Supporting Information:

Figure Legend

Figure *S1*

CID spectrum of $[RGYGGGG+H]^+$

Figure *S2*

CID spectra of the radical cations in **Table 1.**a)-d) $[R(G)_{m-2}YG]^{\bullet+}$ (m=2-5); e)-g) $[R(G)_{m-2}FG]^{\bullet+}$ (m=3-5)

Figure *S3*

CID spectra of a)-f) $[K(G)_{n-2}Y(G)_{7-n}]^{\bullet+}$ and g)-l) $[K(G)_{n-2}F(G)_{7-n}]^{\bullet+}$ (n = 2 – 5). Formation of $[b_n - H]^{\bullet+}$ and y_n^+ ions.

Figure *S4*

Potential energy surface for the formation of $[b_2 - H]^{\bullet+}$ ion from $[R^{\bullet}FG]^+$. Upper numbers are enthalpies at 0 K, and lower italicized numbers are free energies at 298 K. All numbers (in kcal mol^{-1}) are relative to the enthalpy of $\mathbf{[R^{\bullet}FG]^+}$**-1**. Selected bond lengths are in Å.

Figure *S5*

The transition states for the formation of $[b_2 - H]^{\bullet+}$ from $[RFG]^{\bullet+}$ and $[KFG]^{\bullet+}$ through the pathway of side-chain attack. Upper numbers are enthalpies at 0 K, and lower italicized numbers are free energies at 298 K. All numbers (in kcal mol^{-1}) are relative to the enthalpy of $\mathbf{[R^{\bullet}FG]^+}$**-1**. Selected bond lengths are in Å.

Figure *S6*

Low-energy structures and potential energy surface for the interconversion of KFG radical cations. Upper numbers are enthalpies at 0 K, and lower italicized numbers are free energies at 298 K. All numbers (in kcal mol^{-1}) are relative to the enthalpy of $\mathbf{[K^{\bullet}FG]^+}$**-1**. Selected bond lengths are in Å.

Figure *S7*

Potential energy surface for the formation of a_2^+ ion from $[K^{\bullet}FG]^+$. Upper numbers are enthalpies at 0 K, and lower italicized numbers are free energies at 298 K. All numbers (in kcal mol^{-1}) are relative to the enthalpy of $\mathbf{[K^{\bullet}FG]^+}$**-1**. Selected bond lengths are in Å

