14972831
H	-1.65341762	3.71060349	-0.39865591
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H	-1.78126505	2.06794797	2.18774186
H	-3.13249989	2.99933029	1.49509440
H	-4.46708779	0.77460234	1.15722856
H	-3.10089050	0.35540816	2.20323027

H	-4.27437880	-1.60894142	1.04400247
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H	-2.17728953	-2.45995815	-1.15317503
H	-2.87912035	-3.58116671	0.03990038
H	-0.60068913	-3.94552873	1.01743209
H	-0.76509961	-4.48931119	-0.64704484
H	2.55980690	-1.23270937	2.22611543
H	4.25313702	-0.88342174	1.74227936
H	2.97950069	0.38179771	1.69868862
H	2.78232432	1.50700601	-3.38730489
H	1.90948978	0.04350661	-2.82058610
H	1.02311707	1.53731532	-3.02992186
H	1.83009149	2.33900696	1.44117038
H	1.22569406	4.02304908	1.61331976
H	0.39013157	2.64021725	2.39709339
H	1.37397865	-2.99687614	1.46942476
H	1.72973616	-4.28152538	0.28817672
H	3.11279693	-2.76153133	-1.04355040
H	3.70204373	-2.95264126	0.60291532
H	4.80679317	-0.64287561	-0.56691906
H	3.56454210	-0.87178157	-1.80555900
H	4.36095017	1.46379155	-1.59762482
H	3.80226821	1.52626879	0.07981149
H	2.73327648	3.27553733	-0.31190850
H	2.46287970	3.49595818	-2.03610344
H	0.02792056	3.09987971	-1.74164537
H	0.65515928	4.47550471	-0.80011053
K	0.40316492	-0.03447983	4.82224318
K	-1.83741131	-0.12396119	-4.40278150

K[Ca@HMHC]K

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Ca	-0.05167296	0.10691951	0.42531147
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N	0.11921662	2.84824504	0.47578530
N	-2.45305868	1.31686534	0.03294471
N	-2.58480992	-1.59370806	0.56662788
N	-0.28805374	-2.69845139	-0.90075235
N	2.24701549	-1.89255258	0.35552015
C	2.69742479	0.80299054	-1.60335684
C	0.20779694	3.34407705	1.84866206
C	-2.86154380	1.14579167	-1.36217433
C	3.52383953	-1.17841131	0.31502556
C	3.38960557	0.28829092	0.66896875

C	2.53779644	2.44525341	0.13354615
C	1.31347146	3.23436667	-0.28023276
C	-1.07837524	3.38166797	-0.17859953
C	-2.35100951	2.74859710	0.34340994
C	-2.32609801	-2.21097786	1.86088039
C	-0.30059500	-2.00565870	-2.18302153
C	2.02745148	-2.47952964	1.67108266
C	-3.41388813	0.71181392	0.96482919
C	-3.76066207	-0.72508772	0.63317358
C	-2.74427980	-2.58994202	-0.48588780
C	-1.51613394	-3.45392430	-0.68992188
C	0.85109365	-3.60051974	-0.79213676
C	2.18944506	-2.89569132	-0.70118363
H	2.47818588	-0.22885394	-1.90323522
H	3.75111444	1.02829964	-1.86712351
H	2.04595586	1.43850406	-2.21793250
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H	-0.66022373	3.02462477	2.43783128
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H	-2.79707432	0.09617127	-1.67338643
H	3.95817994	-1.27583114	-0.68949810
H	4.25952662	-1.64036163	1.00117782
H	3.05414073	0.39551181	1.71570926
H	4.39645668	0.74977828	0.59587187
H	3.43077193	2.87961371	-0.35848047
H	2.70352165	2.54601502	1.21552934
H	1.52279107	4.31649635	-0.15576534
H	1.10866237	3.08003586	-1.35167857
H	-0.98628717	3.20732638	-1.26251568
H	-1.14109206	4.48090603	-0.04413861
H	-2.40967736	2.86506827	1.43489287
H	-3.22213640	3.29220705	-0.07344924
H	-2.31160488	-1.44335220	2.64616318
H	-3.09359975	-2.97305477	2.11598430
H	-1.33525896	-2.68595754	1.88387810
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H	-1.14274732	-1.30371694	-2.25447548
H	0.60884665	-1.40635740	-2.32784447
H	0.99158183	-2.82927173	1.78262935
H	2.71473658	-3.33130075	1.86332104
H	2.17523648	-1.71945613	2.44995245
H	-2.97822319	0.77163482	1.97790939

H	-4.35786513	1.29567272	0.97623705
H	-4.28968658	-0.76264774	-0.32910753
H	-4.48583374	-1.09439247	1.38364860
H	-3.59798353	-3.26775784	-0.26828598
H	-2.99694966	-2.07135294	-1.42267214
H	-1.71533123	-4.13818777	-1.54241427
H	-1.37262251	-4.09816175	0.19002303
H	0.70611858	-4.22598953	0.10101346
H	0.88971652	-4.30041461	-1.65430910
H	2.42107289	-2.40748148	-1.65951941
H	2.96876541	-3.67464798	-0.55499097
K	0.14256799	0.25870570	4.73971377
K	-0.20261751	1.68825908	-5.28494536

K[Ca@HMHC]K

3

Ca	-0.11488652	0.19253122	-0.35829936
N	-2.40702321	1.25881359	0.63105806
N	0.10054692	2.88298666	0.15322237
N	2.45262970	0.98148977	0.05398551
N	2.13934604	-1.74598415	-1.05792860
N	-0.19765525	-2.83507736	0.35665703
N	-2.66458450	-1.47165901	-0.48573241
C	-2.61052656	0.78931497	2.00245865
C	0.00020466	3.66211754	-1.08021711
C	2.91630791	0.47236618	1.34560431
C	-3.82289611	-0.62685378	-0.19156318
C	-3.50438148	0.85260388	-0.25685793
C	-2.32559490	2.72508274	0.62008475
C	-0.97933176	3.24964401	1.07318012
C	1.39879027	3.11263430	0.79260642
C	2.53535035	2.44768713	0.04497882
C	1.71836086	-2.04130439	-2.42123372
C	-0.00996971	-2.43302216	1.74498660
C	-2.60997931	-1.79335645	-1.90593808
C	3.26030468	0.46869662	-1.06064154
C	3.41995139	-1.03775498	-1.05354011
C	2.21969235	-2.95229504	-0.24302952
C	0.89636905	-3.67820007	-0.10769707
C	-1.45729137	-3.54372684	0.17141612
C	-2.68565040	-2.67271353	0.34085626
H	-2.52158535	-0.30163275	2.07041676
H	-3.60394615	1.08528806	2.39757430
H	-1.83989901	1.19504274	2.67142098

H	0.08992370	4.74860629	-0.87185808
H	-0.95178991	3.46996586	-1.58951144
H	0.77721510	3.36628445	-1.79531681
H	2.37397408	0.95262451	2.17101620
H	4.00135669	0.64895588	1.49421513
H	2.72308220	-0.60247388	1.44607795
H	-4.20520613	-0.87675147	0.80773667
H	-4.65653852	-0.83869645	-0.88841434
H	-3.22093645	1.13328365	-1.28670086
H	-4.42965722	1.41159321	-0.00494795
H	-3.11689167	3.15580704	1.26544533
H	-2.54042845	3.06996525	-0.40129078
H	-1.04077769	4.35141804	1.18556281
H	-0.73408369	2.85009675	2.07016370
H	1.34859210	2.72845008	1.82393180
H	1.60796448	4.19884240	0.87467696
H	2.54389148	2.78154180	-1.00230841
H	3.49810667	2.77799311	0.48332072
H	1.76509953	-1.13083045	-3.03359062
H	2.35367032	-2.82358846	-2.88954095
H	0.67078651	-2.37236544	-2.45095195
H	0.01989333	-3.29654871	2.44239616
H	0.92567761	-1.87328265	1.88027963
H	-0.81519032	-1.76765364	2.08575684
H	-1.64256138	-2.23959249	-2.17568626
H	-3.42105996	-2.49262539	-2.20258865
H	-2.69562966	-0.87476727	-2.50179731
H	2.77711141	0.79344841	-1.99913741
H	4.27488085	0.91843832	-1.03870038
H	3.99547452	-1.34204745	-0.16841761
H	4.03902797	-1.33021032	-1.92341756
H	2.95434979	-3.67156334	-0.66555344
H	2.59918549	-2.67714165	0.75226801
H	1.04797710	-4.54514404	0.57058199
H	0.61041548	-4.10083077	-1.08214784
H	-1.45632949	-3.98171353	-0.83760037
H	-1.54230373	-4.39791452	0.87698114
H	-2.78769553	-2.37055923	1.39380324
H	-3.57460541	-3.29941553	0.11175023
K	-0.54581161	1.26657301	-4.52190039
K	0.60240181	0.51267383	5.51651624

