# Supporting Information

## Genuine Quadruple Bonds between Two Main-Group Atoms. Chemical Bonding in $AeF^-$ (Ae = Be - Ba) and Isoelectronic EF (E = B - Tl) and the Particular Role of d Orbitals in Covalent Interactions of Heavier Alkaline-Earth Atoms

Ruiqin Liu,[a] Lei Qin[a], Zhaoyin Zhang[a], Lili Zhao[a,*], Filip Sagan[b], Mariusz Mitoraj[b,*], Gernot Frenking[a,c,*]

[a]Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing 211816, China.
[b]Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, R. Gronostajowa 2, 30-387 Cracow, Poland
[c]Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4, D-35043 Marburg, Germany.
Email: ias_llzhao@njtech.edu.cn; mitoraj@chemia.uj.edu.pl; frenking@chemie.uni-marburg.de

## Table of Contents

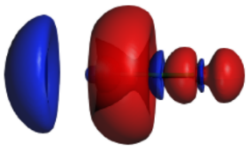
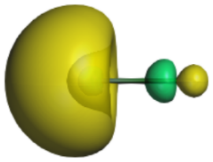
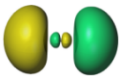
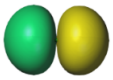
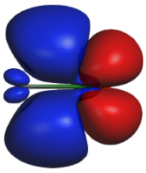
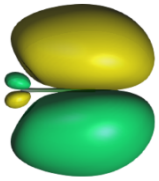
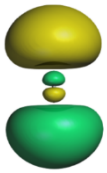
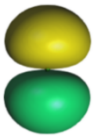
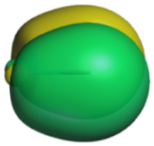
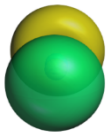
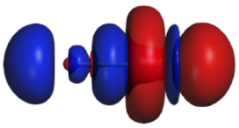
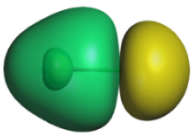
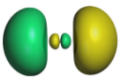
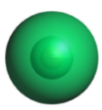
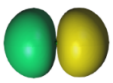
| | Deformation density $MgF^-$ | $MgF^-$ | Orbitals Mg | | $F^-$ |
|---|---|---|---|---|---|
| **a) Δρ1** |  $\Delta E_{\sigma 1}$ = -47.7 kcal/mol $\nu_1 = \pm 0.580$ |  HOMO $\nu_1 = \pm 0.580$ |  $3p_\sigma$ ν= 0.221  4S ν= 0.081  3S ν= -0.222 | ← |  $2p_\sigma$ ν= -0.085 |
| **b) Δρ2** |  $\Delta E_{\pi 1}$ = -8.9 kcal/mol $\nu_2 = \pm 0.225$ |  HOMO-1 $\nu_2 = \pm 0.225$ |  $3p_\pi$ ν= 0.038 | ← |  $2p_\pi$ ν= -0.051 |
| **c) Δρ3** |  $\Delta E_{\pi 2}$ = -8.9 kcal/mol $\nu_3 = \pm 0.225$ |  HOMO-1' $\nu_3 = \pm 0.225$ |  $3p_\pi$' ν= 0.038 | ← |  $2p_\pi$' ν= -0.051 |
| **d) Δρ4** |  $\Delta E_{\sigma 2}$ = -2.7 kcal/mol $\nu_1 = \pm 0.080$ |  HOMO-2 $\nu_3 = \pm 0.080$ |  $3p_\sigma$ ν= 0.003  4S ν= 0.004  3S ν= 0.014 | ← |  $2p_\sigma$ ν= -0.022 |

**Figure S1:** Plot of the deformation densities Δρ of the four most important orbital interactions in $MgF^-$ which indicate the charge flow red→blue. Shape of the most important AOs of Mg and

$F^-$ which built the MOs of $MgF^-$. The eigenvalues υ give the relative size of the charge transfer.

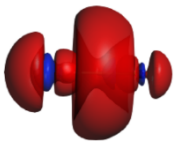
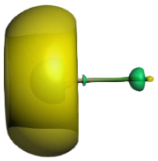
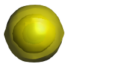
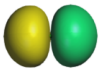
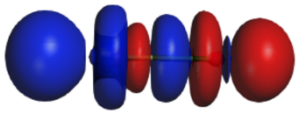
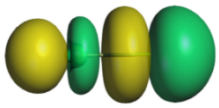
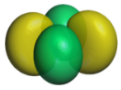
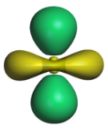
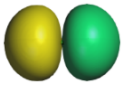
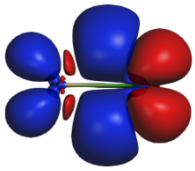
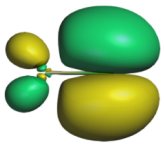
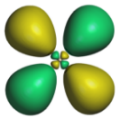
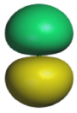
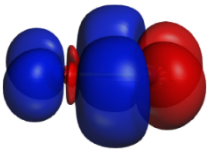
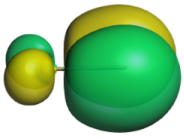
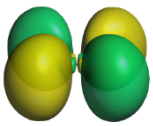
| | Deformation density | Orbitals | | | |
|---|---|---|---|---|---|
| | $SrF^-$ | $SrF^-$ | Sr | | $F^-$ |
| **a) Δρ1** |  $\Delta E_{\sigma 1}$ = -40.6 kcal/mol $\nu_1 = \pm 0.694$ |  HOMO $\nu_1 = \pm 0.694$ |  6S ν = 0.160  $5p_\sigma$ ν = 0.107  5S ν = -0.292 | ← |  $2p_\sigma$ ν= -0.035 |
| **b) Δρ2** |  $\Delta E_{\sigma 2}$ = -17.5 kcal/mol $\nu_2 = \pm 0.328$ |  HOMO-2 $\nu_2 = \pm 0.328$ |  $4d_\sigma$ ν = 0.053  $4d_\sigma$' ν = 0.041 | ← |  $2p_\sigma$ ν= -0.104 |
| **c) Δρ3** |  $\Delta E_{\pi 1}$ = -11.9 kcal/mol $\nu_3 = \pm 0.268$ |  HOMO-1 $\nu_3 = \pm 0.268$ |  $4d_\pi$ ν = 0.067 | ← |  $2p_\pi$ ν = -0.086 |
| **d) Δρ4** |  $\Delta E_{\pi 2}$ = -11.9 kcal/mol $\nu_4 = \pm 0.268$ |  HOMO-1' $\nu_4 = \pm 0.268$ |  $4d_\pi$' ν = 0.067 | ← |  $2p_\pi$' ν = -0.086 |

**Figure S2:** Plot of the deformation densities Δρ of the four most important orbital interactions in $SrF^-$ which indicate the charge flow red→blue. Shape of the most important AOs of Sr and $F^-$ which built the MOs of $SrF^-$. The eigenvalues υ give the relative size of the charge transfer.

