Supporting Information

A supported Cr-Cr sextuple bond in an all-metal cluster

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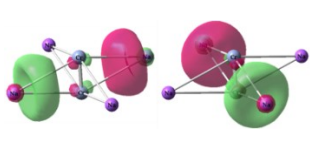
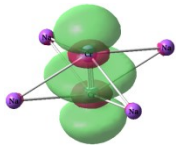
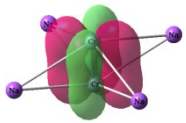
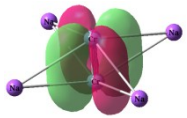
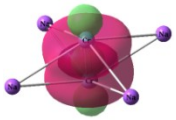
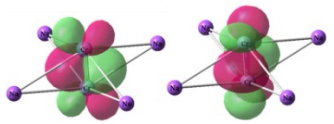
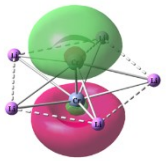
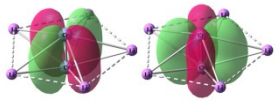
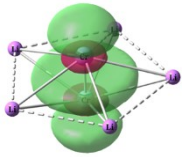
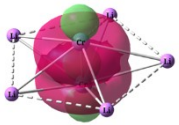
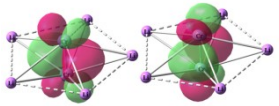
Table S1. The orbital component analysis results of the model structure D_{4h}-$\mathbf{Cr_2Na_4}$ calculated at the CCSD/6-311G(d) level.

$\mathbf{Cr_2Na_4}$	HOMO	HOMO-1	HOMO-2	HOMO-3	HOMO-4	HOMO-5
Diagrams						
Energy/eV	-4.13	-7.17	-7.68	-7.75	-11.16	-11.41
Component	Na_4©3s~77.6% Na_4©3$p_{x,y}$~16.1%	Na_4©3s~12.5% Cr_2©4s~67.6% Cr_2©3d_0~12.1%	Na_4©3$p_{x,y}$~4.7% Cr_2©3d_{+2}~91.53%	Na_4©3s~25.7% Na_4©3$p_{x,y}$~10.3% Cr_2©3d_{-2}~62.4%	Na_4©3s~11.2% Cr_2©4s~35.0% Cr_2©3d_0~51.5%	Cr_2©3$d_{+1,-1}$~86.4% Na_4©3s~6.9%

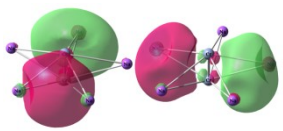
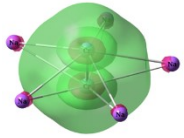
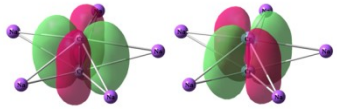
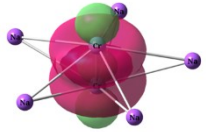
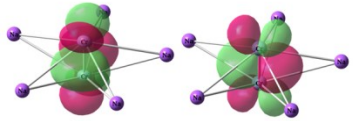
The coefficient of each orbital is given by the contribution of the Na_4 and Cr_2 fragments.

Table S2. The orbital component analysis results of D_{5h}-$\mathbf{Cr_2Li_5}$ calculated at the CCSD/6-311G(d) level (only present the α orbitals).

$\mathbf{Cr_2Li_5}$	HOMO(SOMO)	HOMO-1(α)	HOMO-2(α)	HOMO-3(α)	HOMO-4(α)	HOMO-5(α)
Diagrams						
Energy/eV	-4.60	-5.06	-7.63	-8.40	-11.31	-11.38
Component	Cr_2©4s~96.9%	Li_5©2s~79.1% Li_5©$2p_{x,y}$~15.6%	Li_5©2s~30.1% Li_5©$2p_{x,y}$~15.1% Cr_2©$3d_{-2}$~52.6%	Cr_2©4s~80.1% Cr_2©$3d_0$~13.4%	Li_5©2s~14.1% Cr_2©4s~34.1% Cr_2©$3d_0$~44.8%	Li_5©2s~11.4% Cr_2©$3d_{+1,-1}$~79.1%

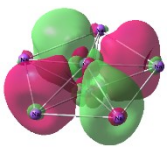
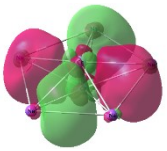
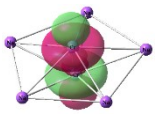
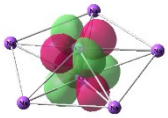
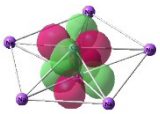
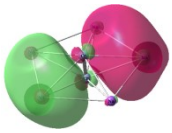
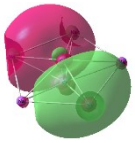
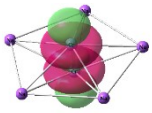
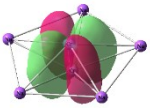
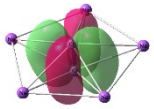
The coefficient of each orbital is given by the contribution of the Li_5 and Cr_2 fragments.

Table S3. The orbital component analysis results of D_{5h}-$\mathbf{Cr_2Na_5^+}$ calculated at the CCSD/6-311G(d) level.

$\mathbf{Cr_2Na_5^+}$	HOMO	HOMO-1	HOMO-2	HOMO-3	HOMO-4
Diagrams					
Energy/eV	-7.67	-10.63	-10.96	-14.51	-14.71
Component	Na_5©3s~73.1% Na_5©3$p_{x,y}$~20.9%	Na_5©3s~15.0% Cr_2©4s~61.0% Cr_2©3d_0~12.0%	Na_5©3s~20.7% Na_5©3$p_{x,y}$~10.9% Cr_2©3$d_{+2,-2}$~64.8%	Na_5©3s~6.9% Cr_2©4s~29.4% Cr_2©3d_0~56.5%	Cr_2©3$d_{+1,-1}$~89.8%

The coefficient of each orbital is given by the contribution of the Na_5 and Cr_2 fragments.

Table S4. The patterns and corresponding occupancy numbers of active orbitals of D_{5h}-$Cr_2Na_5^+$ with CASSCF(10,10)/6-311G(d) level.

Diagram					
Occupy number	0.020	0.020	0.197	0.314	0.314
Diagram					
Occupy number	1.992	1.992	1.798	1.676	1.676

The Cr-Cr length is 1.579 Å.

The D_{5h}-$Cr_2Na_5^+$ structure was optimized at the CASSCF(10,10)/6-311G(d) level. The final Cr-Cr length shows 1.579 Å, which is slightly longer than that with other levels (Table S5). The active orbitals of D_{5h}-$Cr_2Na_5^+$ are including two quasi-π orbitals, two δ orbitals and one σ bonding orbital, as well as their corresponding anti-bonding orbitals. The lower two Cr-Cr π orbitals and one σ orbital were not included in the active space due to the energy difference over 2 eV at the B3LYP/6-311G(d) level.

Table S5. The R_{Cr-Cr}, WBI_{Cr-Cr}, ω_{Cr-Cr}, NPA_{Cr} and the δ bond energy data of Cr-Cr bonding structures calculated at the different methods and basis sets.

Molecule	Methods	Sym	R_{Cr-Cr} (Å)	NPA_{Cr} (|e|)	WBI_{Cr-Cr}	ω_{Cr-Cr} (cm^{-1})	δ– energy (eV)
Cr_2	CCSD/6-311G(d)	D	1.530	0.000	6.018	987.09	-3.780
Cr_2Na_4	CCSD/6-311G(d)	D_{4h}	1.561	0.303	5.399	897.52	-5.514
	TPSSH/6-311G(d, p)	D_{4h}	1.570	0.310	5.383	871.38	-4.921*
	B3LYP/6-311G(d)	D_{4h}	1.572	0.361	5.301	827.01	-7.677
$Cr_2Na_5^0$	B3LYP/6-311G(d)	D_{5h}	1.576	0.084	4.827	847.25	-5.144
	BP86/Def2-TZVP	D_{5h}	1.613	-0.400	5.478	740.09	-4.441
$Cr_2Na_5^+$	B3LYP/6-311G(d)	D_{5h}	1.562	0.333	5.348	895.67	-9.950
	CCSD/6-311G(d)	D_{5h}	1.571	0.390	5.251	839.87	-7.670
	CASSCF(10,10)/6-311G(d)	D_{5h}	1.579	0.720†	/	/	/
	CCSD/Def2-TZVP	D_{5h}	1.574	-0.281	5.746	822.99	-10.481
	BP86/Def2-TZVP	C1	1.600	-0.351*	5.678	772.22	-7.650*
	B3LYP/6-311+G(d)	C1	1.569	-1.060	6.327	860.41	-8.494
$Cr_2Li_5^0$	CCSD/6-311G(d)	D_{5h}	1.591	0.151	/	821.82	-5.559
	B3LYP/6-311G(d)	D_{5h}	1.590	0.196	4.701	813.58	-5.056
	CCSD/def2-TZVP	D_{5h}	1.589	0.307	5.481	/	-7.388
	BP86/def2-TZVP	D_{5h}	1.627	-0.459	5.476	717.33	-4.738
$Cr_2Li_5^+$	CCSD/6-311G(d)	D_{5h}	1.570	0.381	5.238	884.56	-7.207

*average value.
†mulliken charge.