K[Sr@HMHC]K

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Sr	0.15216575	0.05387287	-0.13964601
N	2.90388313	-0.57449060	-0.58527765
N	1.92475925	2.28402668	0.08329573
N	-1.07330386	2.67121415	-0.30296615
N	-2.72816558	0.39972005	0.76120783
N	-1.93701654	-2.05138454	-0.79589674
N	0.86195203	-2.74604130	0.04905644
C	3.21189489	-0.81903713	-1.99252192
C	2.13227559	2.71109116	1.46516533
C	-1.67261343	2.68591641	-1.63415820
C	2.29552630	-2.95869833	-0.18300455
C	3.15352415	-1.77309181	0.21953950
C	3.70549092	0.54244340	-0.07520989
C	3.20149118	1.90290959	-0.52906943
C	1.29502869	3.34806072	-0.70281313
C	-0.07781858	3.74385719	-0.19046525
C	-2.52903903	0.02361849	2.15729285
C	-2.14101121	-1.67700649	-2.19174216
C	0.52386606	-3.09261977	1.42638779
C	-2.07885389	2.81052239	0.75177057
C	-3.19443646	1.78411729	0.67406765
C	-3.67276149	-0.49833053	0.10336014
C	-3.17400971	-1.92570535	-0.03066964
C	-1.42082184	-3.41810672	-0.71121385
C	0.07964396	-3.51832414	-0.91768059
H	2.47779969	-1.49259455	-2.45423164
H	4.22978495	-1.24665116	-2.11555379
H	3.14733276	0.11030875	-2.57040594
H	2.66178423	3.68654735	1.51203310
H	2.71628527	1.96565086	2.01748176
H	1.18191676	2.78828324	2.00978511
H	-0.88784431	2.71443444	-2.40123556
H	-2.34286828	3.55995951	-1.77715146
H	-2.24536332	1.76809689	-1.82947129
H	2.44942029	-3.18699234	-1.24652487
H	2.64657261	-3.85253292	0.36946124
H	2.96560721	-1.51906307	1.27675061
H	4.22024612	-2.07469187	0.14617864
H	4.76464659	0.43074782	-0.38622916
H	3.69796711	0.49049524	1.02405114
H	3.97767739	2.66439095	-0.30838703
H	3.06710275	1.90461504	-1.62134544
H	1.21690299	2.99984204	-1.74692942
H	1.93708823	4.25463903	-0.71355975

H	-0.00929818	4.05089496	0.86210767
H	-0.41574217	4.64233776	-0.74357695
H	-1.88636283	0.75382933	2.66659906
H	-3.49169744	-0.04477372	2.70797177
H	-2.00675180	-0.93912288	2.24872941
H	-2.97655472	-2.24525100	-2.65391226
H	-2.34951569	-0.60317324	-2.29862333
H	-1.22994137	-1.85712795	-2.77752488
H	-0.47832199	-2.73239243	1.69922048
H	0.56674026	-4.18878117	1.60026118
H	1.21568100	-2.59836689	2.12078660
H	-1.56428774	2.73617068	1.72414484
H	-2.54906414	3.81650792	0.71289354
H	-3.74264855	1.91189207	-0.26958252
H	-3.92527961	2.00445149	1.47826580
H	-4.63698819	-0.52862020	0.65505168
H	-3.90171312	-0.09146707	-0.89267019
H	-3.98693144	-2.52459862	-0.49488863
H	-3.00868830	-2.35509650	0.96849261
H	-1.68222246	-3.83251737	0.27228605
H	-1.91792519	-4.07318399	-1.45497158
H	0.34605728	-3.16747389	-1.92849524
H	0.35098902	-4.59471604	-0.86901528
K	1.16024992	0.03303202	4.69763073
K	0.49650810	0.55352780	-5.04349017

K[Sr@HMHC]K

2

Sr	0.06104421	0.20875201	0.39494580
N	2.75836629	-0.37376898	-0.24473080
N	1.85947970	2.44632543	0.56097160
N	-1.15632951	2.74877242	0.08821255
N	-2.93380486	0.39609942	0.57087989
N	-1.69091664	-1.84658694	-0.92095193
N	0.91024328	-2.67026090	0.24273627
C	2.85873077	-0.61354816	-1.68299500
C	2.20329129	2.72948187	1.95223021
C	-1.56029483	2.91073579	-1.30704791
C	2.36473956	-2.81183707	0.13122563
C	3.12192851	-1.56073261	0.53553533
C	3.62839870	0.74149311	0.14469991
C	3.06185216	2.10582118	-0.20462264
C	1.18892508	3.59954118	-0.04583336
C	-0.22210087	3.81300483	0.47167286

C	-3.07845249	-0.23942618	1.87574729
C	-1.34936096	-1.27864909	-2.22158749
C	0.45951947	-3.06233949	1.57337646
C	-2.30618647	2.76930538	0.99774673
C	-3.39831789	1.78520198	0.62248424
C	-3.63804841	-0.34400971	-0.47166082
C	-3.12605152	-1.75915531	-0.66561542
C	-1.26809794	-3.24102621	-0.82485268
C	0.23674395	-3.43436518	-0.80280450
H	2.08333031	-1.30879897	-2.03102765
H	3.85039451	-1.02278506	-1.96800554
H	2.69466397	0.31493310	-2.24517981
H	2.89766881	3.59291526	2.02622537
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H	1.30442980	2.94023443	2.54479948
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H	2.61850387	-3.07624947	-0.90440952
H	2.72651351	-3.65560862	0.75013715
H	2.93537712	-1.33467510	1.60020580
H	4.20705264	-1.77483492	0.43410795
H	4.62278338	0.63684030	-0.33484226
H	3.80289358	0.67370814	1.22819721
H	3.85299776	2.86801048	-0.04648125
H	2.80832304	2.14270502	-1.27593836
H	1.16875335	3.44967774	-1.13693238
H	1.77359457	4.52653379	0.12939912
H	-0.21353309	3.87816012	1.56925285
H	-0.58897592	4.79407002	0.10750176
H	-2.61641598	0.38332896	2.65426789
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H	-2.55208106	-1.20444449	1.91282508
H	-1.84359650	-1.80713827	-3.06306459
H	-1.63493788	-0.21895774	-2.28950840
H	-0.26605142	-1.31177190	-2.40717779
H	-0.58760700	-2.77233293	1.74408780
H	0.55343144	-4.15713407	1.73605394
H	1.04420492	-2.53783686	2.34176538
H	-1.93561485	2.55139397	2.01490838
H	-2.75994711	3.78264126	1.02738066
H	-3.81758745	2.05715226	-0.35583329
H	-4.23151401	1.89491485	1.34333858
H	-4.72455112	-0.41060263	-0.24808920

H	-3.55266565	0.21767282	-1.41397914
H	-3.70374952	-2.22018555	-1.49454876
H	-3.34909675	-2.35668385	0.23052331
H	-1.70672040	-3.66719741	0.08938850
H	-1.67617831	-3.83679969	-1.66860916
H	0.66574637	-3.14626927	-1.77424724
H	0.43111824	-4.52254226	-0.68880826
K	0.37691791	0.12747491	4.86088206
K	0.77208582	1.70039482	-5.22953382

K[Sr@HMHC]K

3

Sr	0.13416570	0.15120892	-0.37655275
N	1.85000782	2.19513979	0.57333971
N	2.91359539	-0.56978919	-0.22292354
N	0.63868477	-2.62517966	-0.12176906
N	-2.11110804	-1.77183325	-0.92045300
N	-2.64432820	0.70481238	0.62288045
N	-0.92189867	2.96158090	-0.23669753
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C	3.52960300	-0.53395184	-1.54702127
C	0.23900227	-3.05440685	1.21695787
C	0.13521070	3.93506000	0.05121928
C	1.53109634	3.39748109	-0.20289881
C	3.25290172	1.83309374	0.34261569
C	3.57010785	0.38590744	0.67340929
C	2.99037909	-1.92015199	0.34133430
C	2.06148355	-2.90834146	-0.34058088
C	-2.44003122	-1.29219955	-2.25808363
C	-2.19865362	0.39667148	1.97834712
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C	-0.14826168	-3.28660782	-1.16727043
C	-1.64781589	-3.16130101	-0.97318832
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C	-3.70019598	-0.20758908	0.19262476
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C	-2.04228447	3.13066126	0.68349794
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H	2.11529040	3.29247760	2.39237743
H	1.95776042	1.51952454	2.57636197
H	4.60369009	-0.81151308	-1.49753052
H	3.43691964	0.46205655	-1.99744217
H	3.01531398	-1.21237439	-2.23894367
H	0.91261097	-2.63772205	1.97700985