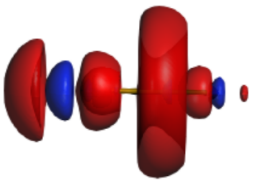
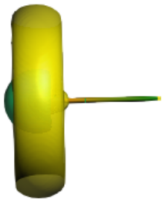
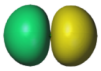
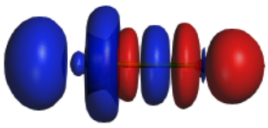
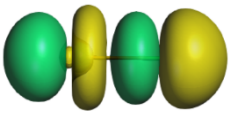
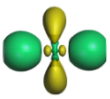
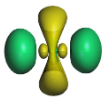
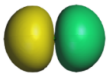
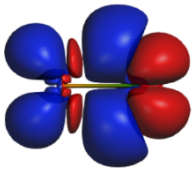
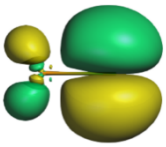
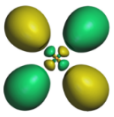
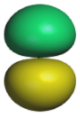
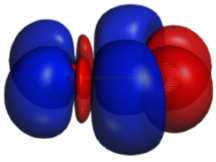
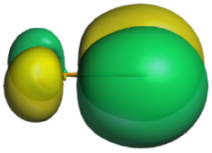
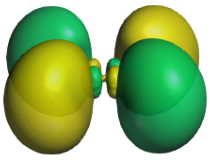
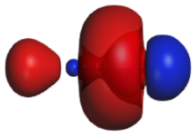
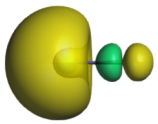
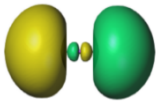
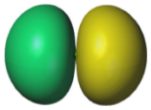
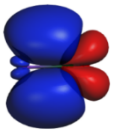
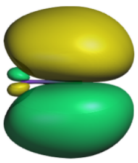
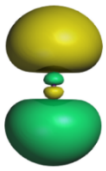
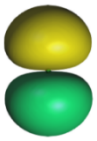
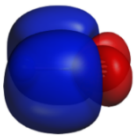
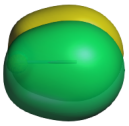
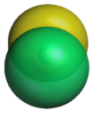
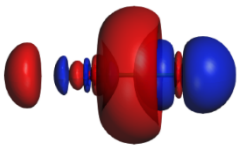
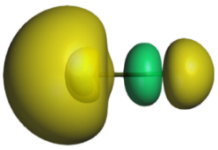
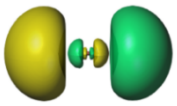
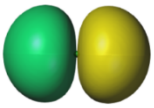
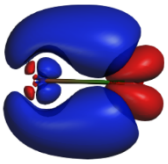
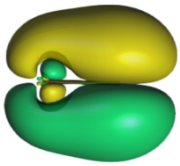
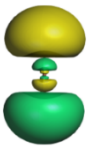
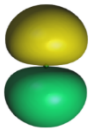
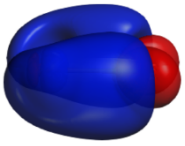
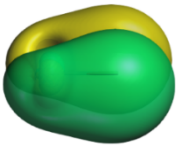
| | Deformation density | | Orbitals | | |
|---|---|---|---|---|---|
| | $BaF^-$ | $BaF^-$ | Ba | | $F^-$ |
| **a)** **Δρ1** |  $\Delta E_{\sigma 1}$ = -39.0 kcal/mol $\nu_1 = \pm 0.735$ |  HOMO $\nu_1 = \pm 0.735$ |  7S ν = 0.165  $6p_\sigma$ ε= -1.18 eV ν = 0.083  6S ν= -0.318 | ← |  $2p_\sigma$ ν= -0.021 |
| **b)** **Δρ2** |  $\Delta E_{\sigma 2}$ = -25.5 kcal/mol $\nu_2 = \pm 0.375$ |  HOMO-1 $\nu_2 = \pm 0.375$ |  $5d_\sigma$ ν = 0.075  $5d_\sigma$' ν = 0.043  $6p_\sigma$ ν = 0.017 | ← |  $2p_\sigma$ ν= -0.148 |
| **c)** **Δρ3** |  $\Delta E_{\pi 1}$ = -14.1 kcal/mol $\nu_3 = \pm 0.280$ |  HOMO-1' $\nu_3 = \pm 0.280$ |  $5d_\pi$ ν = 0.047 | ← |  $2p_\pi$ ν = -0.056 |
| **d)** **Δρ4** |  $\Delta E_{\pi 2}$ = -14.1 kcal/mol $\nu_4 = \pm 0.280$ |  HOMO-2 $\nu_4 = \pm 0.280$ |  $5d_\pi$' ν = 0.047 | ← |  $2p_\pi$'ν = -0.056 |

**Figure S3:** Plot of the deformation densities Δρ of the four most important orbital interactions in $BaF^-$ which indicate the charge flow red→blue. Shape of the most important AOs of Ba and $F^-$ which built the MOs of $BaF^-$. The eigenvalues υ give the relative size of the charge transfer.