Table S6. The NPA, Generalized Atomic Polar Tensors (GAPT) and Mulliken charge of Cr in our manuscript calculated at the B3LYP/6-311G(d) level.

Molecule	$R_{Cr\text{-}Cr}$(Å)	NPA_{Cr}(|e|)	$GAPT_{Cr}$ (|e|)	$Mulliken_{Cr}$
Cr_2	1.530	0.000	0.000	0.000
$Cr_2(CHO_2)_4$	1.731	1.094	1.124	1.025
$Cr_2(Ar')_2$	1.605	0.763	0.215	0.765
D_{4h}-Cr_2Na_4	1.561	0.303	-0.088	0.495
D_{5h}-$Cr_2Na_5^0$	1.576	0.084	-0.123	0.342
D_{5h}-$Cr_2Na_5^+$	1.562	0.333	0.040*	0.579
D_{5h}-$Cr_2Li_5^0$	1.591	0.151	-0.023	0.498
D_{5h}-$Cr_2Li_5^+$	1.570	0.381	-0.089	0.669

*average value

Table S7. The topological analysis results at Cr-Cr's BCP calculated at the B3LYP/6-311G(d) level.

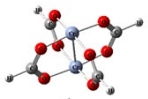
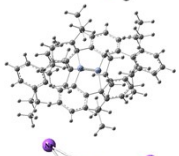
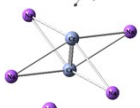
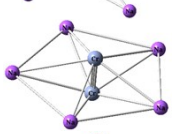
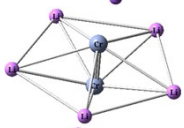
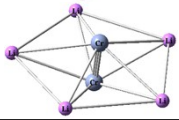
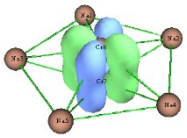
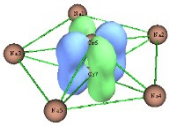
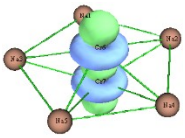
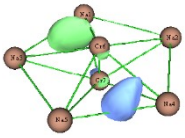
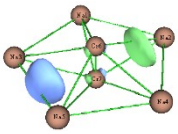
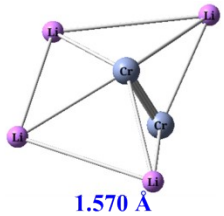
Molecule	diagram	R_{Cr-Cr} (Å)	Laplacian of electron density	G(r)	V(r)	|V(r)|/G(r)	$\rho_{(BCP)}$ (a.u.)
Cr_2		1.530	2.492	1.102	-1.581	1.435	0.448
$Cr_2(CHO_2)_4$		1.731	1.156	0.525	-0.762	1.451	0.275
$Cr_2(Ar')_2$		1.605	1.875	0.832	-1.196	1.438	0.367
D_{4h}-Cr_2Na_4		1.561	2.238	0.977	-1.394	1.427	0.408
D_{5h}-Cr_2Na_5		1.576	2.112	0.926	-1.323	1.429	0.393
D_{5h}-$Cr_2Na_5^+$		1.562	2.218	0.973	-1.392	1.431	0.408
D_{5h}-Cr_2Li_5		1.591	1.983	0.872	-1.248	1.431	0.378
D_{5h}-$Cr_2Li_5^+$		1.570	2.139	0.940	-1.345	1.431	0.399

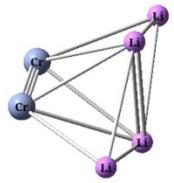
Table S8. The NEVPT2 calculation results following CASSCF(10,11)/6-311G(d) for D_{5h}-$Cr_2Na_5^+$ in ORCA 4.2.1.

Five mainly occupied orbitals in active space and their occupy number are given below. The occupy number of other six orbitals is 0.313, 0.314, 0.197, 0.043, 0.043 and 0.026 respectively.

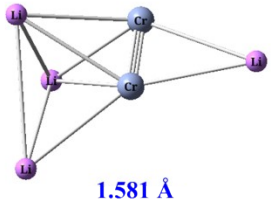
Diagram					
Occupy number	1.680	1.680	1.798	1.952	1.952