Figure *S1*

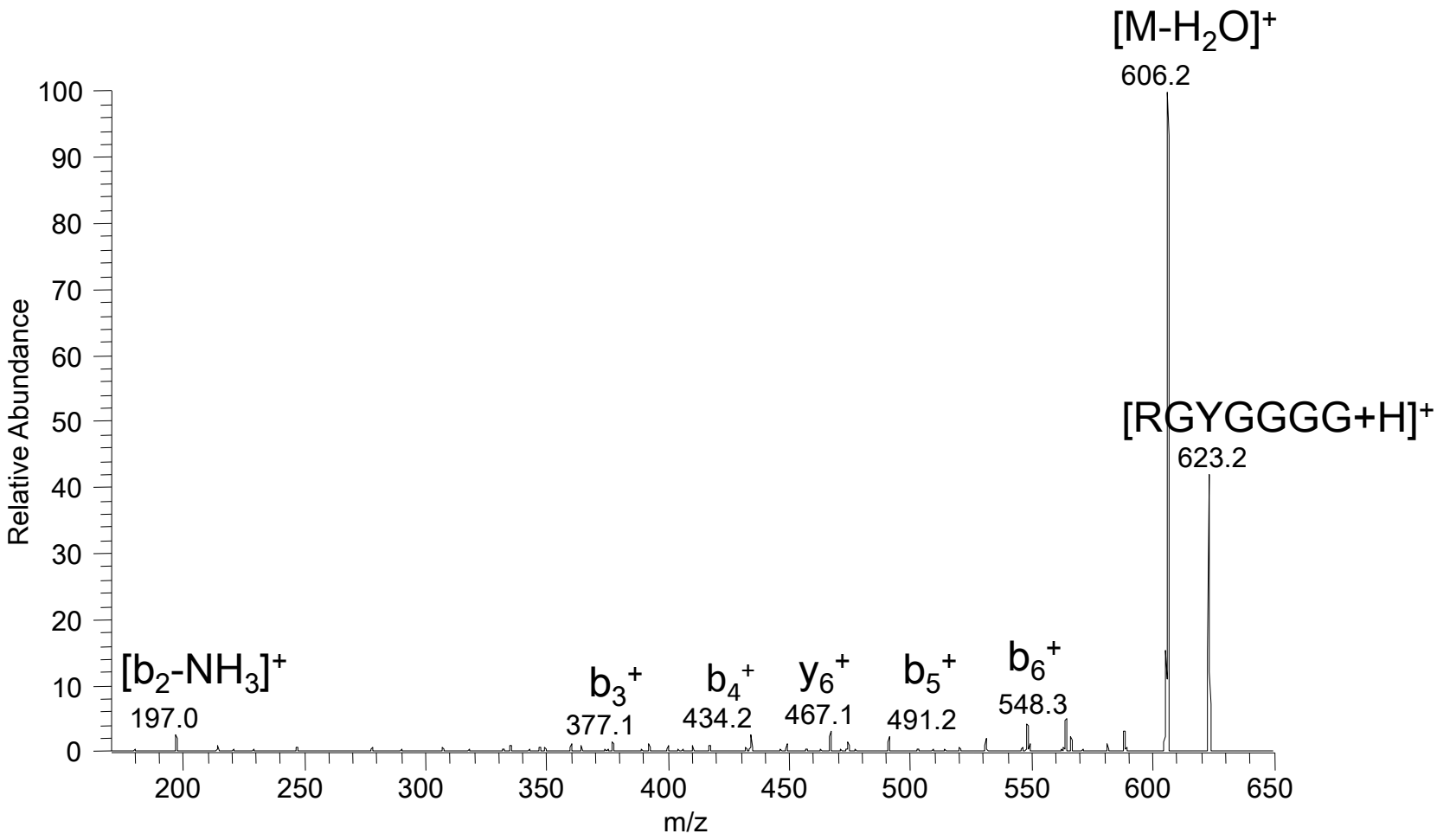


Figure S2

Supplementary Material (ESI) for PCCP

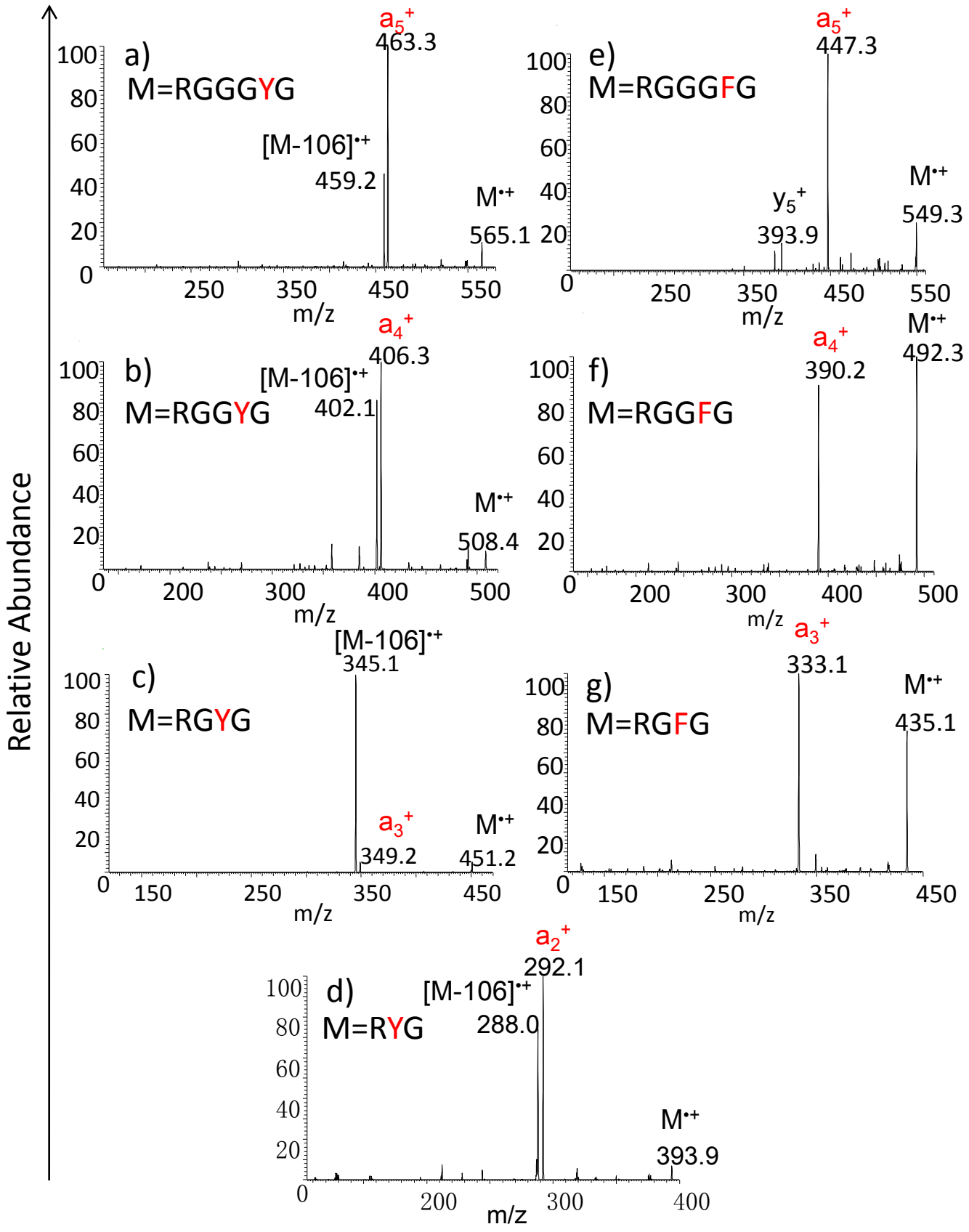


Figure S3

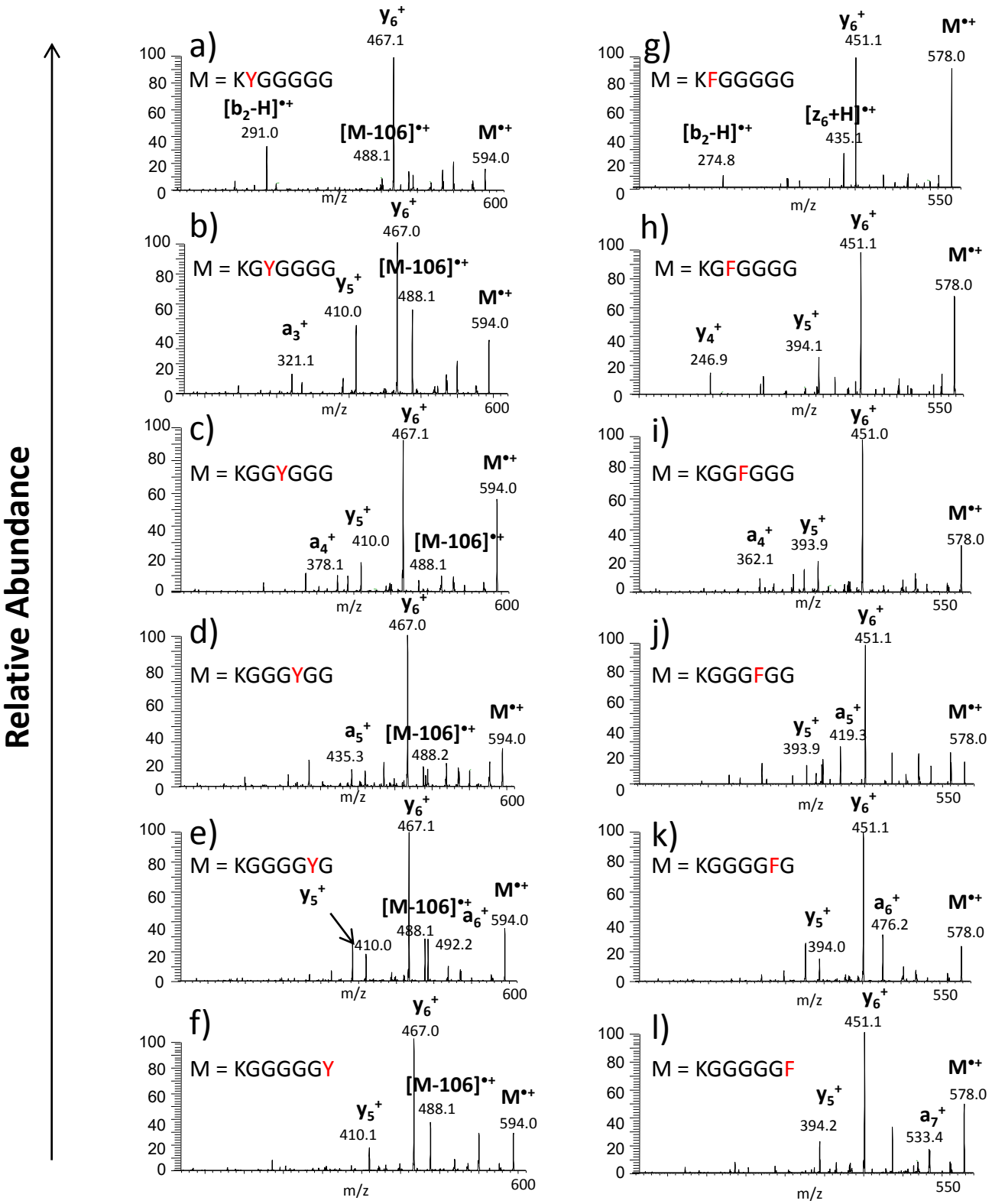

Relative Abundance
a)
M = KYGGGGG
[b2-H]•+
291.0
[M-106]•+
488.1
M•+
594.0
y6+
467.1
b)
M = KGYGGGG
y5+
410.0
a3+
321.1
[M-106]•+
488.1