| | Deformation density EF | EF | Orbitals E ($^2$P) | | F ($^2$P) |
|---|---|---|---|---|---|
| | | | **AlF** | | |
| Δρ1 |  $\Delta E_{\sigma 1}$ = -261.7 kcal/mol $\nu_1 = \pm 1.235$ |  HOMO $\nu_1 = \pm 1.235$ |  $3p_\sigma$ ν= -0.749 | ↔ |  $2p_\sigma$ ν= 0.818 |
| Δρ2 |  $\Delta E_{\pi 1}$ = -9.4 kcal/mol $\nu_2 = \pm 0.304$ |  HOMO-1 $\nu_2 = \pm 0.304$ |  $3p_\pi$ ν= 0.065 | ← |  $2p_\pi$ ν= -0.102 |
| Δρ3 |  $\Delta E_{\pi 2}$ = -9.4 kcal/mol $\nu_3 = \pm 0.304$ |  HOMO-1' $\nu_3 = \pm 0.304$ |  $3p_\pi$' ν= 0.065 | ← |  $2p_\pi$' ν= -0.102 |
| | | | **InF** | | |
| Δρ1 |  $\Delta E_{\sigma 1}$= -191.1 kcal/mol $\nu_1 = \pm 1.220$ |  HOMO $\nu_1 = \pm 1.220$ |  $5p_\sigma$ ν= -0.774 | ↔ |  $2p_\sigma$ ν= 0.790 |
| Δρ2 |  $\Delta E_{\pi 1}$ = -4.0 kcal/mol $\nu_2 = \pm 0.311$ |  HOMO-1 $\nu_2 = \pm 0.311$ |  $5p_\pi$ ν= 0.057 | ← |  $2p_\pi$ ν= -0.070 |
| Δρ3 |  $\Delta E_{\pi 2}$ = -4.0 kcal/mol $\nu_3 = \pm 0.311$ |  HOMO-1' $\nu_3 = \pm 0.311$ |  $5p_\pi$' ν= 0.057 | ← |  $2p_\pi$' ν= -0.070 |
| | | | **TlF** | | |

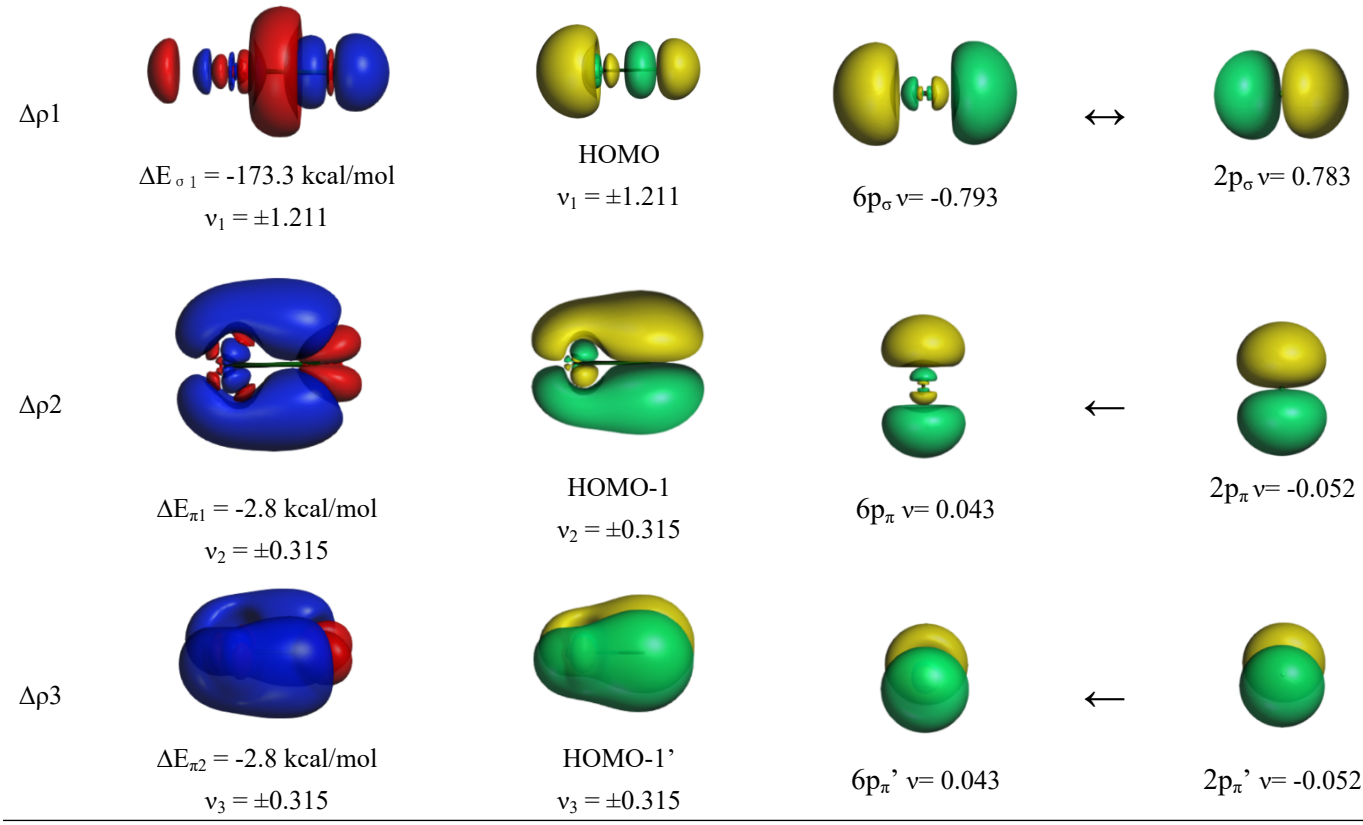



**Figure S4.** Plot of the deformation densities Δρ of the three most important orbital interactions in AlF、InF and TlF which indicate the charge flow red→blue. Shape of the most important AOs of the atoms which built the MOs of $EF^-$. The eigenvalues υ give the relative size of the charge transfer.