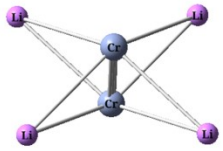
1.570 Å
Cs
0.0



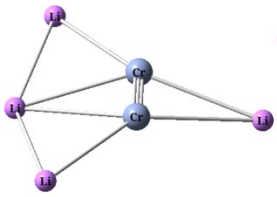
1.572 Å
C2v
0.04



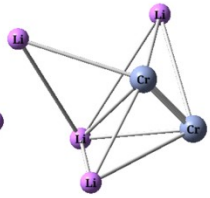
1.581 Å
Cs
0.9



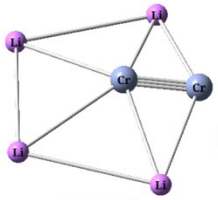
1.559 Å
D4h
1.0



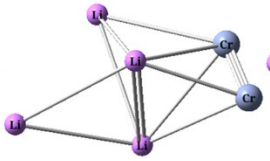
1.562 Å
Cs
1.1



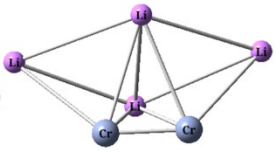
1.564 Å
Cs
2.4



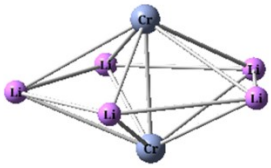
1.573 Å
Cs
3.3



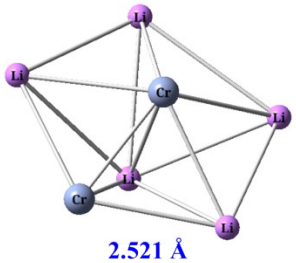
1.581 Å
Cs
7.8



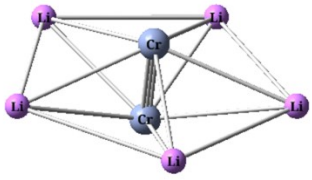
1.733 Å
C2v
37.7



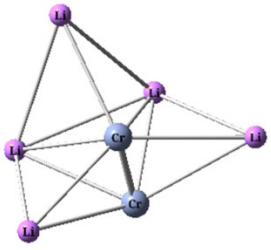
2.506 Å
C1
0.0



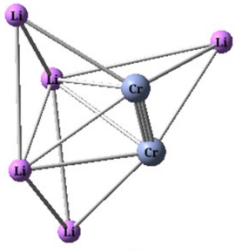
2.521 Å
Cs
0.5



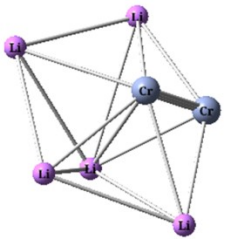
1.577 Å
D5h
46.3



1.581 Å
Cs
54.0



1.571 Å
Cs
57.5



1.579 Å
Cs
58.7

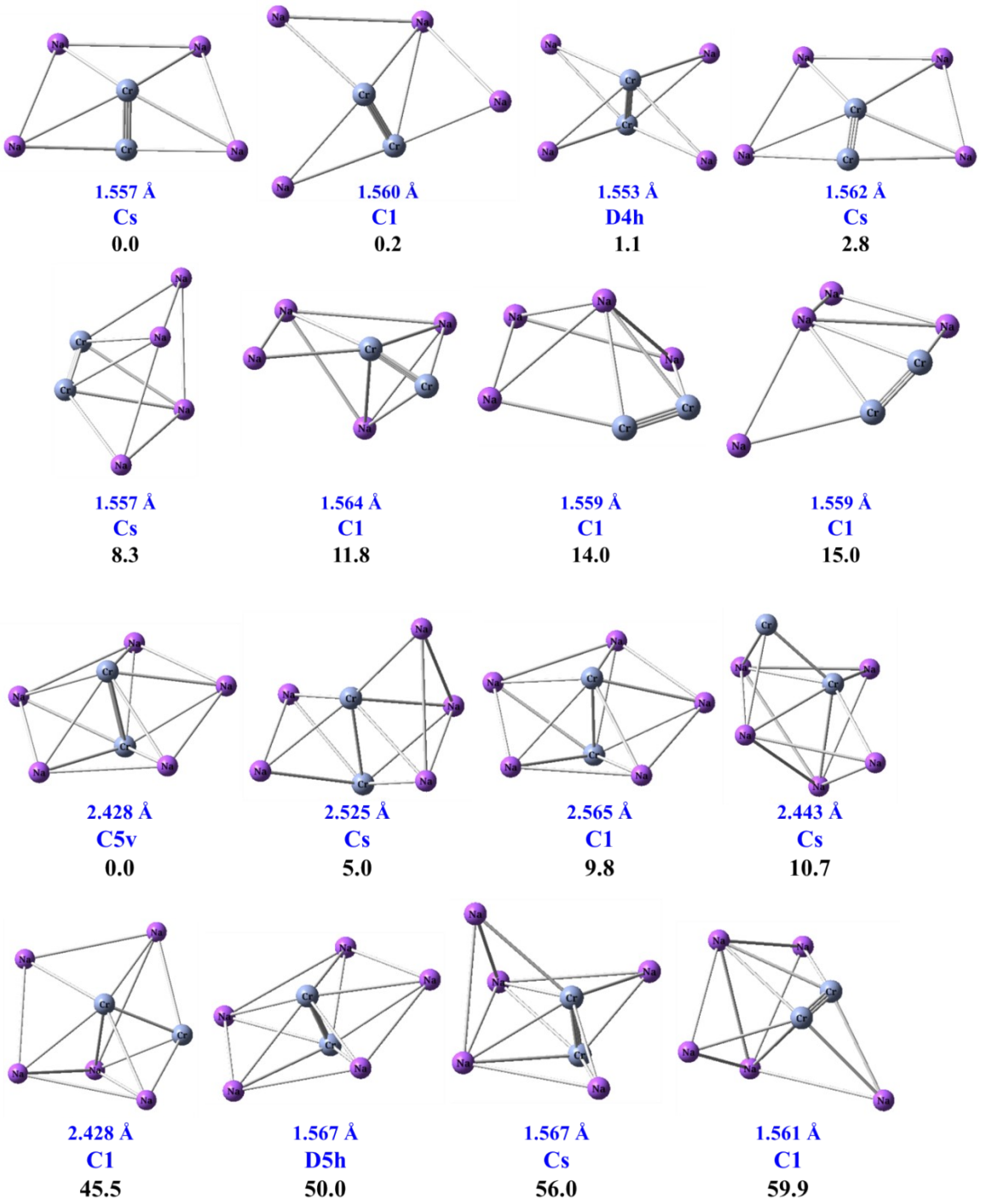


Fig. S1. The lowest-lying isomers of Cr_2Li_4, Cr_2Li_5, Cr_2Na_4 and Cr_2Na_5 with energy in kcal/mol. The distance between Cr-Cr is also given. These structures are re-optimized and filtrated at the B3LYP/6-31G(d) level after searched by CALYPSO program. Structures with imaginary frequencies are considered.

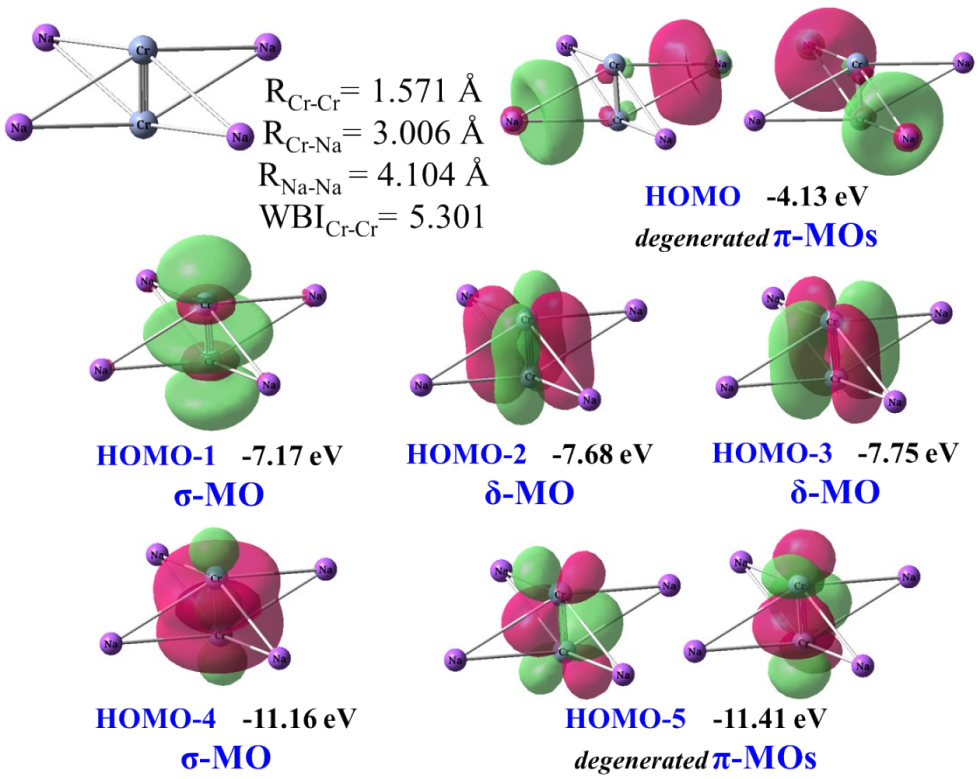


Fig. S2. The skeleton and the important FMOs of the D_{4h}-Cr_2Na_4 at the CCSD/6-311G(d) level.

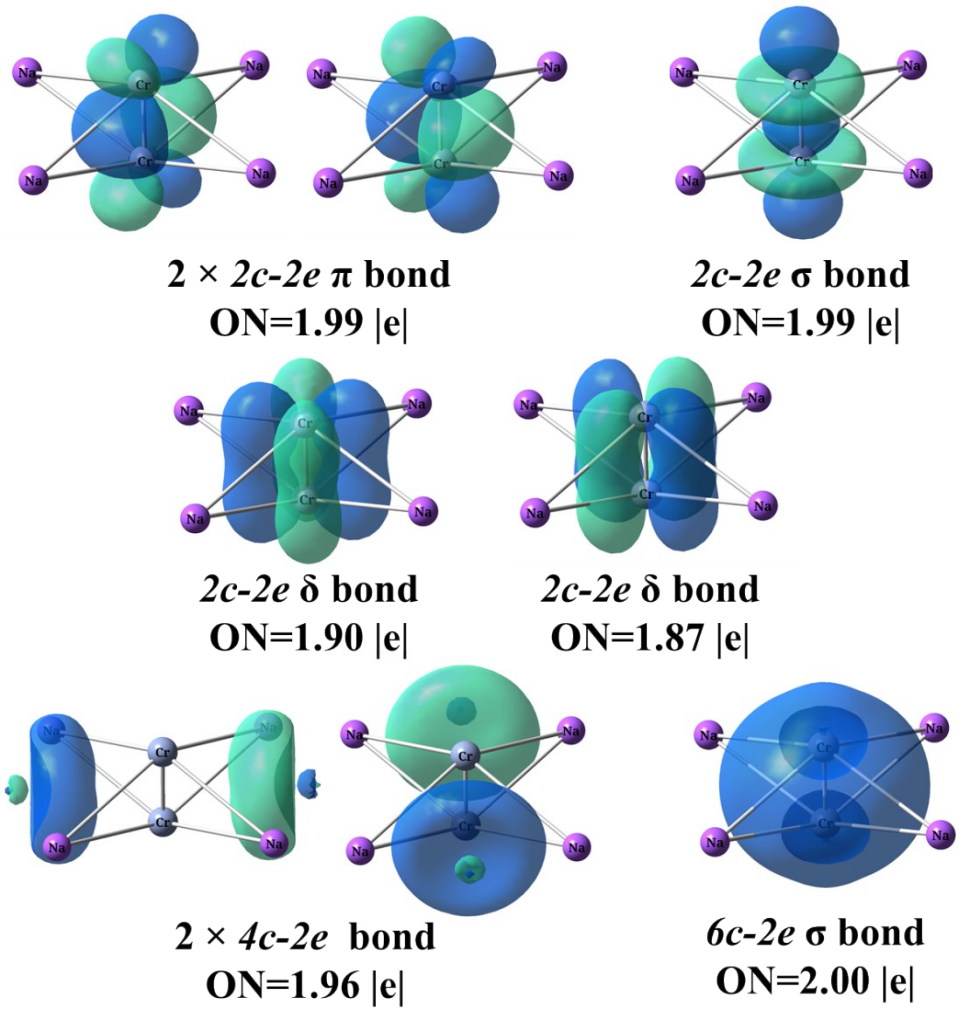


Fig. S3. The AdNDP pattern of D_{4h}-Cr_2Na_4 at the CCSD/6-311G(d) level.