H	0.24195772	-4.15986698	1.31722666
H	-0.76184912	-2.68502997	1.47696917
H	0.04961398	4.25439970	1.09885747
H	-0.00135730	4.85389807	-0.55124902
H	1.65092188	3.15012140	-1.27242284
H	2.25297545	4.21008944	0.02553046
H	3.92031901	2.48786915	0.93888502
H	3.48718137	2.03710342	-0.71213677
H	4.67142989	0.25073045	0.64753430
H	3.25621284	0.16025426	1.70486718
H	2.74833674	-1.85796987	1.41413992
H	4.02781684	-2.30967814	0.27926652
H	2.24476699	-2.90911875	-1.42474278
H	2.30758530	-3.92968740	0.01437431
H	-1.60514170	-1.48475290	-2.94603619
H	-3.35466723	-1.77881189	-2.65872331
H	-2.59096044	-0.20278577	-2.26808145
H	-3.01098164	0.49171902	2.72850873
H	-1.80405964	-0.62695802	2.05312295
H	-1.38119321	1.05929791	2.29738496
H	-1.98385711	2.21682818	-1.91765507
H	-1.90177916	4.00678872	-1.82272371
H	-0.47334818	3.02369761	-2.29493683
H	0.14418696	-2.84830098	-2.13772776
H	0.09743539	-4.36884362	-1.21227169
H	-1.94194507	-3.67030569	-0.04515203
H	-2.15391303	-3.71412163	-1.78813538
H	-4.11577942	-2.22300623	-0.36729269
H	-2.95781855	-2.08038099	0.96166541
H	-4.53714002	-0.21579277	0.92260539
H	-4.12009582	0.17763359	-0.74819498
H	-3.61236252	2.20027939	-0.45514924
H	-3.90955392	2.28022929	1.28425837
H	-1.65219451	3.11316449	1.71221899
H	-2.52046929	4.12490959	0.55039877
K	0.89721356	0.59324686	-4.76669275
K	0.87977608	-0.86213972	5.34905107

Computational details on the electronic contribution (β_{ijk}^{e}) and a nuclear relaxation contribution (β_{ijk}^{nr}, $i, j, k = x, y, z$).

Using the Born-Oppenheimer approximation, β_0 can be written into an electronic contribution (β_{ijk}^{e}, $i, j, k = x, y, z$) and a vibrational contribution (β_{ijk}^{v}), and the latter can be further divided into nuclear relaxation and curvature terms (β_{ijk}^{nr} and β_{ijk}^{curv}). Then, the following equation is obtained:

$$\beta_{ijk} = \beta_{ijk}^{e} + \beta_{ijk}^{v} = \beta_{ijk}^{e} + \beta_{ijk}^{nr} + \beta_{ijk}^{curv} \quad (1)$$

β_{ijk}^{curv} is usually smaller and far more computationally expensive than β_{ijk}^{nr}. For this reason, β_{ijk}^{curv} is frequently neglected. β_{ijk}^{nr} is given in terms of vibronic energies and dipole moment matrix elements over the vibronic wave functions.[1]

According to Bishop and co-workers,[2] if we denote the equilibrium molecular geometry with an OEEF (F_i) present by R_F and without the field present, by R_0, then we may define:

$$(\Delta\mu_i)_{R_0} = \mu_i(F, R_0) - \mu_i(0, R_0) \quad (2)$$

$$(\Delta\mu_i)_{R_F} = \mu_i(F, R_F) - \mu_i(0, R_0) \quad (3)$$

β_{ijk}^{e} can be derived from the expansion of eq 5&6. And β_{ijk}^{nr} can be derived from the expansion of eq 6:

$$(\Delta\mu_i)_{R_0} = (\alpha_{ij}^{e}(0;0)) \times F_j + \frac{1}{2}(\beta_{ijk}^{e}(0;0,0)) \times F_j F_k + \cdots \quad (4)$$

$$(\Delta\mu_i)_{R_F} = (\alpha_{ij}^{e}(0;0) + \alpha_{ij}^{nr}(0;0)) \times F_j + \frac{1}{2}(\beta_{ijk}^{e}(0;0,0) + \beta_{ijk}^{nr}(0;0,0)) \times F_j F_k + \cdots \quad (5)$$

This approach is used in this paper to compute the $\beta_{zzz}^{e}(F)$ and $\beta_{zzz}^{nr}(F)$ contributions within a permanent static electric field.

References

[1] R. Zaleśny, M. Garcia-Borràs, R. W. Góra, M. Medved, J. M. Luis, *Phys. Chem. Chem. Phys.* **2016**, 18, 22467.

[2] D. M. Bishop, M. Hasan, B. Kirtman, *J. Chem. Phys.* **1995**, 103, 4157.

Table S1. NPA charge of alkali metal atoms with with ωB97XD, CAM-B3LYP, and CAM-B3LYP-D3 methods with ma-TZVP basis set including def2-ECP basis set for K[Ca@HMHC]K.

		NPA charge (|e|)		
		ωB97XD	CAM-B3LYP	CAM-B3LYP-D3
1	Q_{K1}	-0.48595	-0.48617	-0.48617
	Q_{K2}	-0.48585	-0.48607	-0.48607
	Q_{AE}	1.04943	1.04295	1.04295
2	Q_{K1}	-0.27814	-0.29127	-0.29127
	Q_{K2}	-0.73982	-0.72691	-0.72691
	Q_{AE}	1.08384	1.07835	1.07835

Table S2. Total energy (E_{tot}, a.u.) and relative energy (E_{rel}, kcal/mol) of K[Ca@HMHC]K between singlet and triplet states at ωB97XD/ma-SVP/def2-ECP level.

		Singlet state	Triplet state
1	E_{tot}	-2915.84952587	-2915.81645031
	E_{rel}	0.00	20.76
2	E_{tot}	-2915.85013289	-2915.83024318
	E_{rel}	0.00	12.48
3	E_{tot}	-2915.85013289	-2915.83024318
	E_{rel}	0.00	12.48

Considering the different spin states for each configuration of K[Ca@HMHC]K, from Fig. S2 ~ S3, the strengths of both bending vibration of C-H bond (ε_{BV}) and stretching vibration of C-H bond (ε_{SV}) are obviously different. These are also different among singlet isomers for both AE = Ca and Sr. Compared between singlet and triplet states; it is the triplet structure owns the significantly larger ε value for BV but it is the singlet one holds the larger ε value for SV of **1** with two equal Ca-K distances. The situation is exactly the opposite that the triplet structure is significantly larger in ε value of BV but smaller in ε value of SV than the singlet one for **2** or **3** of K[Ca@HMHC]K with two unequal Ca-K distances.

Table S3. Dipole moment (μ_0, D) and static first hyperpolarizabilities (β_0, au) as well as their components in axes.

	μ_0	μ_x	μ_y	μ_z	β_0	β_{xxx}	β_{yyy}	β_{zzz}
2 (AE = Ca)	10.114	-1.163	-0.010	-10.047	65579	-1121	266	-52901
1 (AE = Ca)	2.651	2.651	0.002	-0.002	656	10	1	1858
3 (AE = Ca)	10.114	1.163	0.010	10.114	65579	1121	-266	52901
2 (AE = Sr)	8.573	-0.689	-0.001	-8.546	49474	6229	13	-45233
1 (AE = Sr)	3.201	1.564	0.487	2.747	4875	1240	434	2735
3 (AE = Sr)	8.573	0.689	0.001	8.546	49474	-6229	-13	45233

For both K[Ca@HMHC]K and K[Sr@HMHC]K (see Table 3), there is a rationale fact that there is no difference between NPA charges in K1 and K2 of 1 but large in that of 2&3. As a result, μ_0 of 1 is small (2.651 (AE = Ca) and 3.197 D (AE = Sr)) and not in the z-axis while that of 2&3 are as large as 10.114 (AE = Ca) and 8.546 D (AE = Sr) and in the z-axis. For 2, |NPA K1| < |NPA K2|, then, $\mu_z < 0$. From 1 to 2 or 3 (see Fig. 4), the μ_0 value are, respectively, increased by more than 2.8 and 1.6 times for AE = Ca and Sr, respectively.