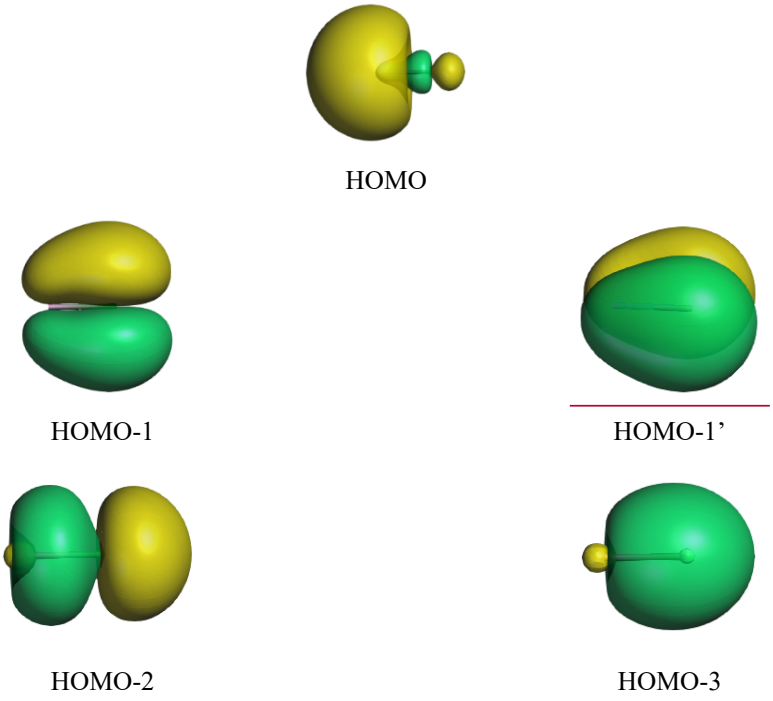



**Figure S5.** Molecular orbital results of BF at the BP86/DZP//BP86/def2-QZVPP level of theory.

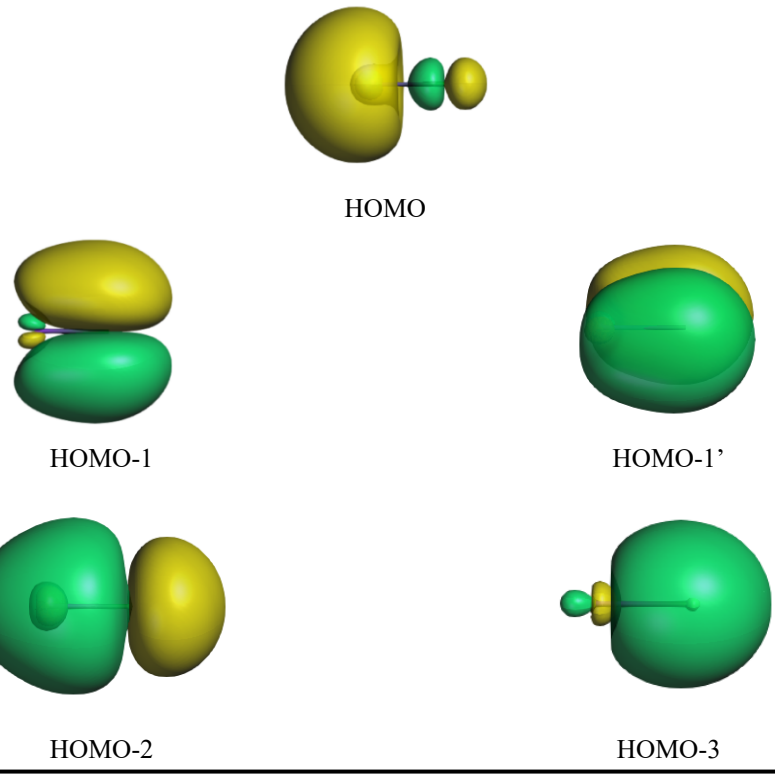



**Figure S6.** Molecular orbital results of AlF at the BP86/DZP//BP86/def2-QZVPP level of theory.

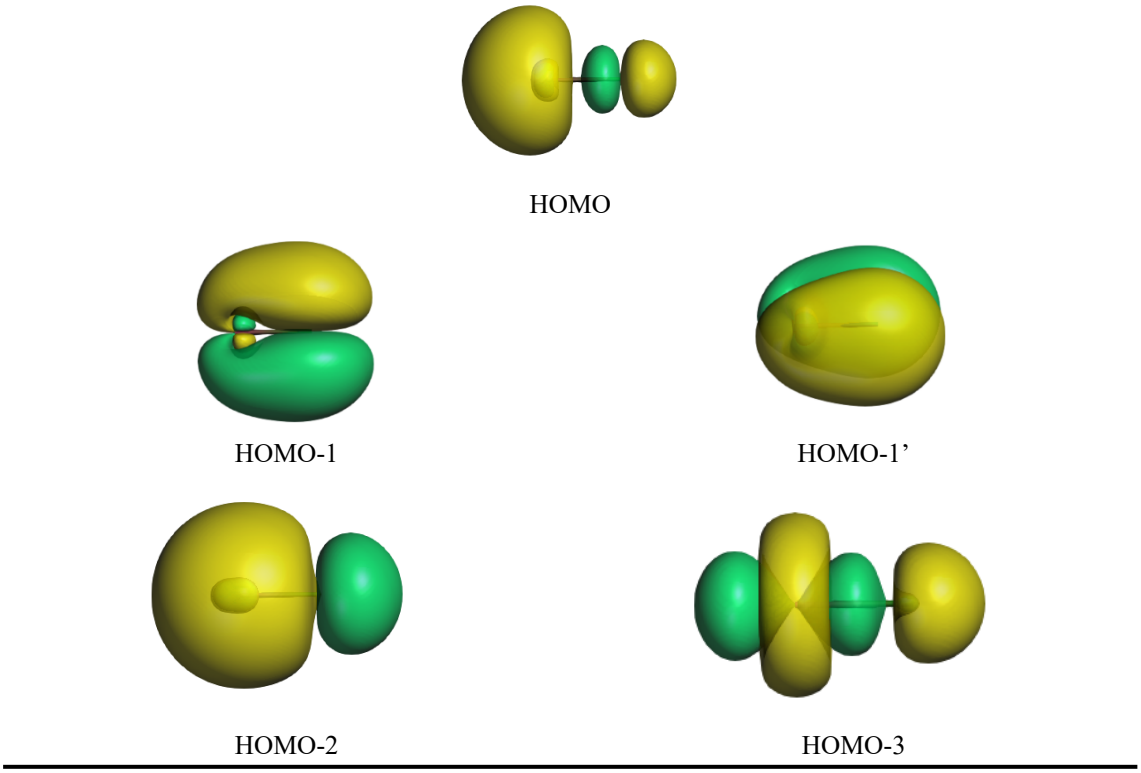



**Figure S7.** Molecular orbital results of GaF at the BP86/DZP//BP86/def2-QZVPP level of theory.

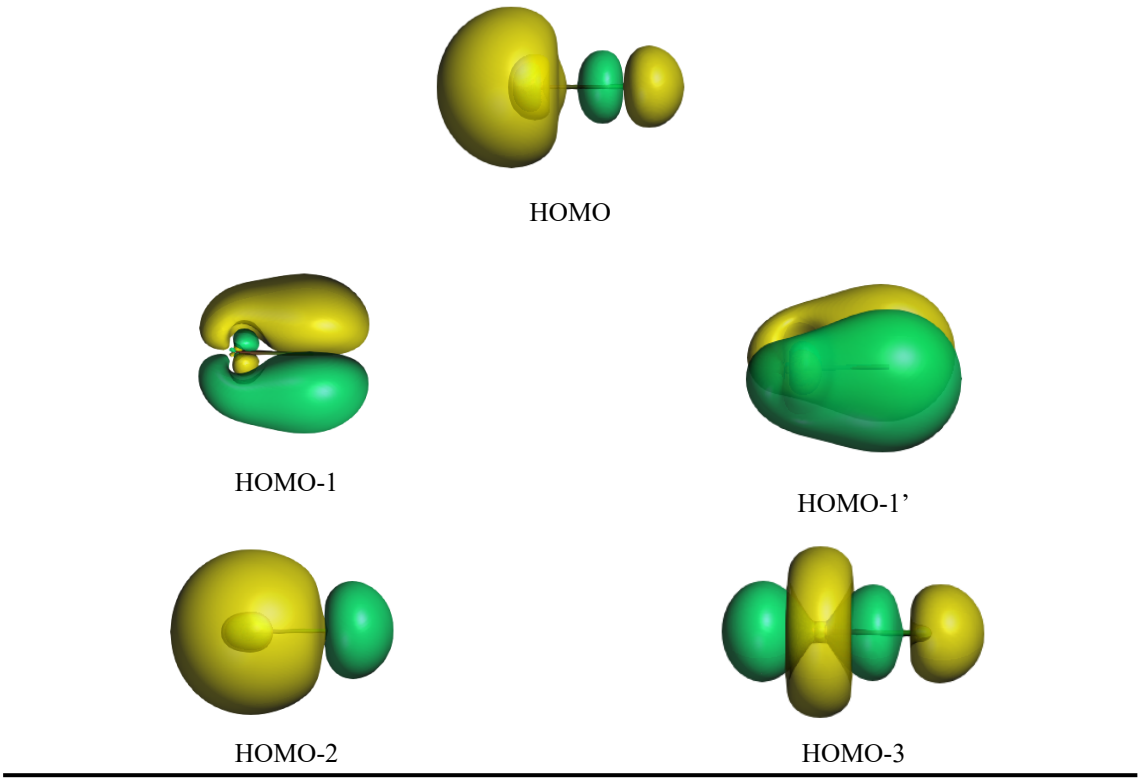



**Figure S8.** Molecular orbital results of InF at the BP86/DZP//BP86/def2-QZVPP level of theory.

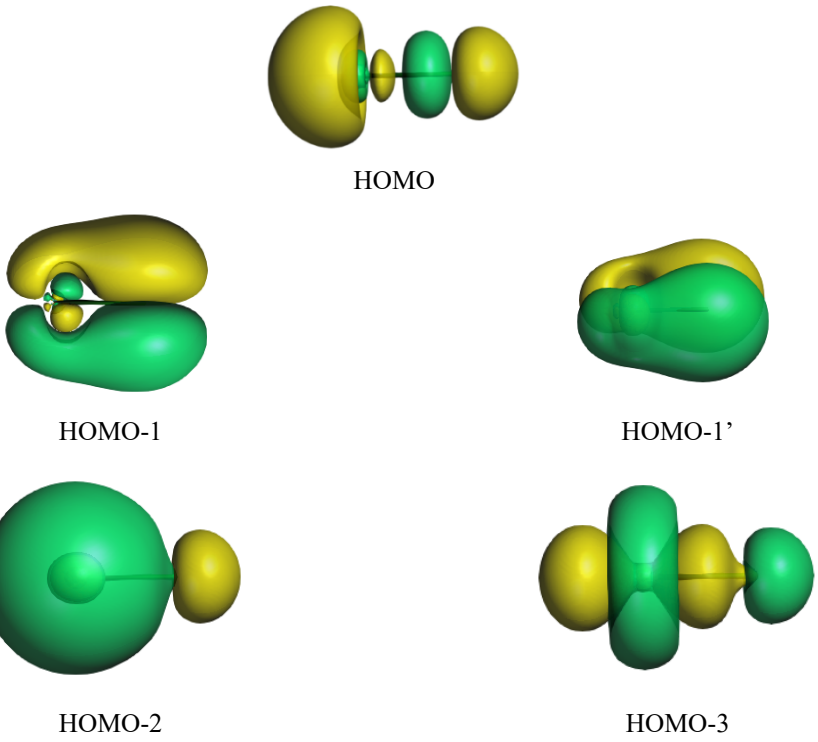



**Figure S9.** Molecular orbital results of TlF at the BP86/DZP//BP86/def2-QZVPP level of theory.

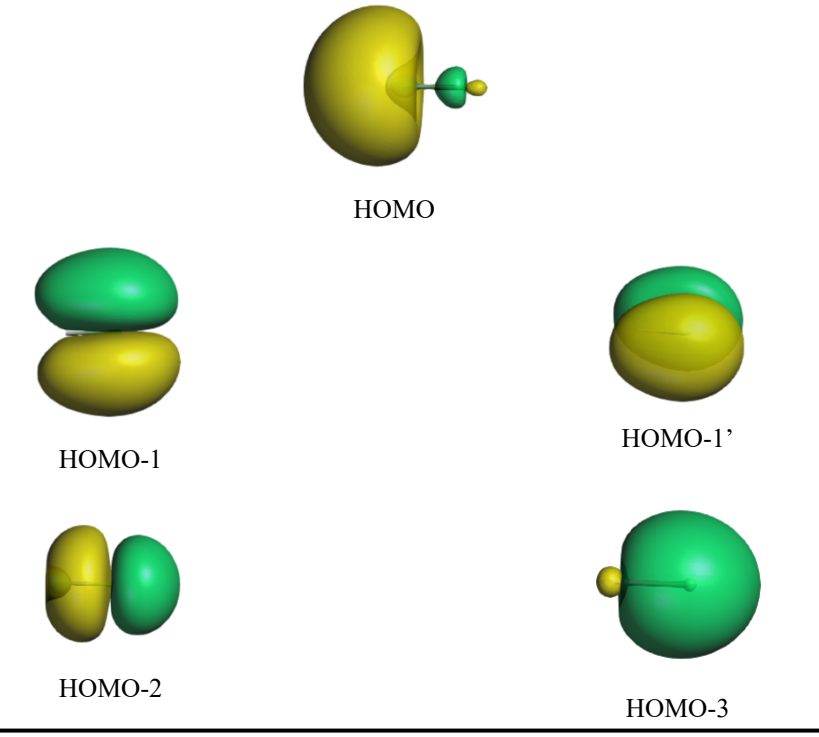



**Figure S10.** Molecular orbital results of $BeF^-$ at the BP86/DZP//BP86/def2-QZVPP level of theory.

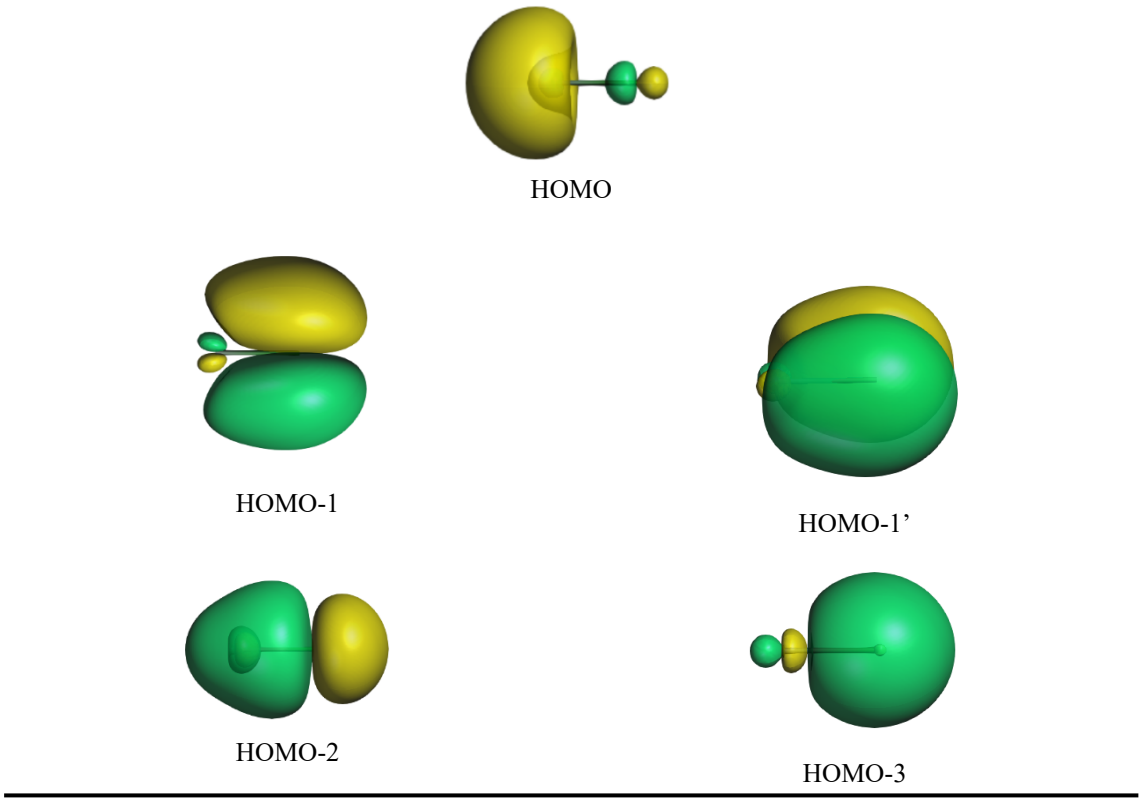



**Figure S11.** Molecular orbital results of $MgF^-$ at the BP86/DZP//BP86/def2-QZVPP level of theory.

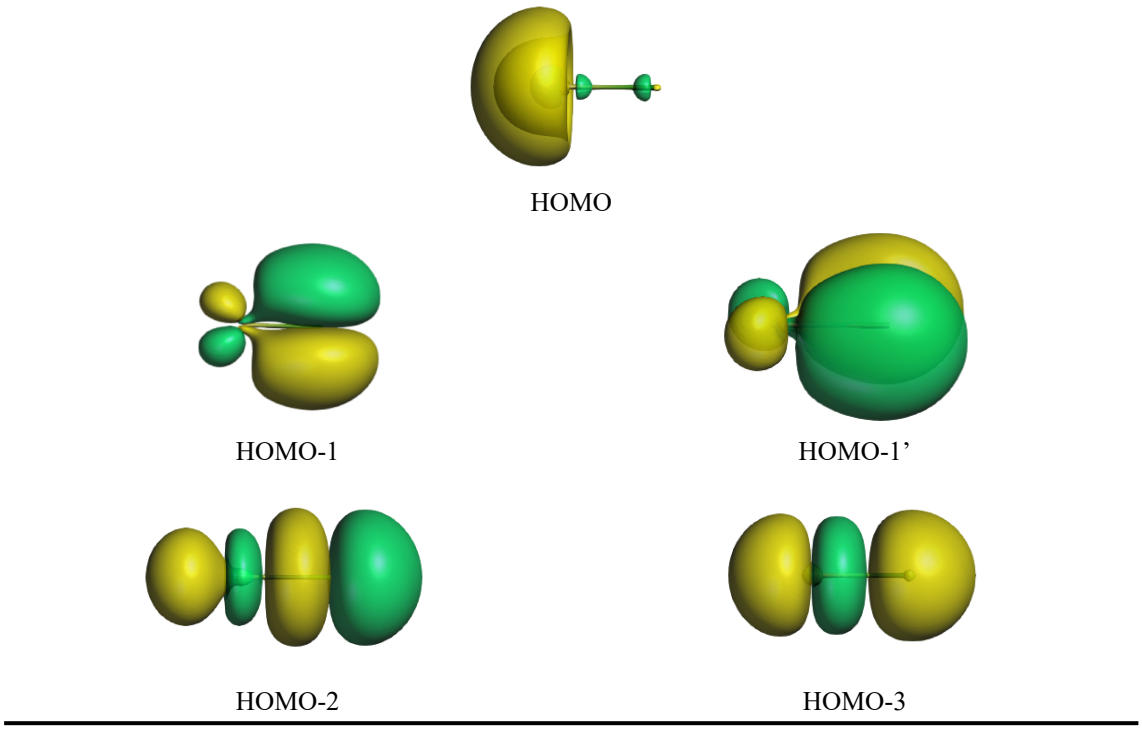