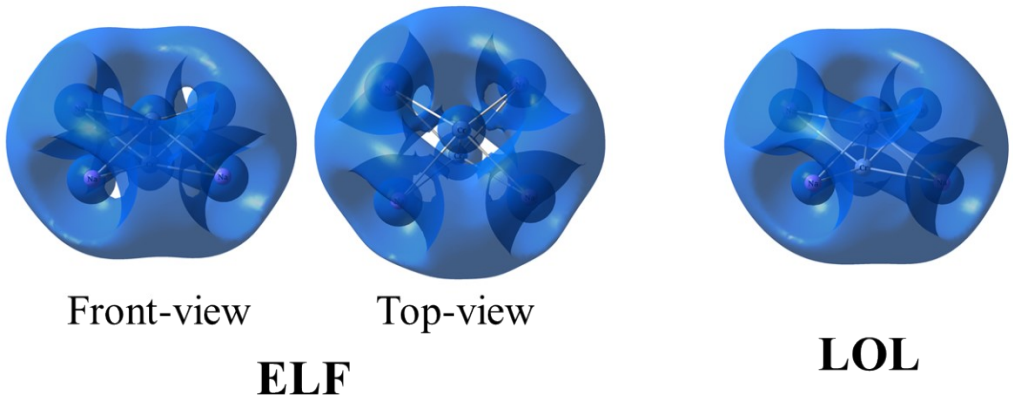


Fig. S4. The ELF (surface value = 0.40) and LOL (surface value = 0.20) plots of D_{4h}-Cr_2Na_4 at the CCSD/6-311G(d) level.

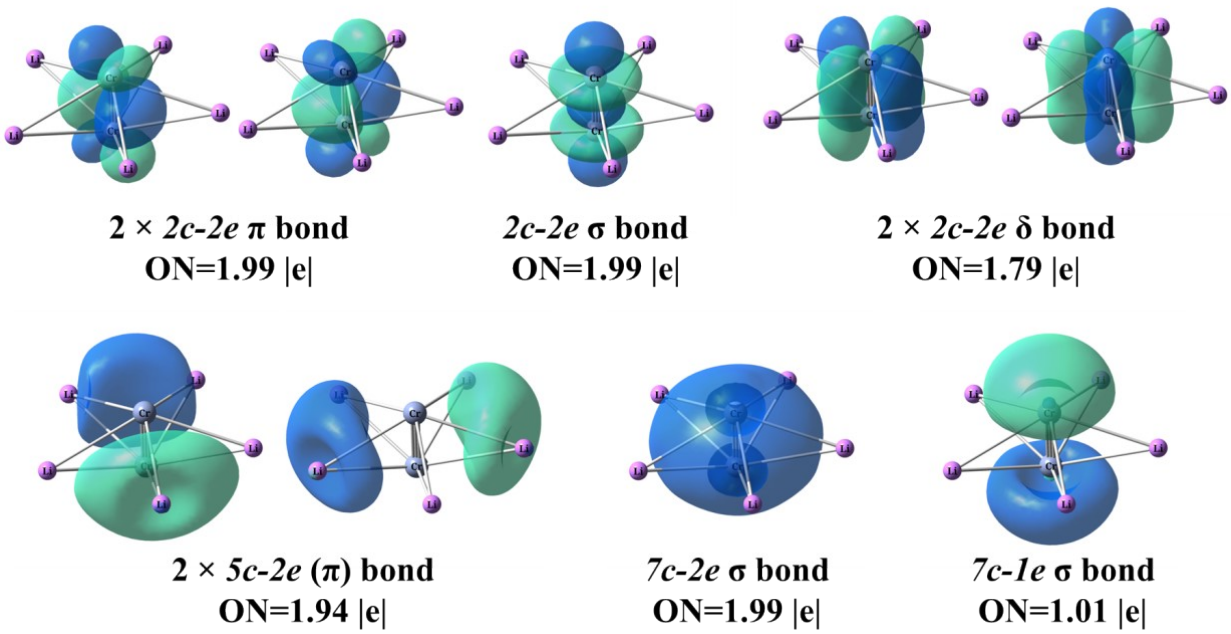


Fig. S5. The AdNDP patterns of D_{5h}-Cr_2Li_5 at the CCSD/6-311G(d) level.

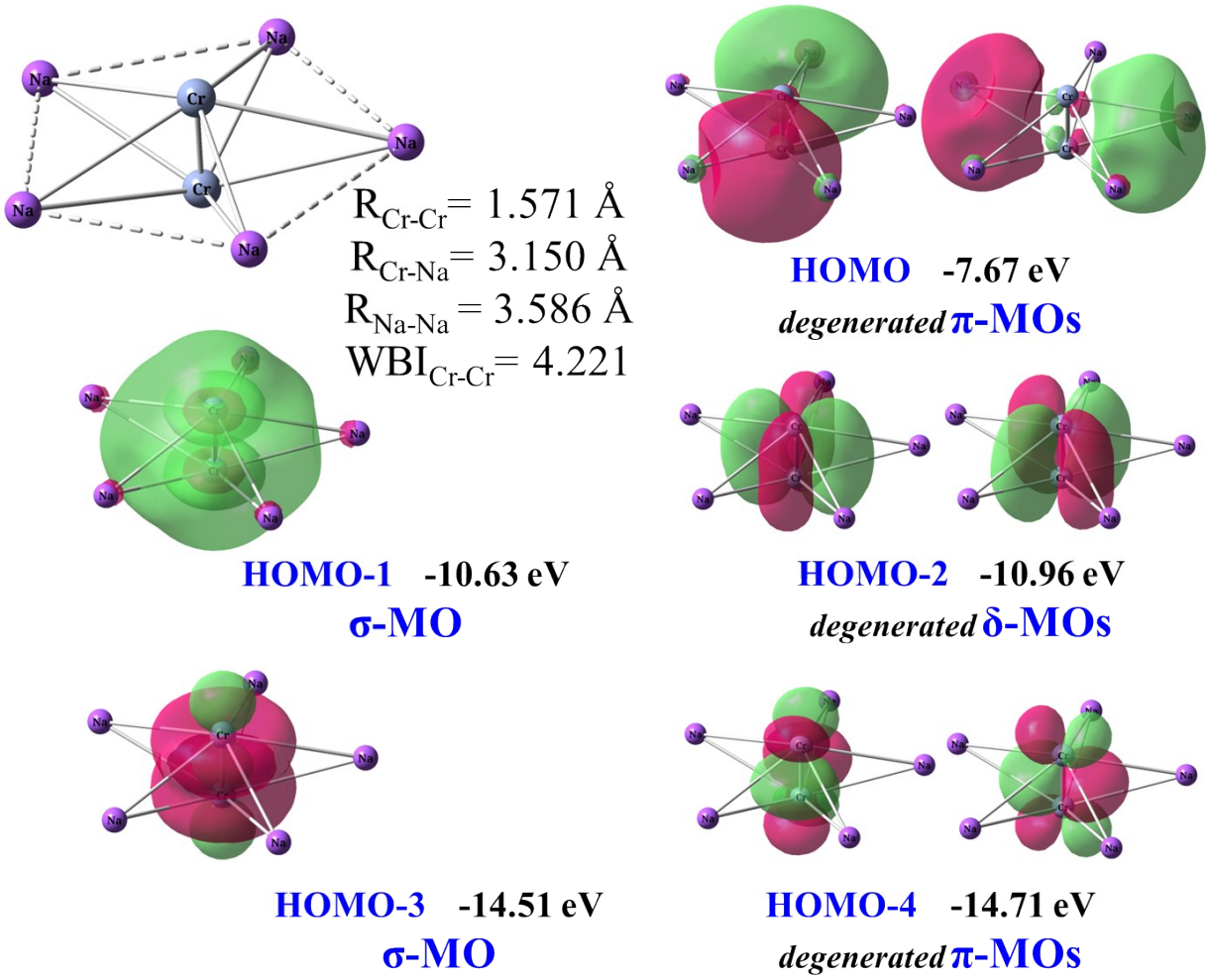


Fig. S6. The structure information and the mainly frontier molecular orbitals of D_{5h}-$Cr_2Na_5^+$ at the CCSD/6-311G(d) level.