The similar condition but significantly difference in value occurs in the static first hyperpolarizability. The direction of β_0 or β_{zzz} is just same to that of μ_0 or μ_z. β_0 or β_{zzz} direction is not in z-axis for 1 but in z-axis and from the K atom (K1 for 2 and K2 for 3) with a small negative NPA charge to another K atom (K2 for 2 and K1 for 3) with a large negative NPA charge for 2&3. The β_0 or β_{prj} or β_{HRS} value is quite small for 1 but considerably large for 2&3. The β_0 value and β_{HRS} values are, respectively, increased by more than 114 times and 22 times from 1 to 2 or 3 (see Fig. 4) of K[Ca@HMHC]K and the corresponding increasing multiples are 11 times and 9 for from 1 to 2 or 3 of K[Sr@HMHC]K. Then, 1 is the off form and both 2 and 3 are the on forms of the SPDT NLO-MS. From 1 to 2 or 3, the increases in β_0 or β_{prj} or β_{HRS} value constitutes 1 ~ 2 orders of magnitude improvement for K[Ca@HMHC]K but an order of magnitude improvement for K[Sr@HMHC]K. Thus, there are more excellent in SPDT switching behaviour of β for K[Ca@HMHC]K than for K[Sr@HMHC]K.

Table S4. Dipole moment between ground state and crucial excited state ($\Delta\mu$), oscillator strength (f_0), and transition energy (ΔE) of crucial excited state (CES) and their components for K[Ca@HMHC]K.

CES	Wavelength (nm)	f_0	f_0^z	$\Delta\mu_0$ (au)	$\Delta\mu^z$ (au)	ΔE (eV)
1						
1	1076	0.5305	0.5008	4.3362	0.0576	1.1517
4	779	0.3000	0.0167	2.7745	1.0227	1.5912
5	776	0.6437	0.0002	4.0572	0.0826	1.5969
6	763	0.3358	0.0187	2.9049	-0.6962	1.6246
7	754	0.4676	0.4412	3.4065	0.1428	1.6441
24	531	0.1097	0.1032	1.3844	-0.0887	2.3339
2						
1	1263	0.1413	0.1360	2.4236	-11.8054	0.9813
2	1028	0.1065	0.0002	1.8992	-6.5809	1.2059
3	1017	0.1122	0.0006	1.9393	-5.7671	1.2185
4	888	0.2450	0.2426	2.6763	-7.1489	1.3966
5	833	0.2139	0.0003	2.4240	-9.6028	1.4872
6	819	0.2552	0.0283	2.6245	-7.3671	1.5131
7	785	0.5170	0.4947	3.6565	-2.7766	1.5779
10	706	0.1061	0.0793	1.5706	-0.6619	1.7566
11	702	0.3282	0.0005	2.7554	-2.4897	1.7652
12	694	0.1464	0.0018	1.8296	-3.1030	1.7868
17	600	0.1868	0.1823	1.9203	-1.0879	2.0649
3						

1	1263	0.1413	0.1360	2.4236	11.8054	0.9813
2	1028	0.1065	0.0002	1.8992	6.5809	1.2059
3	1017	0.1122	0.0006	1.9393	5.7671	1.2185
4	888	0.2450	0.2426	2.6763	7.1489	1.3966
5	833	0.2139	0.0003	2.4240	9.6028	1.4872
6	819	0.2552	0.0283	2.6245	7.3671	1.5131
7	785	0.5170	0.4947	3.6565	2.7766	1.5779
10	706	0.1061	0.0793	1.5706	0.6619	1.7566
11	702	0.3282	0.0005	2.7554	2.4897	1.7652
12	694	0.1464	0.0018	1.8296	3.1030	1.7868
17	600	0.1868	0.1823	1.9203	1.0879	2.0649

Table S5. Dipole moment between ground state and crucial excited state ($\Delta\mu$), oscillator strength (f_0), and transition energy (ΔE) of crucial excited state (CES) and their components for K[Sr@HMHC]K.

CES	Wavelength (nm)	f_0	f_0^z	$\Delta\mu_0$ (au)	$\Delta\mu^z$ (au)	ΔE (eV)
1						
1	1012	0.5879	0.5821	4.4260	-0.0151	1.2246
4	788	0.5809	0.0012	3.8823	-0.174	1.5734
5	781	0.6788	0.0001	4.1790	-0.0248	1.587
6	765	0.4747	0.4720	3.4590	0.0123	1.6189
7	736	0.0903	0.0002	1.4791	0.0757	1.6837
22	539	0.1219	0.1225	1.4697	0.0275	2.3014
2						
1	1093	0.2331	0.2266	2.8956	-10.2915	1.1347
2	1009	0.1099	0.0056	1.9115	-4.9958	1.2289
3	1004	0.1043	0.0005	1.8580	-5.5294	1.2346
4	862	0.3127	0.3103	2.9789	-6.1386	1.4382
5	811	0.2822	0.0172	2.7464	-6.9365	1.528
6	811	0.2594	0.0000	2.6333	-9.019	1.5281
7	748	0.4285	0.3996	3.2499	-2.0712	1.6556
8	727	0.2431	0.0220	2.4134	-1.2379	1.7045
9	724	0.1743	0.0007	2.0390	-1.9088	1.7123
10	700	0.1766	0.0008	2.0193	-4.1065	1.7693
17	616	0.1369	0.1269	1.6659	-1.267	2.0127
3						
1	1093	0.2331	0.2266	2.8956	10.2915	1.1347
2	1009	0.1099	0.0056	1.9115	4.9958	1.2289
3	1004	0.1043	0.0005	1.8580	5.5294	1.2346
4	862	0.3127	0.3103	2.9789	6.1386	1.4382
5	811	0.2822	0.0172	2.7464	6.9365	1.528
6	811	0.2594	0.0000	2.6333	9.019	1.5281
7	748	0.4285	0.3996	3.2499	2.0712	1.6556
8	727	0.2431	0.0220	2.4134	1.2379	1.7045
9	724	0.1743	0.0007	2.0390	1.9088	1.7123
10	700	0.1766	0.0008	2.0193	4.1065	1.7693