**Figure S12.** Molecular orbital results of $CaF^-$ at the BP86/DZP//BP86/def2-QZVPP level of theory.

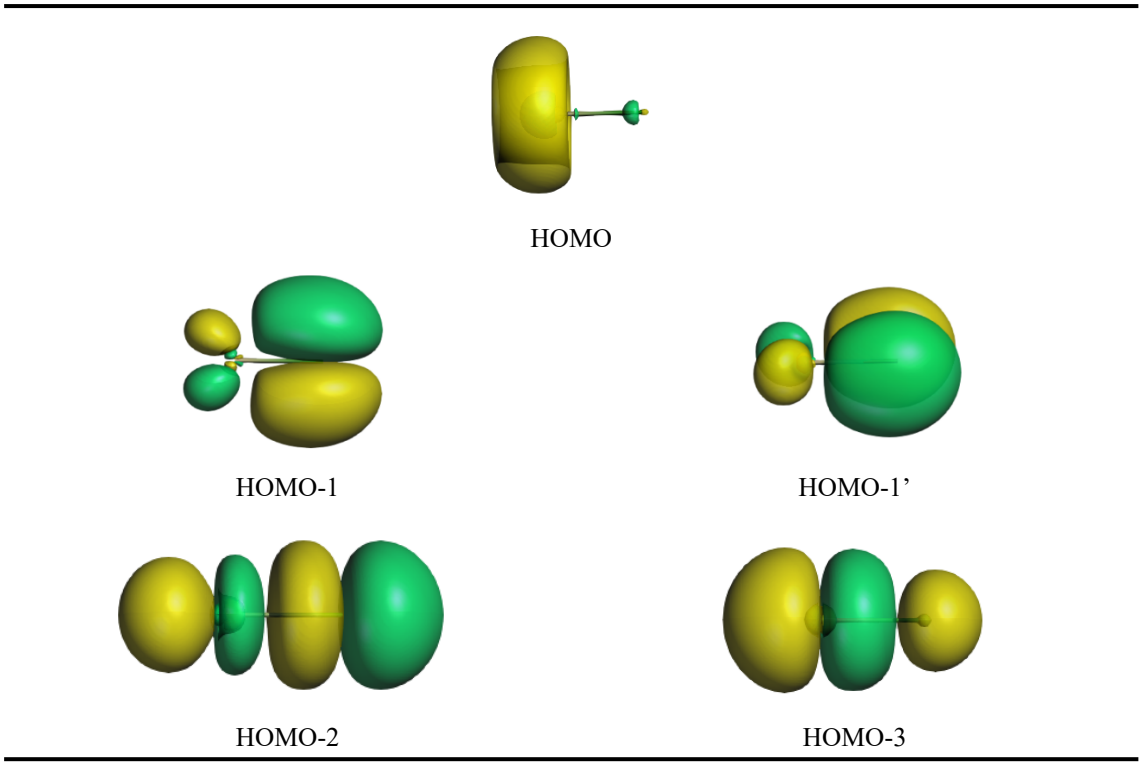



**Figure S13.** Molecular orbital results of $SrF^-$ at the BP86/DZP//BP86/def2-QZVPP level of theory.

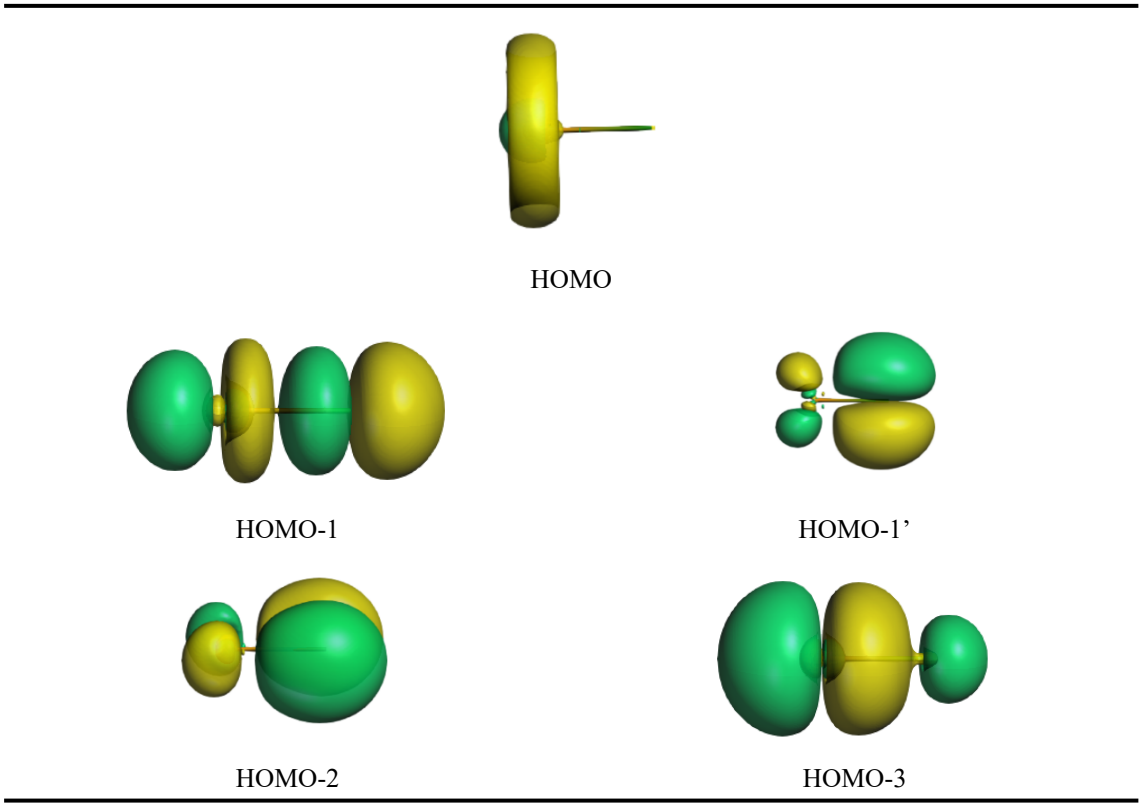



**Figure S14.** Molecular orbital results of $BaF^-$ at the BP86/DZP//BP86/def2-QZVPP level of theory.

**Table S1.** Coordinates and energies (in hartrees) of the calculated structures at the BP86/def2-QZVPP level

**BF**
Energy = -124.7152906

| | | | |
|---|---|---|---|
| B | 0.000000000 | 0.000000000 | -0.819193000 |
| F | 0.000000000 | 0.000000000 | 0.455107000 |

**AlF**
Energy = -342.4192829

| | | | |
|---|---|---|---|
| Al | 0.000000000 | 0.000000000 | 0.688356000 |
| F | 0.000000000 | 0.000000000 | -0.994292000 |

**GaF**
Energy = -2025.1153596

| | | | |
|---|---|---|---|
| Ga | 0.000000000 | 0.000000000 | 0.406232000 |