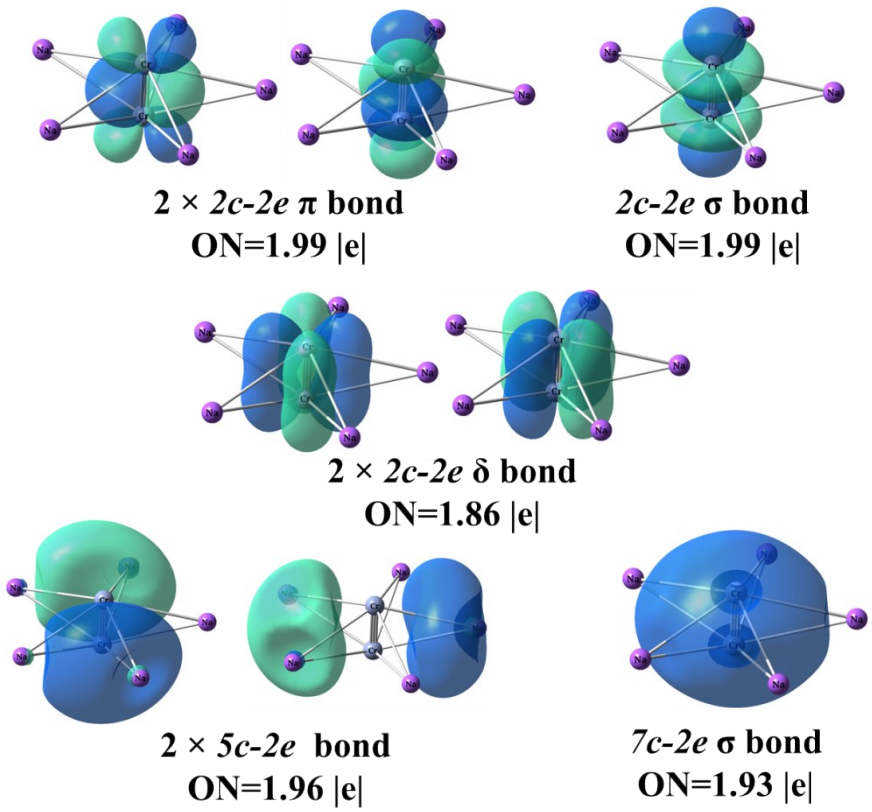
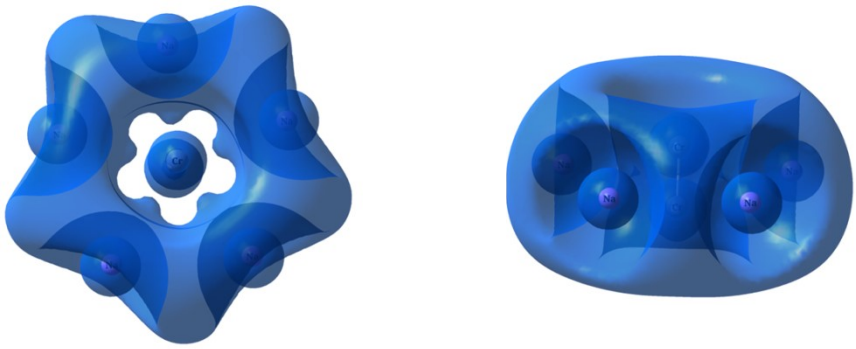
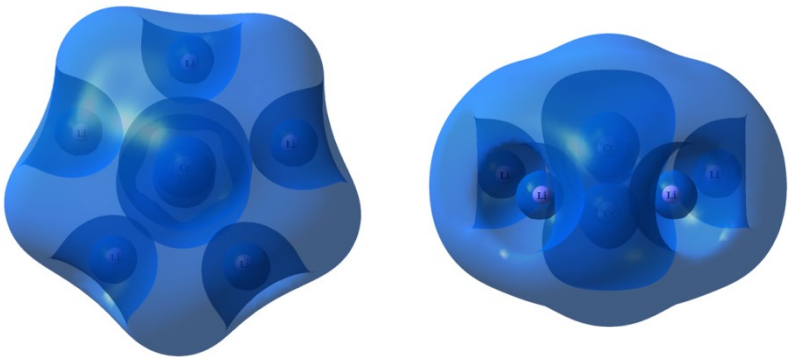


Fig. S7. The AdNDP patterns of D_{5h}-$Cr_2Na_5^+$ at the CCSD/6-311G(d) level.



ELF-Top-view **ELF-**Front-view

Fig. S8. The ELF plots (iso-surface = 0.40) of D_{5h}-$Cr_2Na_5^+$ at the CCSD/6-311G(d) level.



ELF-Top-view **ELF-**Front-view

Fig. S9. The ELF plots (surface value = 0.40) of D_{5h}-Cr_2Li_5 at the CCSD/6-311G(d) level.

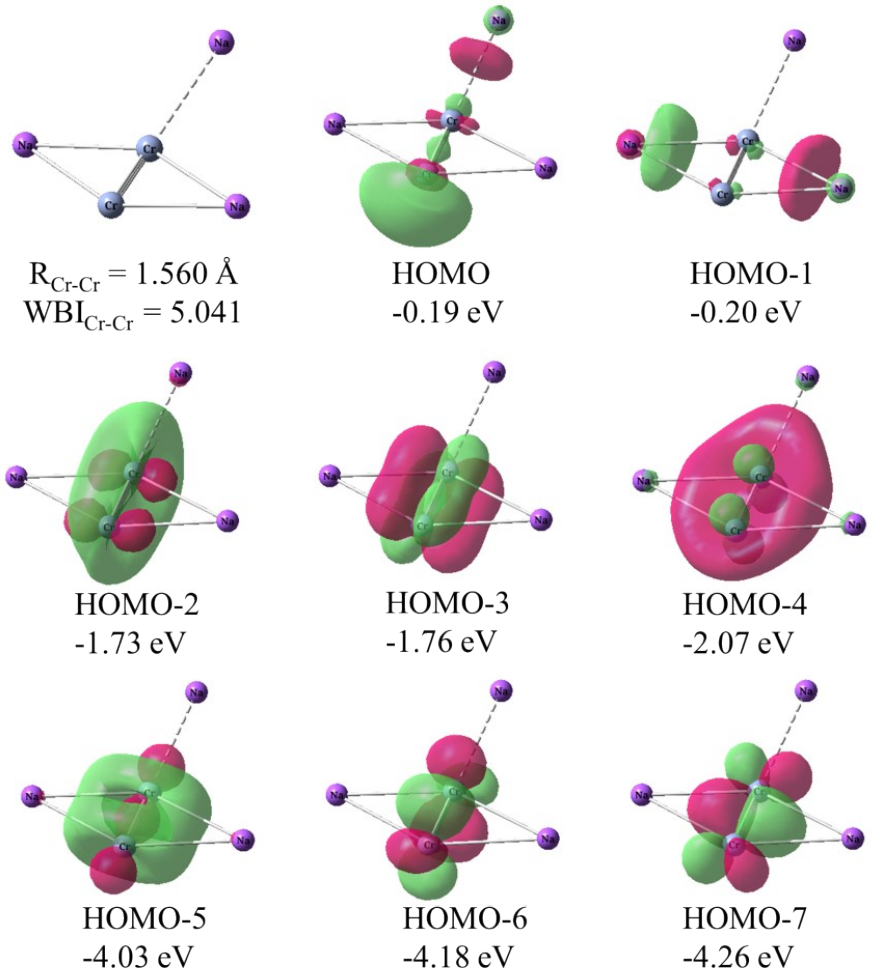


Fig. S10. The structure information and the mainly frontier molecular orbitals of C_{2v}-$Cr_2Na_3^-$ at the B3LYP/6-311G(d) level.

