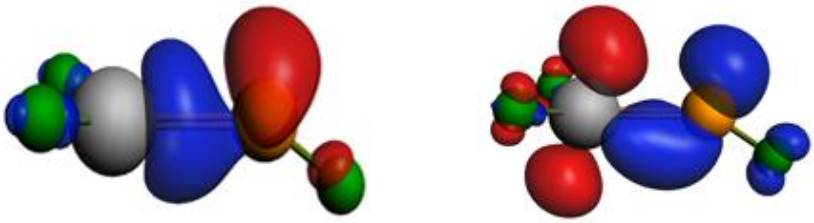
molecules

MDPI

Supplementary Materials

F_2BMF (M = B and Al) Molecules: A Matrix Infrared Spectra and Theoretical Calculations Investigation



$\Delta E_{orb}(\sigma)$= -39.5;
$|\upsilon(\sigma)|$= 0.58

$\Delta E_{orb}(\pi)$= -91.9;
$|\upsilon(\pi)|$= 0.88

ΔE_{int}	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{orb}	ΔE_{σ}	ΔE_{π}	ΔE_{orb}(rest)	ΔE_{dist}
-122.0	59.1	-46.8 (25.8%)	-134.7 (74.2%)	-39.5 (29.3%)	-91.9 (68.3%)	-3.3 (2.4%)	0. 39

Figure S1. Plot of the deformation densities $\Delta\rho$ of the $BF \rightarrow AlF_2$ σ donation and $AlF_2 \rightarrow BF$ π back-donation in $FBAlF_2$ with the associated interaction energy ΔE_{orb} and charge eigenvalues $|\nu_n|$(in e). The charge flow is from red → blue.

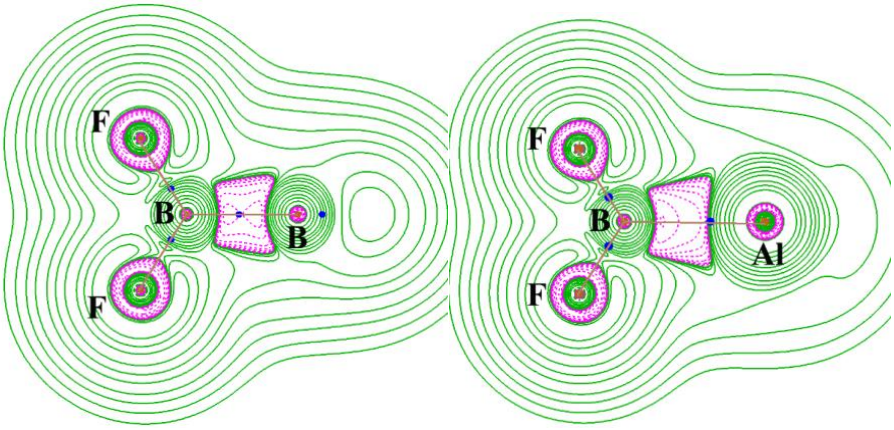


Figure S2. Contour line diagrams of the Laplacian of the electronic density of F_2BMF (M = B, Al). Red lines are in regions of the negative charge concentrations ($\nabla^2 \rho(r) < 0$); Green lines are in regions of the positive charge depletion ($\nabla^2 \rho(r) > 0$).

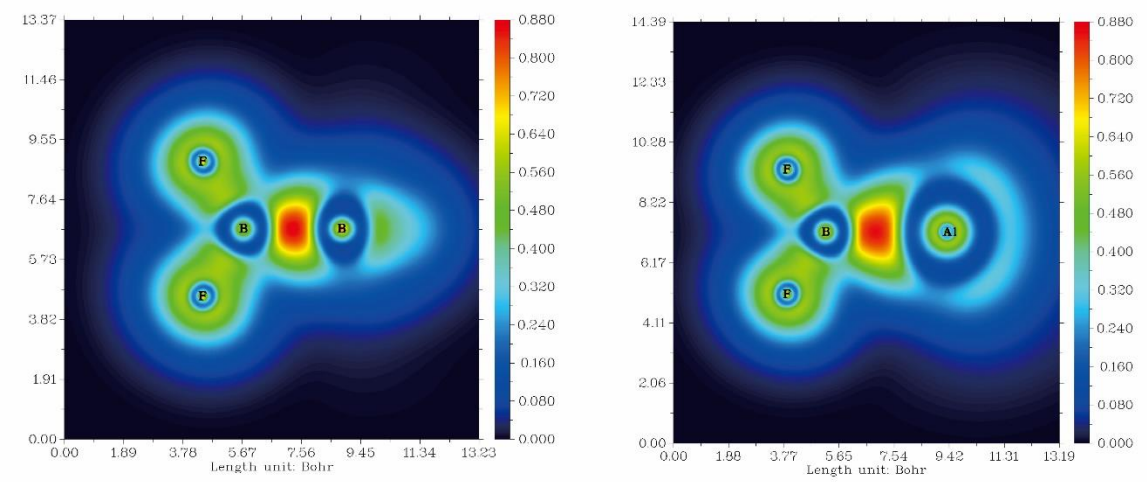


Figure S3. Color-filled maps of localized orbital locator of F_2BMF molecules (M = B, Al) at B3LYP/def2-TZVPP level.