| F | 0.000000000 | 0.000000000 | -1.399244000 |

**InF**
Energy = -290.2134576

| | | | |
|---|---|---|---|
| In | 0.000000000 | 0.000000000 | 0.313141000 |
| F | 0.000000000 | 0.000000000 | -1.704880000 |

**TlF**
Energy = -272.6189483

| | | | |
|---|---|---|---|
| Tl | 0.000000000 | 0.000000000 | 0.212245000 |
| F | 0.000000000 | 0.000000000 | -1.910206000 |

**$BeF^-$**
Energy = -114.6950633

| | | | |
|---|---|---|---|
| Be | 0.000000000 | 0.000000000 | -0.988605000 |
| $F^-$ | 0.000000000 | 0.000000000 | 0.439380000 |

**MgF-**
Energy = -300.0838313

| | | | |
|---|---|---|---|
| Mg | 0.000000000 | 0.000000000 | 0.791494000 |
| $F^-$ | 0.000000000 | 0.000000000 | -1.055325000 |

**CaF-**
Energy = -777.6606903

| | | | |
|---|---|---|---|
| Ca | 0.000000000 | 0.000000000 | 0.618059000 |
| $F^-$ | 0.000000000 | 0.000000000 | -1.373464000 |

**SrF-**

Energy = -130.7484136

| | | | |
|---|---|---|---|
| Sr | 0.000000000 | 0.000000000 | 0.408590000 |