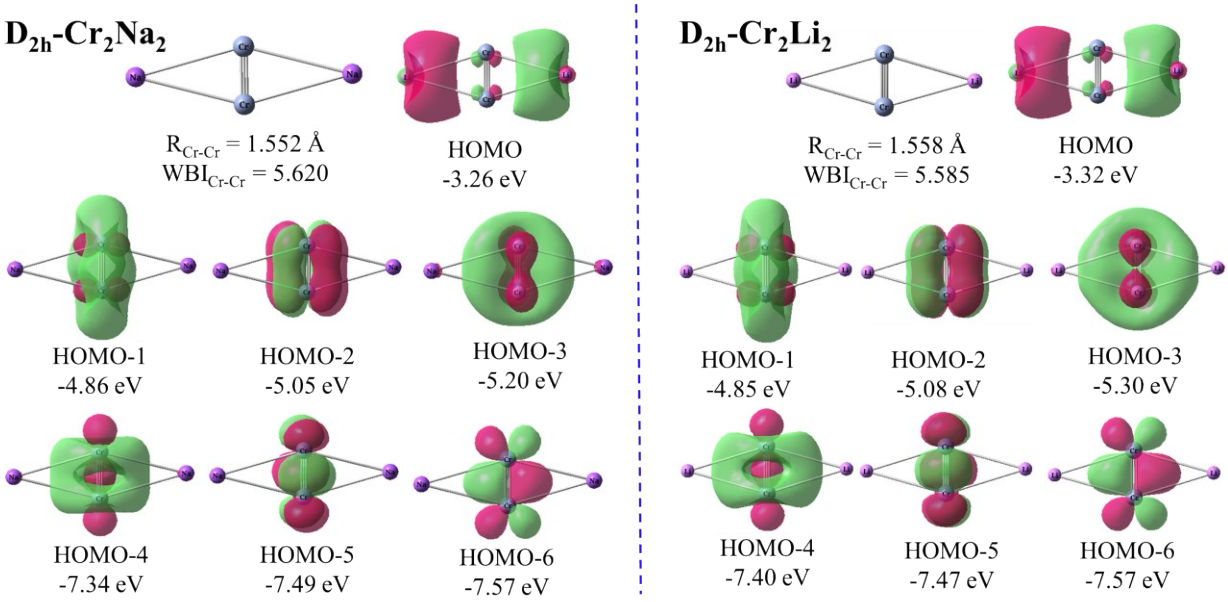


Fig. S11. The structure information and the mainly frontier molecular orbitals of D_{2h}-Cr_2Na_2 and D_{2h}-Cr_2Li_2 optmized at the B3LYP/6-311G(d) level.

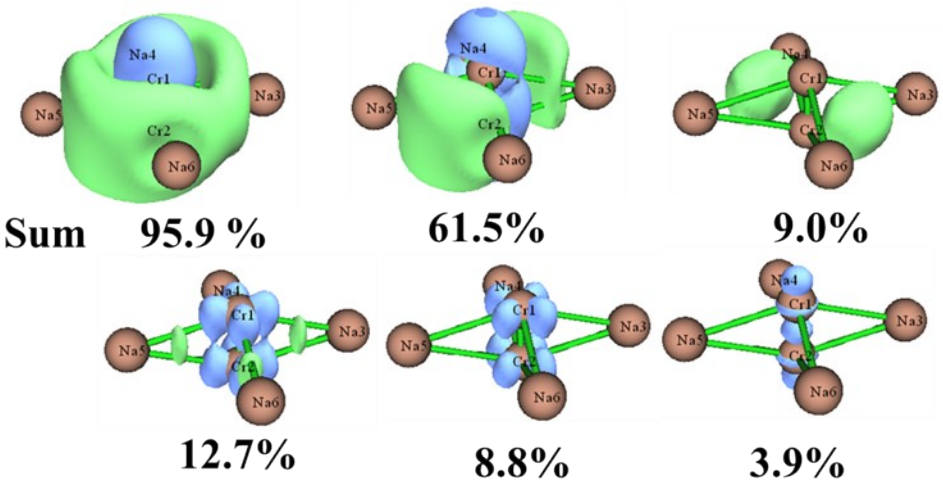


Fig. S12. The mainly five NOCV pairs and their corresponding contribution (Donation from Blue to Green area) of ETS-NOCV calculation for D_{4h}-Cr_2Na_4 at the B3LYP/6-311G(d) level.

The total of mainly 5 NOCV pairs' contribution is up to 95.9%, and the electrons are mainly transferred from the Cr_2 fragment to the Na_4 fragment, which proves that using alkali metal atoms from the radial direction of Cr-Cr cannot form new π bonds like that in Zn-Zn and Be-Be.

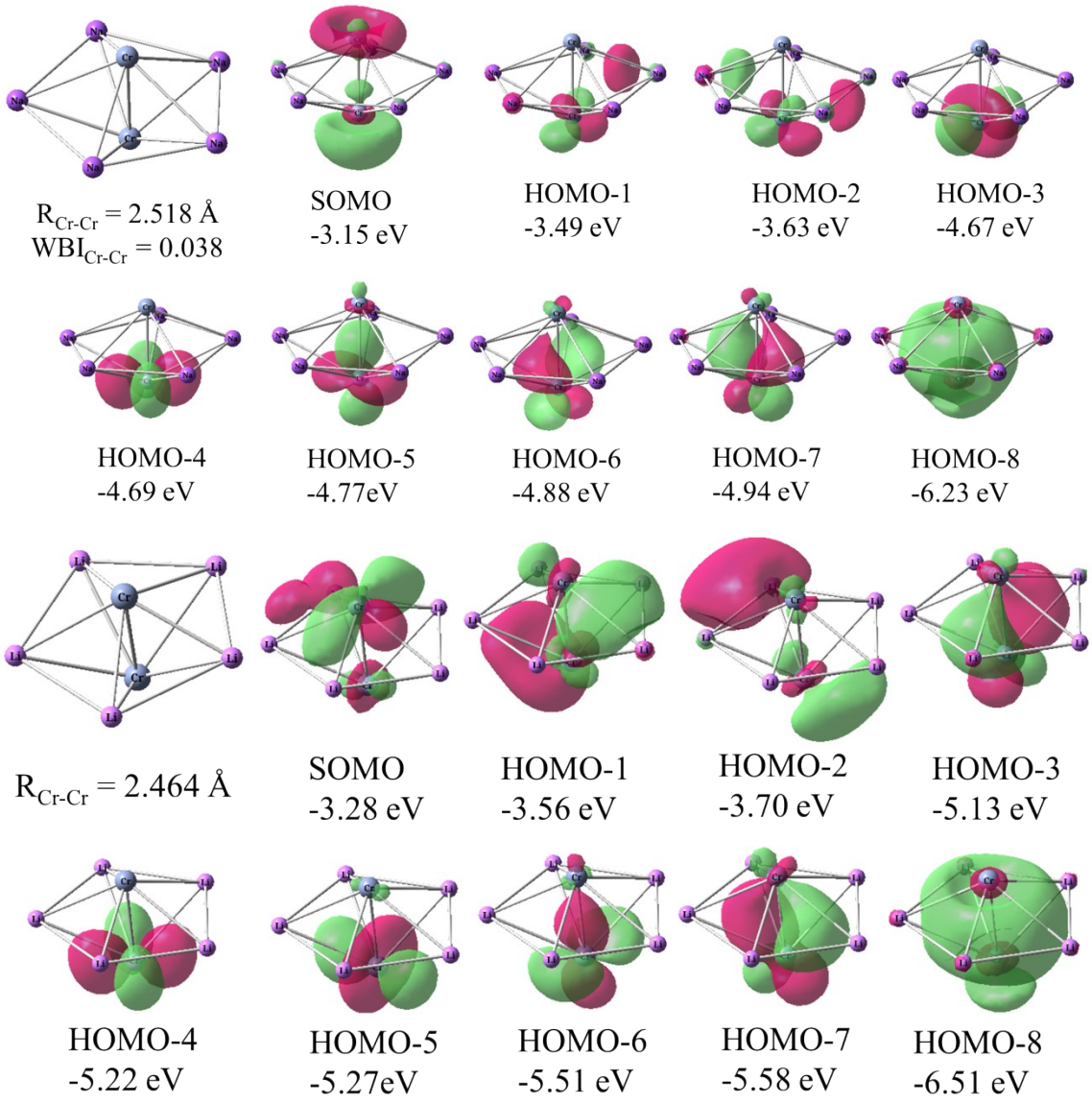


Fig. S13. The structure information and the mainly frontier molecular orbitals (only present α orbitals) of D_{5h}-Cr_2Na_5 (top) and D_{5h}-Cr_2Li_5 (bottom) with longer Cr-Cr length calculated at the B3LYP/6-311G(d) level.