17	616	0.1369	0.1269	1.6659	1.2670	2.0127

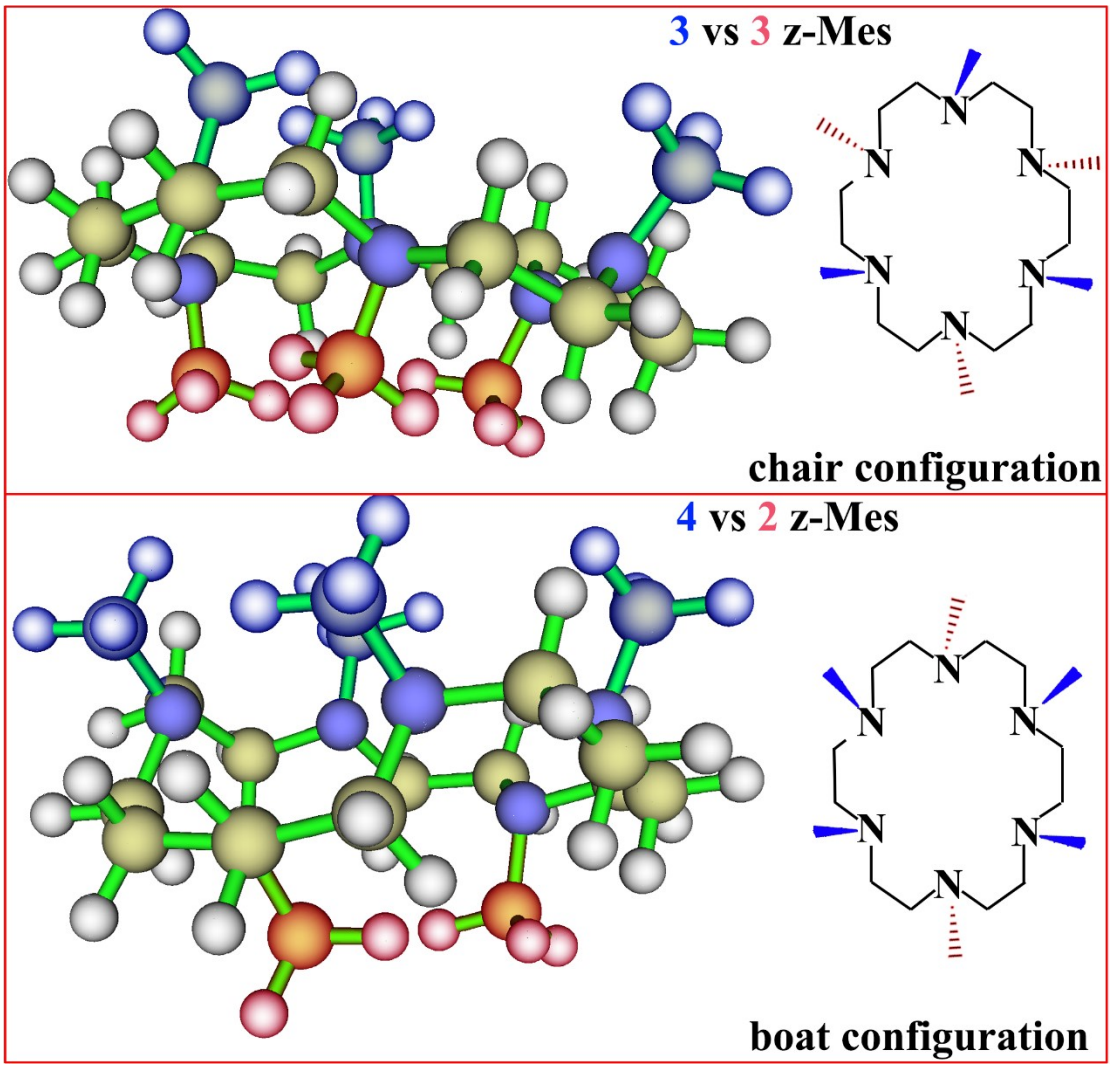


Fig. S1. Boat and chair configurations of HMHC. The z-axial methyl groups (z-Mes) in the upper and lower sides are highlighted in blue and magenta, respectively.

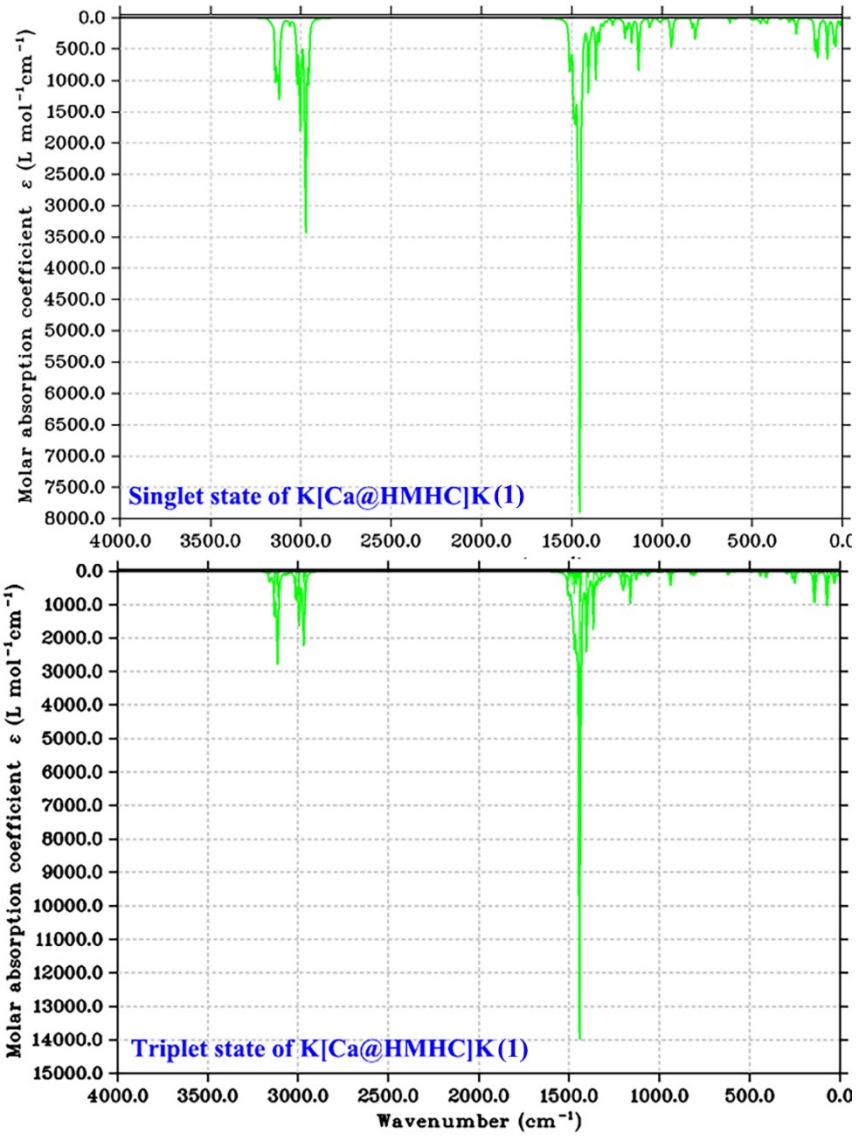


Fig. S2. Infrared spectrum of singlet and triplet states of $K^{\delta-}[Ca^{+}@HMHC]K^{\delta-}$ (**1**)

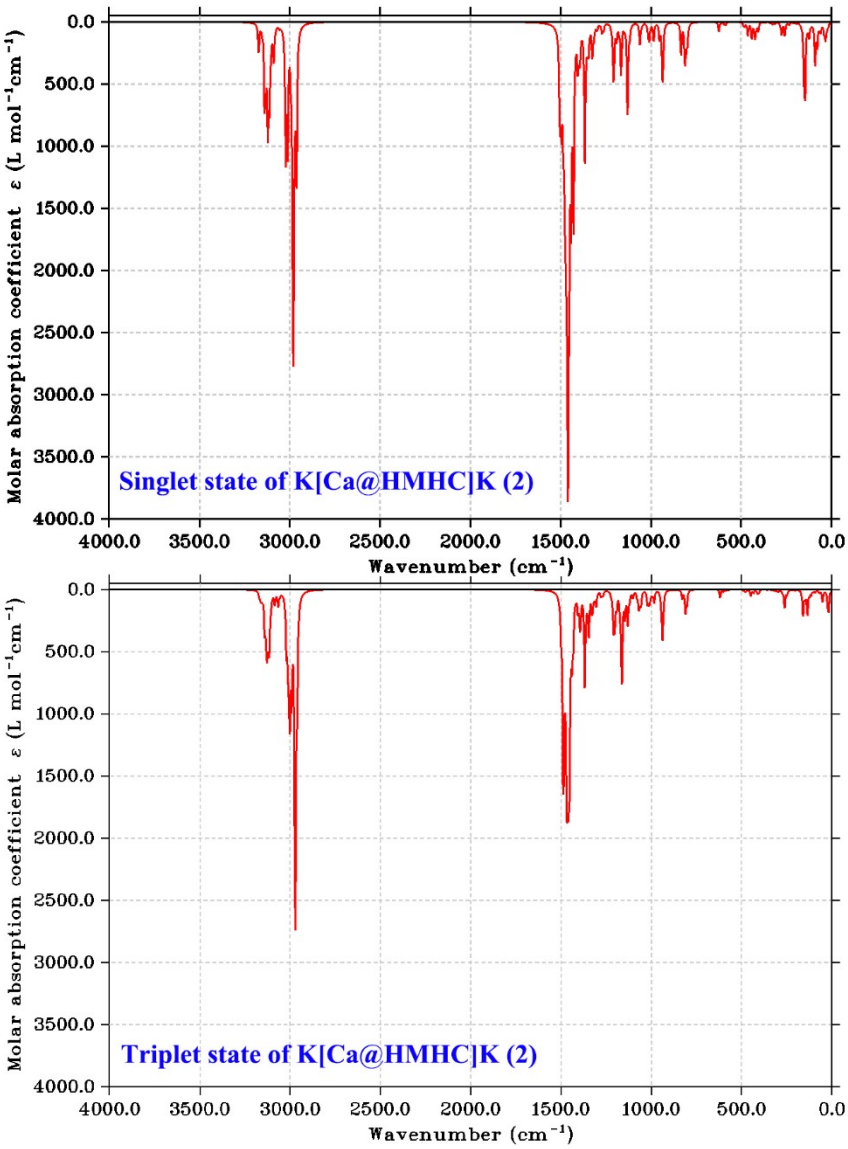


Fig. S3. Infrared spectrum of singlet and triplet states of $K^{\delta-}[Ca^{+}@HMHC]K^{\delta-}$ (**2**)