| $F^-$ | 0.000000000 | 0.000000000 | -1.725156000 |

**BaF-**

Energy = -125.5447411

| | | | |
|---|---|---|---|
| Ba | 0.000000000 | 0.000000000 | 0.309329000 |
| $F^-$ | 0.000000000 | 0.000000000 | -1.924712000 |

**Table S2.** Coordinates and energies (in hartrees) of the calculated structures at the CCSD(T)/def2-TZVPP level

**$BeF^-$**

Energy = -114.4774285

| | | | |
|---|---|---|---|
| Be | 0.000000000 | 0.000000000 | -0.989218000 |
| $F^-$ | 0.000000000 | 0.000000000 | 0.439652000 |

**$MgF^-$**

Energy = -299.4693446

| | | | |
|---|---|---|---|
| $F^-$ | 0.000000000 | 0.000000000 | -1.051416000 |
| Mg | 0.000000000 | 0.000000000 | 0.788562000 |

**$CaF^-$**

Energy = -776.6118451

| | | | |
|---|---|---|---|
| $F^-$ | 0.000000000 | 0.000000000 | -1.451243000 |
| Ca | 0.000000000 | 0.000000000 | 0.653059000 |

**$SrF^-$**

Energy = -130.216534

| | | | |
|---|---|---|---|
| $F^-$ | 0.000000000 | 0.000000000 | -1.808251000 |