Table S1. Compositions of Natural Bond Orbitals from NBO Analysis of F_2BMF molecules (M = B, Al).

Molecule	Bond	NBO	OCC
F_2BBF	B^1-B^4 σ	34.50%$B^1(s^{0.29}p^{0.71})$+65.50%$B^4(s^{0.66}p^{0.34})$	α 0.95
		47.41%$B^1(s^{0.41}p^{0.59})$+52.59%$B^4(s^{0.62}p^{0.38})$	β 0.99
	B^1-B^4 π	34.13%$B^1(s^{0.15}p^{0.85})$+66.87%$B^4(p)$	α 0.96
	F^1-B^1 σ	17.42%$B^1(s^{0.28}p^{0.71}d^{0.01})$+82.58%$F^1(s^{0.44}p^{0.56})$	α 1.00
		17.42%$B^1(s^{0.29}p^{0.70}d^{0.01})$+82.58%$F^2(s^{0.44}p^{0.56})$	β 1.00
	F^2- B^1σ	17.42%$B^1(s^{0.28}p^{0.71}d^{0.01})$+82.58%$F^1(s^{0.44}p^{0.56})$	α 1.00
		17.42%$B^1(s^{0.29}p^{0.70}d^{0.01})$+82.58%$F^2(s^{0.44}p^{0.56})$	β 1.00
	B^4-F^3 σ	16.05%$B^4(s^{0.35}p^{0.65})$+83.95%$F^3(s^{0.44}p^{0.56})$	α 1.00
		15.97%$B^4(s^{0.36}p^{0.64})$+84.03%$F^3(s^{0.45}p^{0.55})$	β 1.00
F_2BAlF	B-Al σ	76.09%$B(s^{0.44}p^{0.56})$+25.57%$Al(s^{0.16}p^{0.82}d^{0.02})$	α 0.99
		50.50% $B(s^{0.39}p^{0.61})$+49.50%$Al(s^{0.83}p^{0.17})$	β 0.99
	Al (LP)	100%$Al(s^{0.75}p^{0.25})$	α 0.98
	F^1-B σ	16.14%$B(s^{0.28}p^{0.71}d^{0.01})$+83.86%$F^1(s^{0.46}p^{0.54})$	α 0.99
		16.43%$B(s^{0.30}p^{0.69}d^{0.01}$+83.57%$F^1(s^{0.45}p^{0.55})$	β 0.99
	F^2-B σ	16.14%$B(s^{0.28}p^{0.71}d^{0.01})$+83.86%$F^1(s^{0.46}p^{0.54})$	α 0.99
		16.43%$B(s^{0.30}p^{0.69}d^{0.01}$+83.57%$F^1(s^{0.45}p^{0.55})$	β 0.99

All the data are calculated by B3LYP hybrid density functional. LP denotes lone pair.

Table S2. Effective Bond Order Computed at B3LYP/def2-TZVPP level of F_2BMF molecules (M = B, Al).

Orbital	F_2BBF	F_2BAlF
a(σ_1)	0.952	0.989
a (σ_1*)	0.084	0.020
a (σ_2)	0.956	0.988
a (σ_2*)	0.117	0.042
a (π)	0.995	/
a (π*)	0.016	/
EBO	1.32	0.96
WBI	1.05	0.69

Table S3. Calculated Fundamental Frequencies of F_2BBF and F_2AlBF isotopomers in the Ground ^2A State.