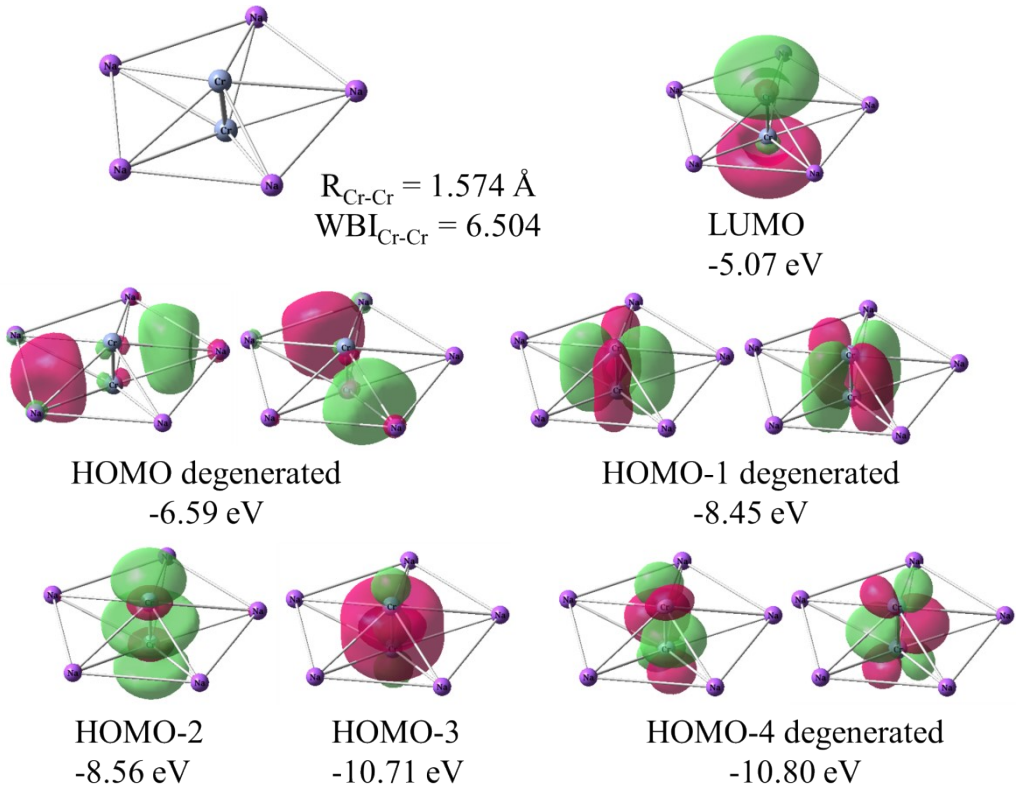


Fig. S14. The structure information and the mainly frontier molecular orbitals of D_{5h}-$Cr_2Na_5^+$ calculated at the B3LYP//6-311G(d)/SDD level based on the structure optimized at the CCSD/6-311G(d) level.

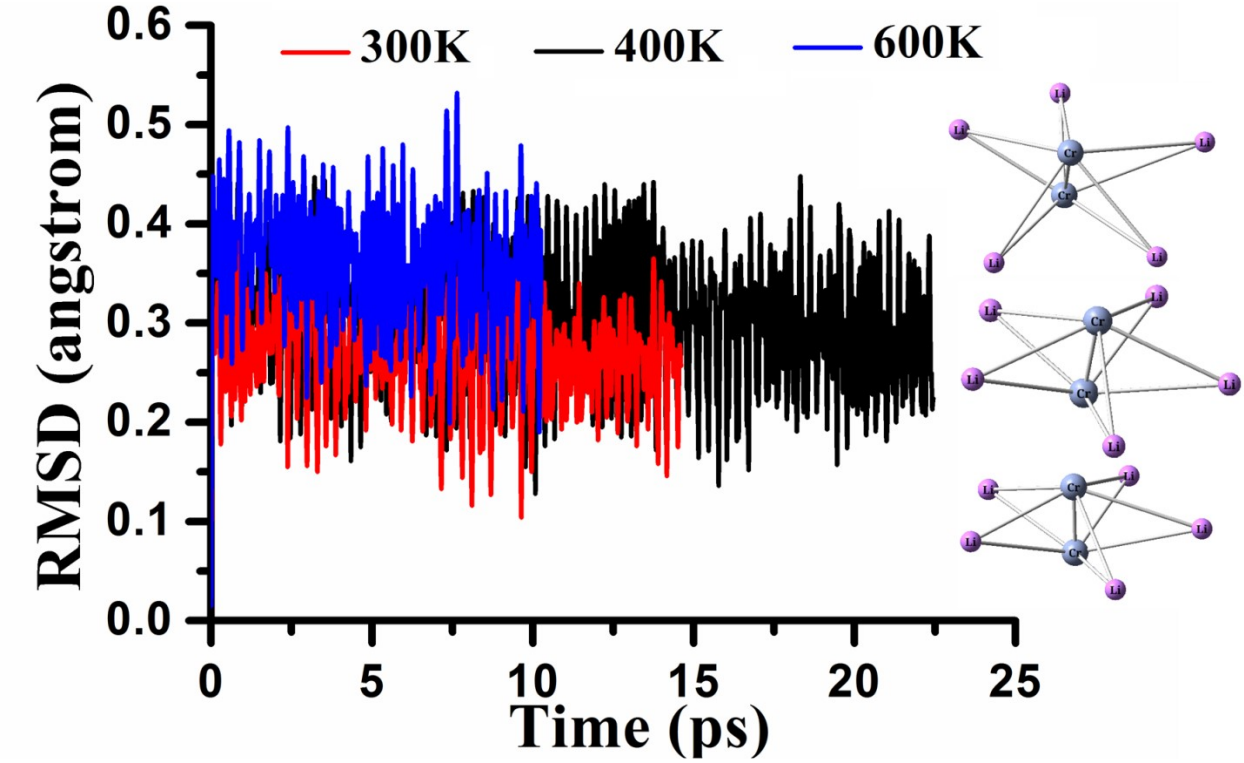


Fig. S15. The RMSD of D_{5h}-Cr_2Li_5 during BOMD calculation at the B3LYP/6-31G(d) level with different temperature.

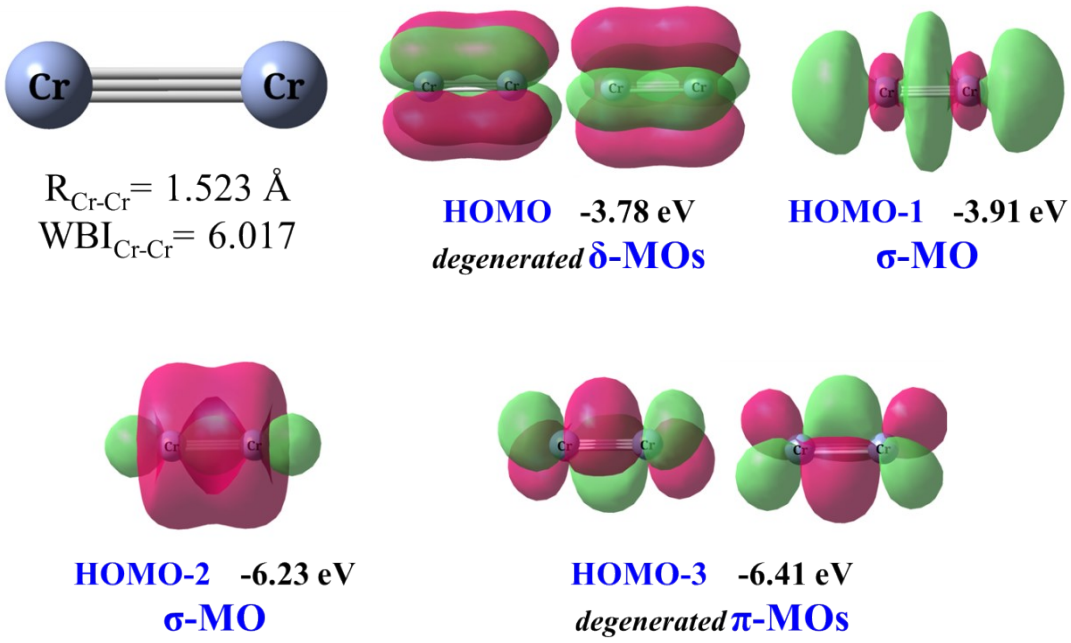


Fig. S16. The structure of Cr_2 and its important FMOs at the B3LYP/6-311G(d) level.