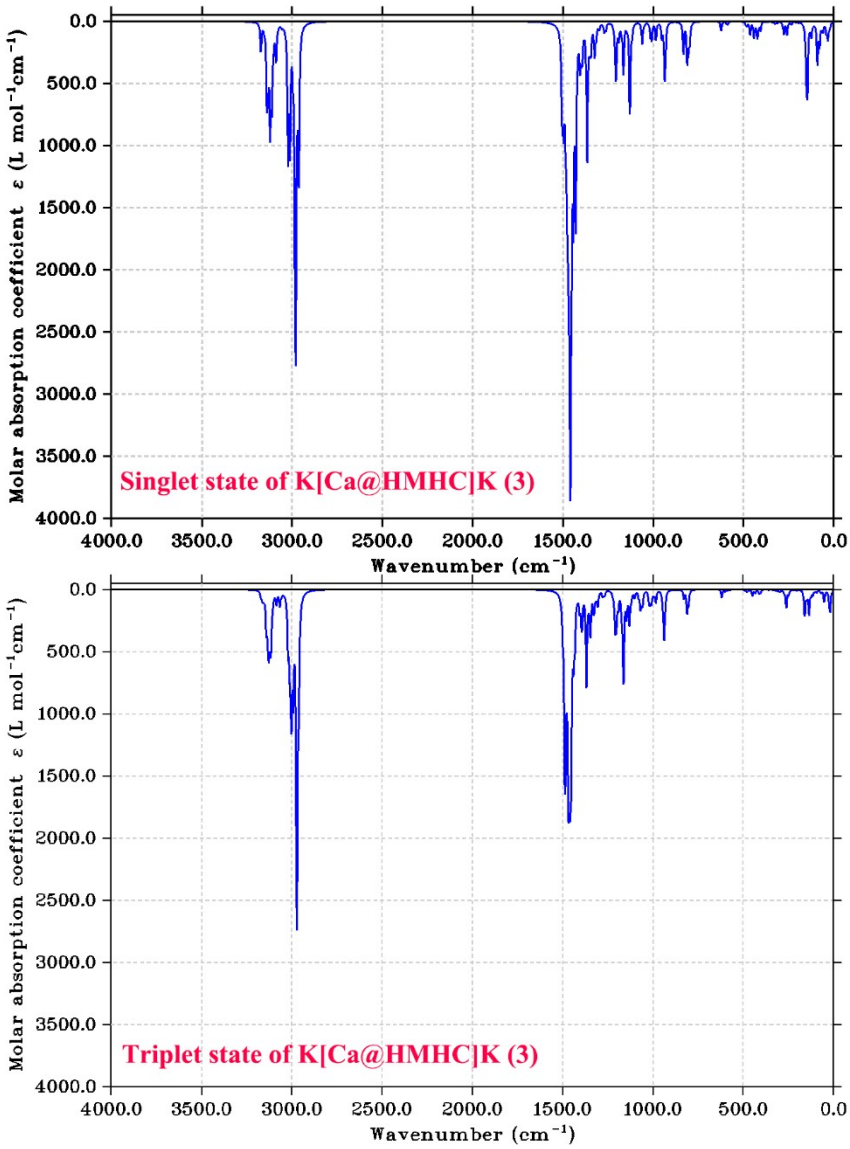


Fig. S4. Infrared spectrum of singlet and triplet states of $K^{\delta-}[Ca^{+}@HMHC]K^{\delta-}$ (**3**)

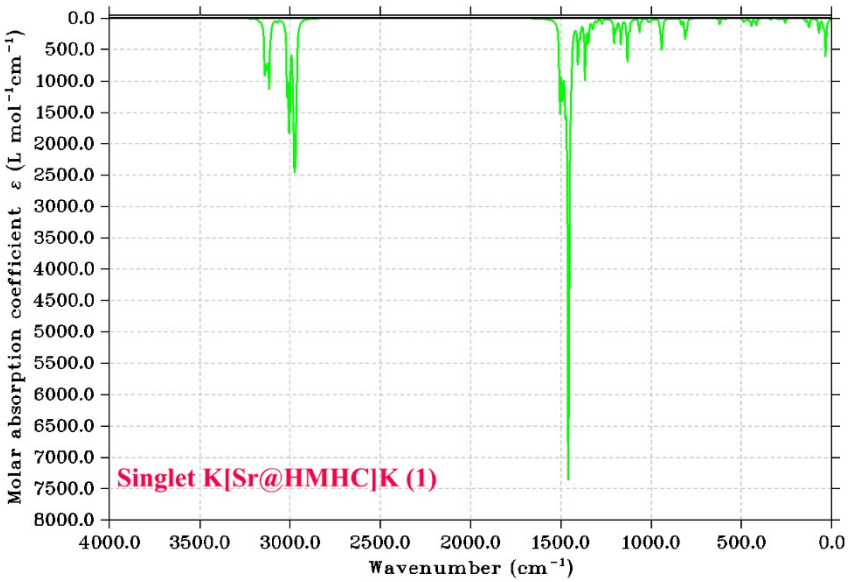


Fig. S5. Infrared spectrum of singlet $K^{\delta-}[Sr^{+}@HMHC]K^{\delta-}$ (**1**)

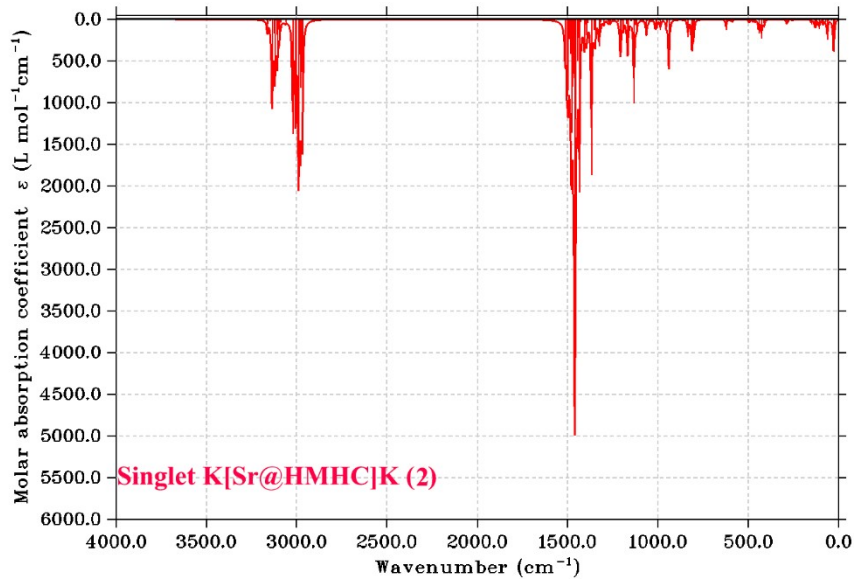


Fig. S6. Infrared spectrum of singlet $K^{\delta-}[Sr^{+}@HMHC]K^{\delta-}$ (**2**)

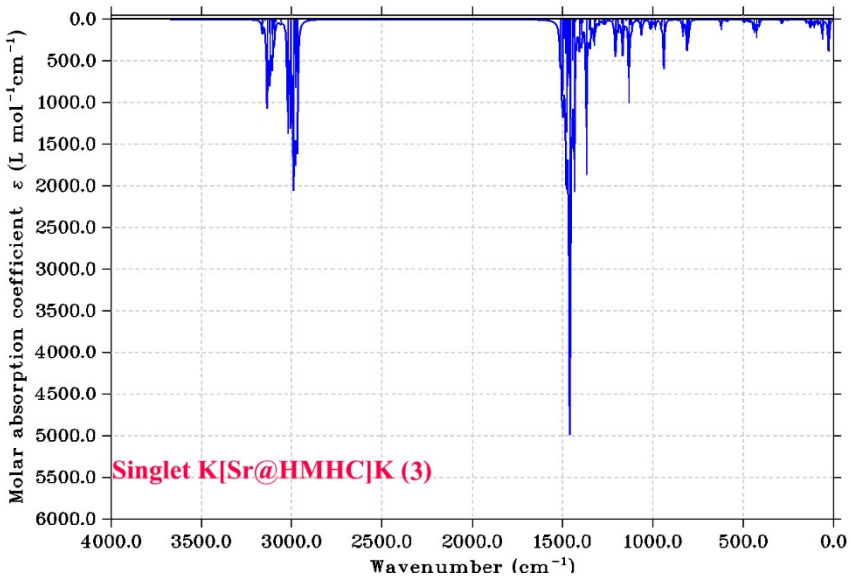


Fig. S7. Infrared spectrum of singlet $K^{\delta-}[Sr^{+}@HMHC]K^{\delta-}$ (**3**)