Approximate description	Cal(int)[a]	Cal(int)[b]	Cal(int)[c]	Cal(int)[d]	Cal(int)[a]	Cal(int)[b]	Cal(int)[c]	Cal(int)[d]
		$F_2{}^{11}B^{11}BF$					$F_2{}^{10}B^{11}BF$	
BBFantisymstr	1458.1(196)	1491.2(52)	1461.7(50)	1466.2	1502.2(312)	1501.4(41)	1471.7(37)	1477.8
BF_2antisymstr	1425.9(204)	1332.3(294)	1286.7(265)	1376.3	1453.7(123)	1378.8(317)	1331.6(284)	1425.1
BF_2symstr	1261.1(370)	1188.9(465)	1150.9(427)	1213.6	1287.1(384)	1221.3(505)	1182.6(465)	1245.4
BF_2scis	762.0(4)	658.5(24)	640.0(18)	674.6	775.5(8)	663.9(22)	644.8(16)	683.5
BF_2B def	661.3(49)	570.9(19)	540.0(13)	605.9	675.6(48)	591.6(20)	560.2(14)	624.1
BF_2 bend	485.2(26)	401.0(1)	387.3(1)	414.1	488.0(27)	401.3(1)	387.6(1)	414.9
FBB wag	465.6(3)	366.5(0)	363.8(0)	335.5	466.7(3)	367.5(0.7)	364.7(0)	336.6
BBF bend	295.8(11)	188.3(15)	182.3(14)	194.3	296.7(11)	188.9(15)	187.8(14)	195.1
BF_2BF def	182.5(6)	125.2(2)	119.5(2)	115.5	183.1(6)	125.6(2.5)	119.9(2)	115.8
		$F_2{}^{11}B^{10}BF$					$F_2{}^{10}B^{10}BF$	
BBFantisymstr	1485.7(89)	1538.6(70)	1508.0(63)	1511.4	1512.1(201)	1546.8(56)	1516.6(49)	1520.8
BF_2antisymstr	1437.5(316)	1332.3(294)	1286.7(265)	1376.3	1478.2(228)	1378.9(324)	1331.6(284)	1425.1
BF_2symstr	1270.5(373)	1192.3(462)	1154.2(424)	1217.9	1301.1(399)	1226.3(505)	1187.3(463)	1251.9
BF_2scis	776.4(3)	663.8(25)	644.9(19)	683.1	789.0(7)	669.3(23)	649.8(17)	682.1
BF_2B def	661.5(3)	572.7(19)	542.1(13)	607.1	676.0(48)	593.0(20)	561.6(14)	624.7
BF_2 bend	493.7(27)	405.5(1)	391.3(1)	419.5	496.9(28)	405.9(0.98)	391.7(1)	420.5
FBB wag	480.8(4)	378.2(0)	375.7(0)	345.6	482.0(4)	379.2(0.1)	376.6 (0)	346.6
BBF bend	298.2(11)	192.6(16)	191.6(15)	197.8	299.2(11)	193.2(16)	192.3(15)	198.7
BF_2BF def	183.7(6)	125.9(2.5)	120.0(2)	116.3	184.4(6)	126.3(2.5)	120.5(2)	116.6
		$F_2{}^{11}$BAlF					$F_2{}^{10}$BAlF	
BF_2antisymmstr	1411.1(300)	1312.0(277)	1270.9(257)	1342.1	1460.4(321)	1357.4(299)	1314.9(275)	
BF_2symstr	1277.2(319)	1172.2(320)	1133.9(309)	1190.3	1317.8(347)	1208.2(378)	1168.8(336)	1227.4
AlFstr	831.0(117)	806.7(106)	780.1(98)	814.5	831.0(116)	806.8(106)	780.2(98)	814.6
BF_2 scis	624.5(15)	566.6(20)	549.5(17)	576.0	631.0(12)	572.5(18)	555.2(15)	582.0
F_2BAlF def	559.0(29)	466.8(32)	453.4(31)	472.9	580.9(33)	484.6(34)	470.4(34)	491.1
F_2BAlF def	338.3(30)	300.7(12)	290.7(8)	311.9	338.8(31)	301.6(13)	291.6(9)	312.8
F_2BAl wag	231.2(1)	162.1(0)	157.3(0)	166.7	232.5(1)	163.1(0)	158.2(0)	167.7
BAlF bend	156.7(15)	118.7(9)	114.3(9)	124.7	1567.0(15)	118.9(9)	114.5(7)	124.9
F_2BAlF def	99.9(8)	49.9(4)	52.9(4)	33.8	99.9(8)	49.9(4)	52.9(4)	33.8

The vibrational frequencies (cm^{-1}) and intensities (km/mol, in parentheses) are calculated using: [a] CAS(9e, 11o)/def2-TZVP basis set; [b] B3LYP/def2-TZVPP basis set.; [c] BPW91/def2-TZVPP basis set; [d]CCSD(T)/def2-TZVP(-f) basis set.

The value predicted by CASSCF method is 1425.9 (1453.7) and 1261.1(1287.1) cm^{-1} for the anti-symmetric and symmetric B-F stretching modes of $F_2{}^{11}B(^{10}B)$-^{11}BF molecule, which is overestimated by about 93.6 cm^{-1} (74.9 cm^{-1}) and 72.2 cm^{-1} (65.8 cm^{-1}) respectively. For $F_2{}^{11}B(^{10}B)$-^{10}BF molecule, the predicted value calculated by CASSCF is also overestimated by 98.0 cm^{-1} (107.6 cm^{-1}) and 69.7 cm^{-1} (59.5 cm^{-1}). Similarly, for the F_2BAlF molecule, the calculated BF_2 anti-symmetric and symmetric mode is at 1411.1 and 1277.2 cm^{-1} by CASSCF method, , being overestimated by about 129.5 cm^{-1} and 96.4 cm^{-1}respectively.