| Sr | 0.000000000 | 0.000000000 | 0.428270000 |

**$BaF^-$**

Energy = -124.9654535

| | | | |
|---|---|---|---|
| $F^-$ | 0.000000000 | 0.000000000 | -2.067115000 |
| Ba | 0.000000000 | 0.000000000 | 0.332215000 |

**BF**

Energy = -124.505751

| | | | |
|---|---|---|---|
| B | 0.000000000 | 0.000000000 | -0.818103000 |
| F | 0.000000000 | 0.000000000 | 0.454502000 |

**AlF**

Energy = -341.8021909

| | | | |
|---|---|---|---|
| F | 0.000000000 | 0.000000000 | -0.983676000 |
| Al | 0.000000000 | 0.000000000 | 0.681006000 |

**GaF**

Energy = -2023.2565034

| | | | |
|---|---|---|---|
| F | 0.000000000 | 0.000000000 | -1.379868000 |
| Ga | 0.000000000 | 0.000000000 | 0.400607000 |

**InF**

Energy = -289.2860866

| | | | |
|---|---|---|---|
| F | 0.000000000 | 0.000000000 | -1.679783000 |
| In | 0.000000000 | 0.000000000 | 0.308532000 |

**TlF**

Energy = -271.724248

| | | | |
|---|---|---|---|
| F | 0.000000000 | 0.000000000 | -1.886248000 |
| Tl | 0.000000000 | 0.000000000 | 0.209583000 |