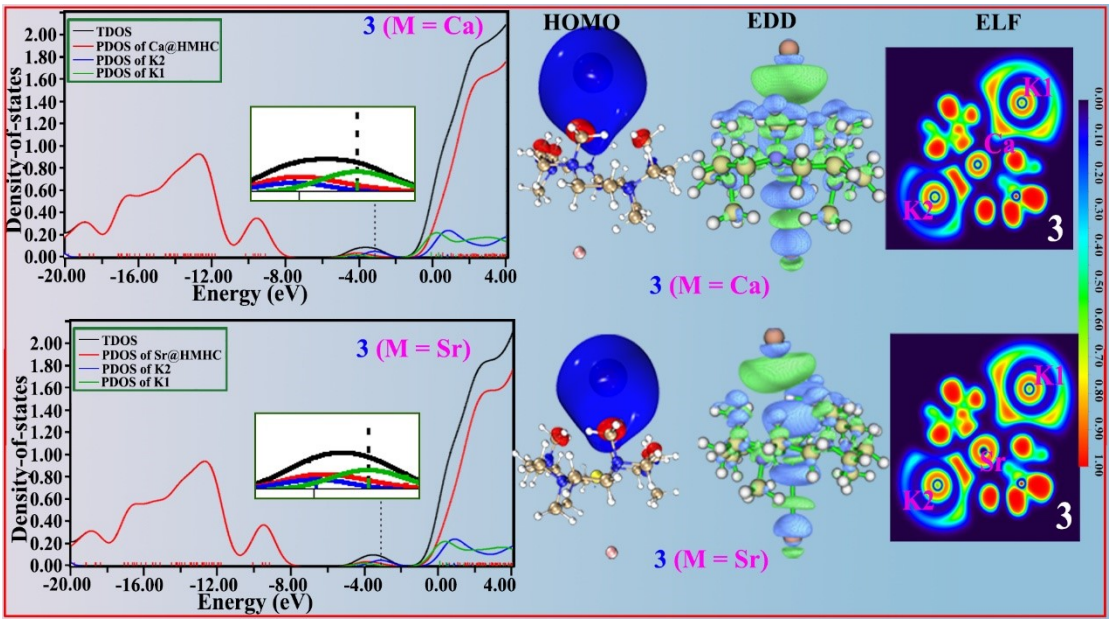
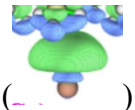
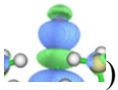
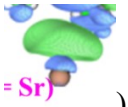


Fig. S8. Partial density of states (PDOS) maps, HOMOs and electron density difference (EDD) maps, and Electron localization function (ELF) maps of **3** of K[AE@HMHC]K (AE = Ca&Sr)

HOMO is the graph of molecular orbital Ψ, not the electron density graph. The electron density is the result of square integration of Ψ. The integrated graph is much smaller than the HOMO orbital graph itself. In EDD maps, the blue and green represent the decrease and increase of the electron density is depicted by blue and green isosurfaces. The green hemisphere around K2 () is obviously larger than that around K1 () for AE = Ca and the same phenomenon occurs in AE = Sr ( → ). For the NPA charge, there is about 0.4 |e| difference between **1** and **2**, which is not big in itself. Then, we think the EDD map can be used to explanation the different in ELF maps. For the ELF map, The ELF is defined as follows:

$$ELF(r) = 1/(1+[D(r)/D_0(r)]^2)$$

$D(r)$ reveals the excess kinetic energy density caused by Pauli repulsion, while $D_0(r)$ can be considered as the Thomas-Fermi kinetic energy density. The ELF's possible values are in the range of 0 ~ 1. ELF = 1 corresponds to the perfect localization and ELF = 1/2 corresponds to the electron gas. Then, ELF maps difference between **1** and **2** may be smaller compared with EDD map.

Reference:

1. A. D. Becke and K. E. Edgecombe, J. Chem. Phys., 1990, 92, 5397–5403

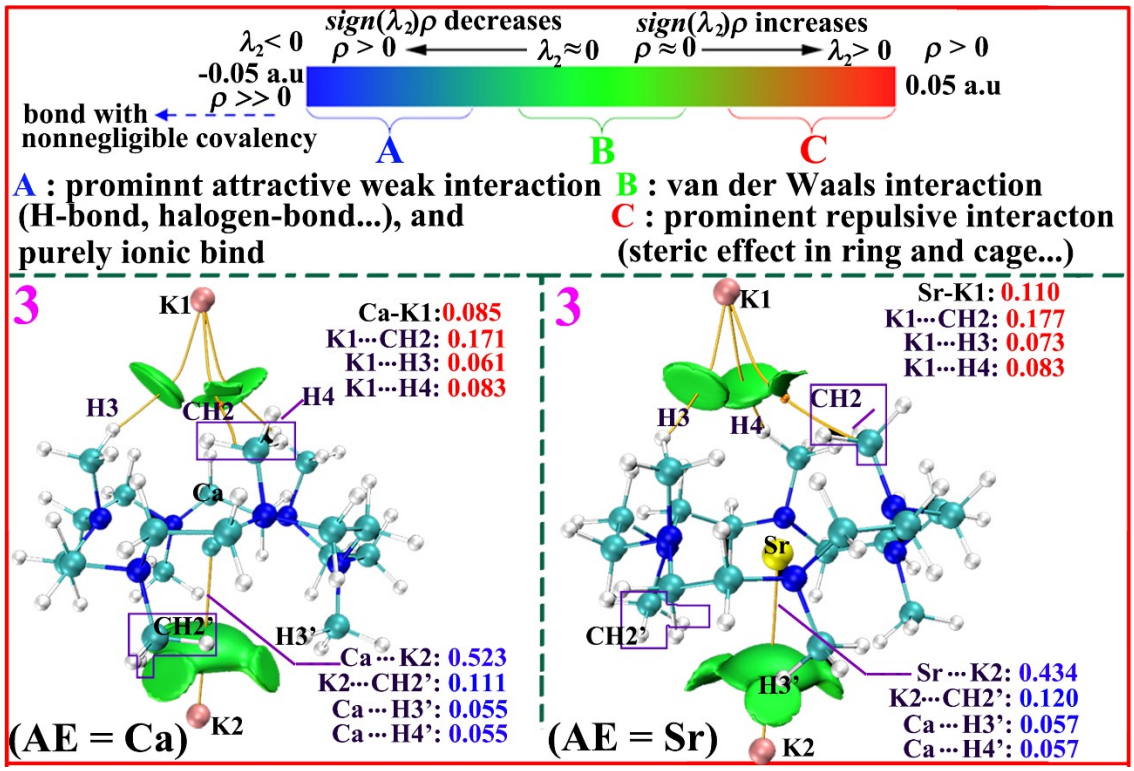


Fig. S9. Color-filled independent gradient model based on Hirshfeld partition (IGMH) isosurfaces and bond order based on the eigenvalues of natural adaptive orbitals (NAdOs of **3** of K[AE@HMHC]K (AE = Ca&Sr). ρ is electron density and the λ_2 term in sign(λ_2)ρ function is obtained as the second largest eigenvalue of the averaged electron density.

$$\text{sign}(\lambda_2)\rho: \quad \Omega(\mathbf{r}) = sign[\lambda_2(\mathbf{r})]\rho(\mathbf{r})$$

where $sign[\lambda_2(\mathbf{r})]$ means the sign of the second largest eigenvalue of electron density Hessian matrix at position **r**. The actual electron density used to evaluate $sign[\lambda 2(\mathbf{r})]$ is approximated by pro-molecular electron density. Promolecular density is simply constructed by superposing electron densities of free-state atoms and hence can be evaluated extremely rapidly

$$\rho^{\text{pro}}(\mathbf{r}) = \sum \rho_{A}^{\text{free.fit}}(\mathbf{r} - \mathrm{R_A})$$

where $\rho_{A}^{\text{free.fit}}$ is pre-fitted spherically averaged electron density of atom *A*.