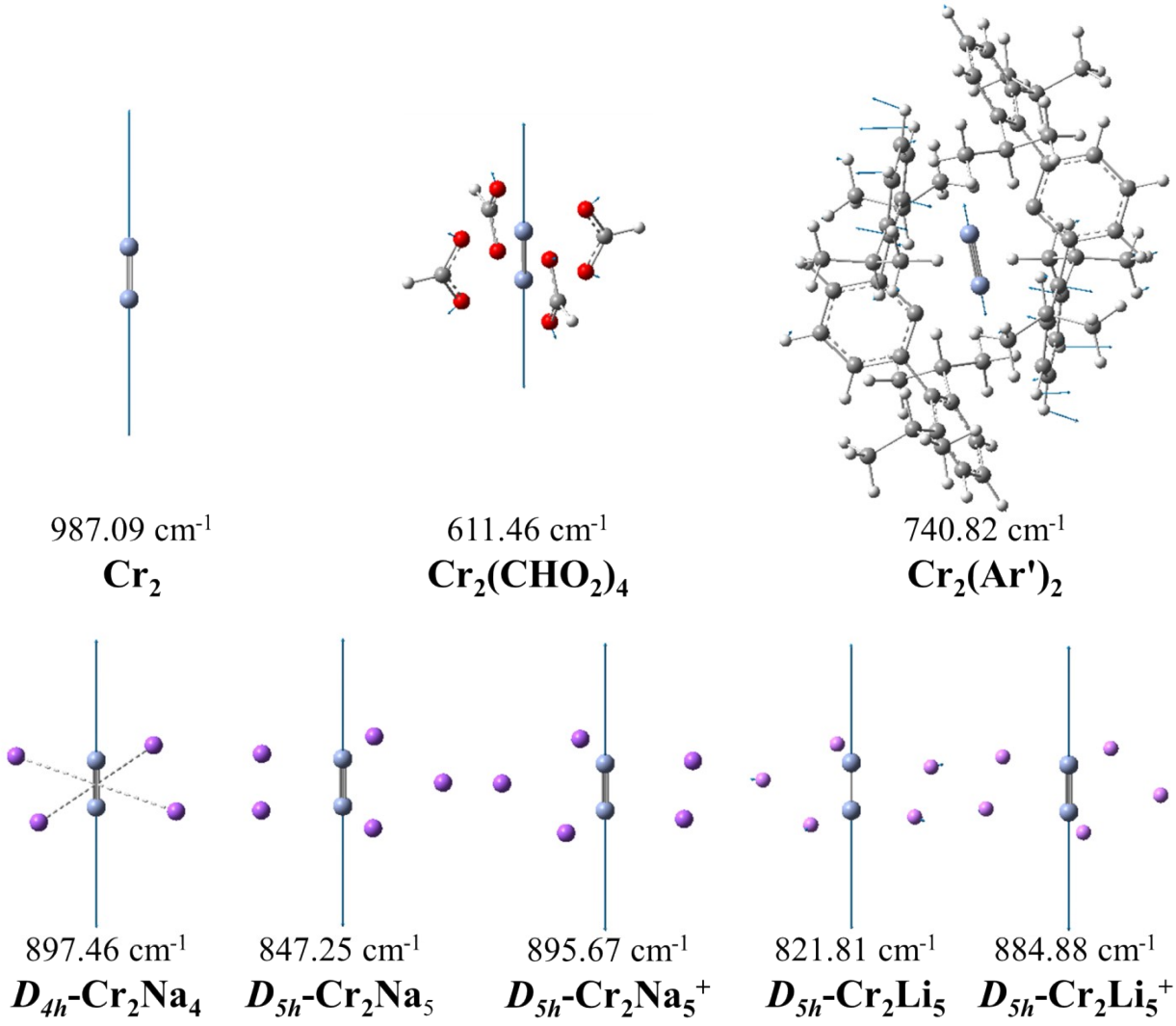


Fig. S17. The Cr-Cr stretching vibrational frequency accompany with their corresponding modes calculated at the B3LYP/6-311G(d) level.

The XYZ coordinates of the D_{2h}-Cr_2Li_2, D_{5h}-Cr_2Li_5, D_{5h}-$Cr_2Li_5^+$, D_{2h}-Cr_2Na_2, C_{2v}-$Cr_2Na_3^-$, D_{4h}-Cr_2Na_4, D_{5h}-Cr_2Na_5 and D_{5h}-$Cr_2Na_5^+$ calculated at the B3LYP/6-311G(d) level.

D_{2h}-Cr_2Li_2,

Li	0.00000000	0.00000000	2.66650300
Li	0.00000000	0.00000000	-2.66650300
Cr	0.00000000	0.77888000	0.00000000
Cr	0.00000000	-0.77888000	0.00000000

D_{5h}-Cr_2Li_5,

Cr	0.00000000	0.00000000	0.79533234
Cr	-0.00000000	0.00000000	-0.79533234
Li	-1.54421169	-2.12542505	0.00000000
Li	-2.49858699	0.81184013	0.00000000
Li	1.54421169	-2.12542505	0.00000000
Li	-0.00000000	2.62716984	0.00000000
Li	2.49858699	0.81184013	0.00000000

D_{5h}-$Cr_2Li_5^+$,

Cr	0.00000000	-0.00000000	0.78500741
Cr	-0.00000000	-0.00000000	-0.78500741
Li	-0.00000000	2.72959272	0.00000000
Li	2.59599694	0.84349054	0.00000000
Li	-2.59599694	0.84349054	0.00000000
Li	1.60441434	-2.20828690	0.00000000

Li	-1.60441434	-2.20828690	0.00000000

D_{2h}-Cr_2Na_2,

Na	0.00000000	0.00000000	2.91420100
Na	0.00000000	0.00000000	-2.91420100
Cr	0.00000000	0.77605400	0.00000000
Cr	0.00000000	-0.77605400	0.00000000

C_{2v}-$Cr_2Na_3^-$,

Cr	0.00000000	0.00000000	-1.29346993
Cr	0.00000000	-0.00000000	0.26639707
Na	0.00000000	2.85484461	-0.47894245
Na	0.00000000	-2.85484461	-0.47894245
Na	0.00000000	0.00000000	3.19877407

D_{4h}-Cr_2Na_4,

Cr	-0.00000000	0.00000000	0.78020996
Cr	-0.00000000	0.00000000	-0.78020996
Na	-0.00000000	2.89425656	0.00000000
Na	0.00000000	-2.89425656	0.00000000
Na	2.89425656	0.00000000	0.00000000
Na	-2.89425656	-0.00000000	0.00000000

D_{5h}-Cr_2Na_5

Cr	0.00000000	0.00000000	0.78407008

Cr	-0.00000000	0.00000000	-0.78407008
Na	0.00000000	2.97088179	0.00000000
Na	2.82547649	0.91805296	0.00000000
Na	-2.82547649	0.91805296	0.00000000
Na	1.74624050	-2.40349386	0.00000000
Na	-1.74624050	-2.40349386	0.00000000

D_{5h}-$Cr_2Na_5^+$

Cr	0.00000000	0.00000000	0.78084077
Cr	-0.00000000	0.00000000	-0.78084077
Na	-0.00000000	3.03091978	0.00000000
Na	2.88257600	0.93660572	0.00000000
Na	-2.88257600	0.93660572	0.00000000
Na	1.78152994	-2.45206561	0.00000000
Na	-1.78152994	-2.45206561	0.00000000