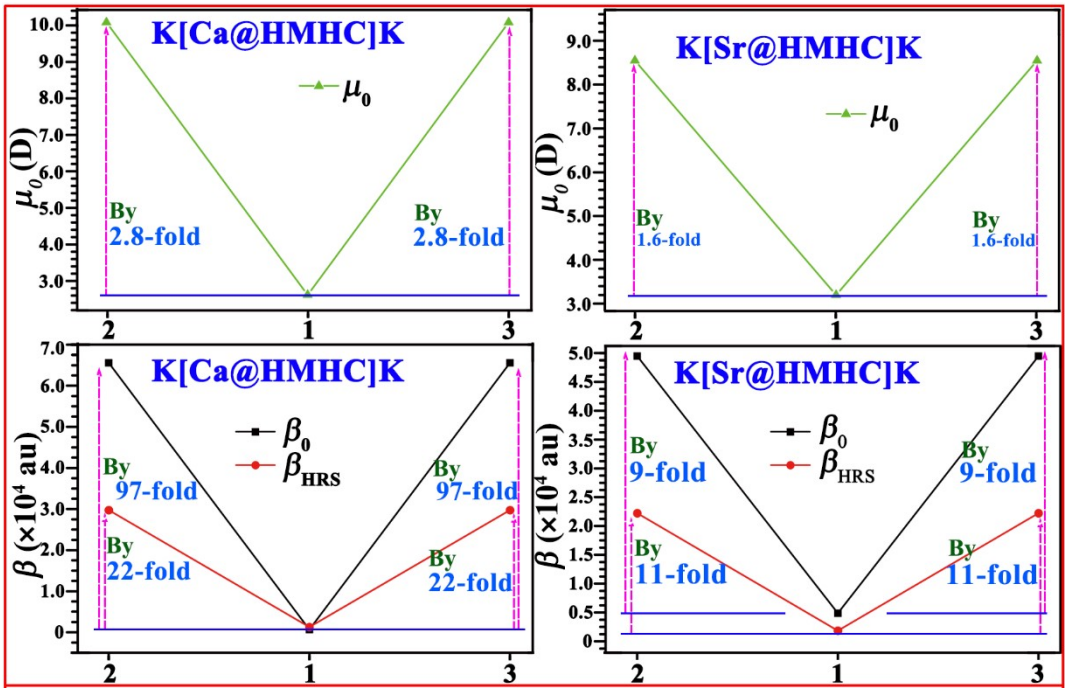


Fig. S10. Evolutions of β_0, β_{HRS}, and m_0 components with respect to the isomers for K[AE@HMHC]K (AE = Ca&Sr). It should be noted that these values are computed as $(\mu_{0,2} - \mu_{0,1})/\mu_{0,1}$ and $(\beta_{i,2} - \beta_{i,1})/\beta_{i,1}$, where i = 0 and HRS.

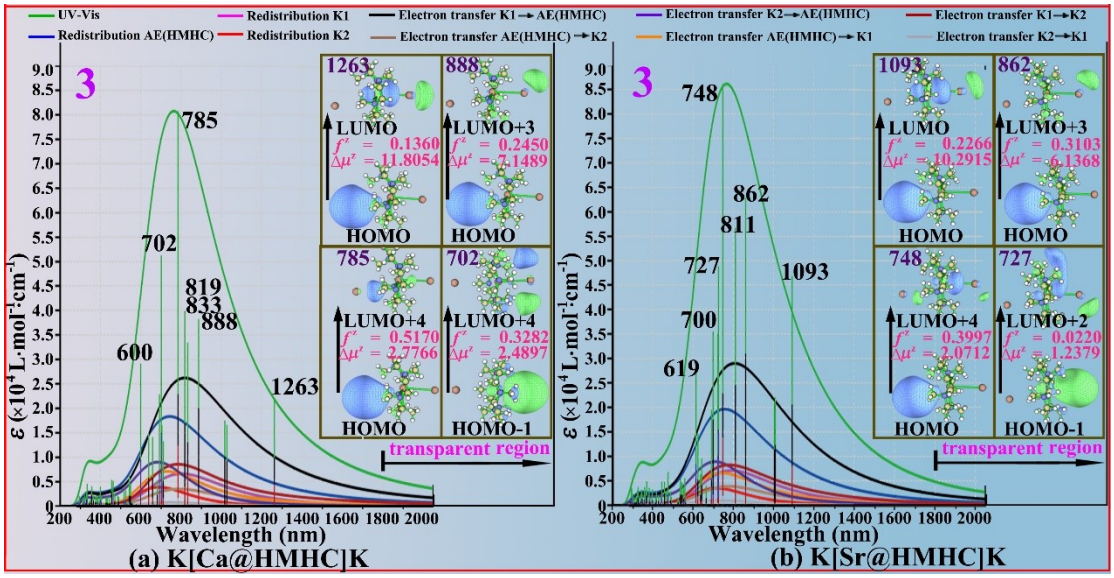


Fig. S11. Charge-transfer spectra (CTS) and real space representation of hole and electron distributions (isovalue = 0.02). (a) **3** of K[Ca@HMHC]K and (b) **3** of K[Ca@HMHC]K. The Gaussian function with full width at half-maximum of 0.667 eV was employed for broadening the theoretical data as spectrum curves.

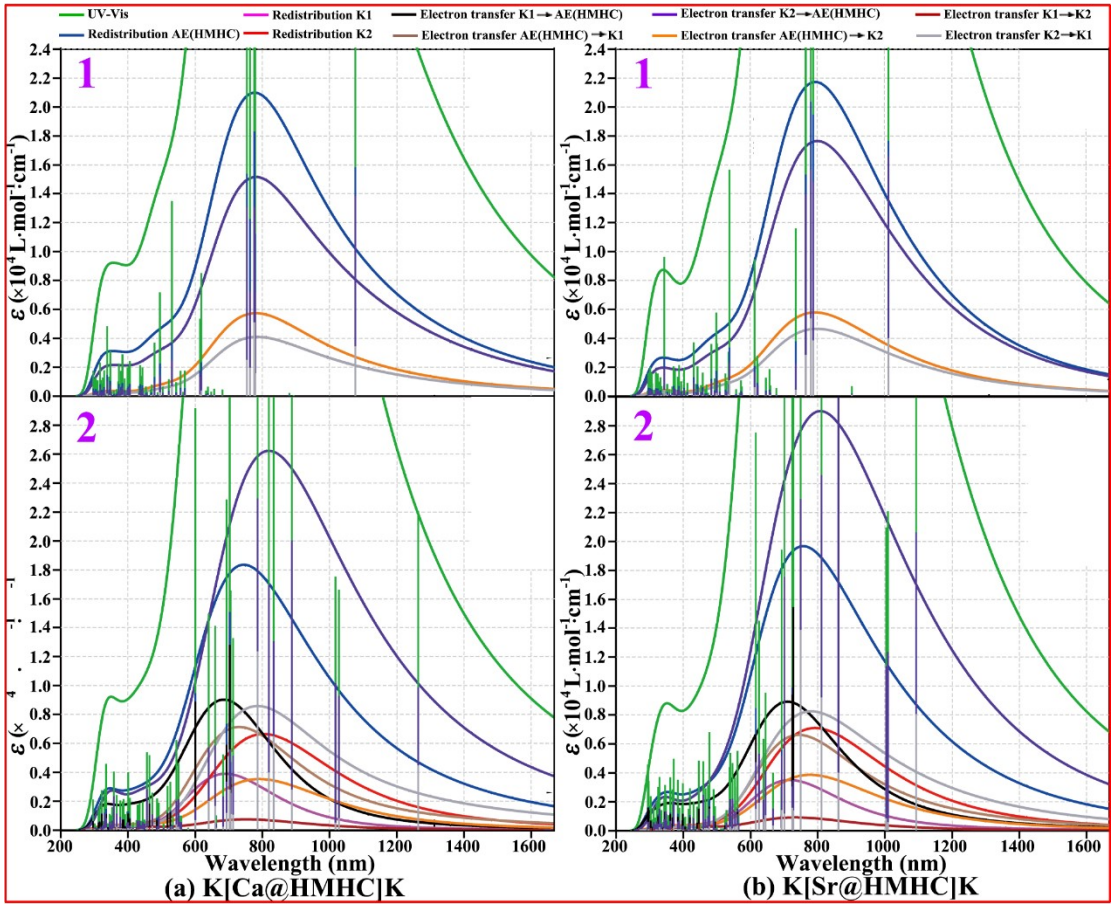


Fig. S12 Charge-transfer spectra (CTS) the spectra with a zoom of Y-axis in the 0 to 3.0×10^4 L mol^{-1} cm^{-1}