M•+
594.0
y6+
467.0
c)
M = KGGYGGG
y5+
410.0
a4+
378.1
[M-106]•+
488.1
M•+
594.0
y6+
467.1
d)
M = KGGGYGG
a5+
435.3
[M-106]•+
488.2
M•+
594.0
y6+
467.0
e)
M = KGGGGYG
y5+
410.0
[M-106]•+
488.1
a6+
492.2
M•+
594.0
y6+
467.1
f)
M = KGGGGGY
y5+
410.1
[M-106]•+
488.1
M•+
594.0
y6+
467.0
g)
M = KFGGGGG
[b2-H]•+
274.8
[z6+H]•+
435.1
M•+
578.0
y6+
451.1
h)
M = KGFGGGG
y4+
246.9
y5+
394.1
M•+
578.0
y6+
451.1
i)
M = KGGFGGG
a4+
362.1
y5+
393.9
M•+
578.0
y6+
451.0
j)
M = KGGGFGG
y5+
393.9
a5+
419.3
M•+
578.0
y6+
451.1
k)
M = KGGGGFG
y5+
394.0
a6+
476.2
M•+
578.0
y6+
451.1
l)
M = KGGGGGF
y5+
394.2
a7+
533.4
M•+
578.0
y6+
451.1
m/z
100
80
60
40
20
0
600
550

Figure *S4*

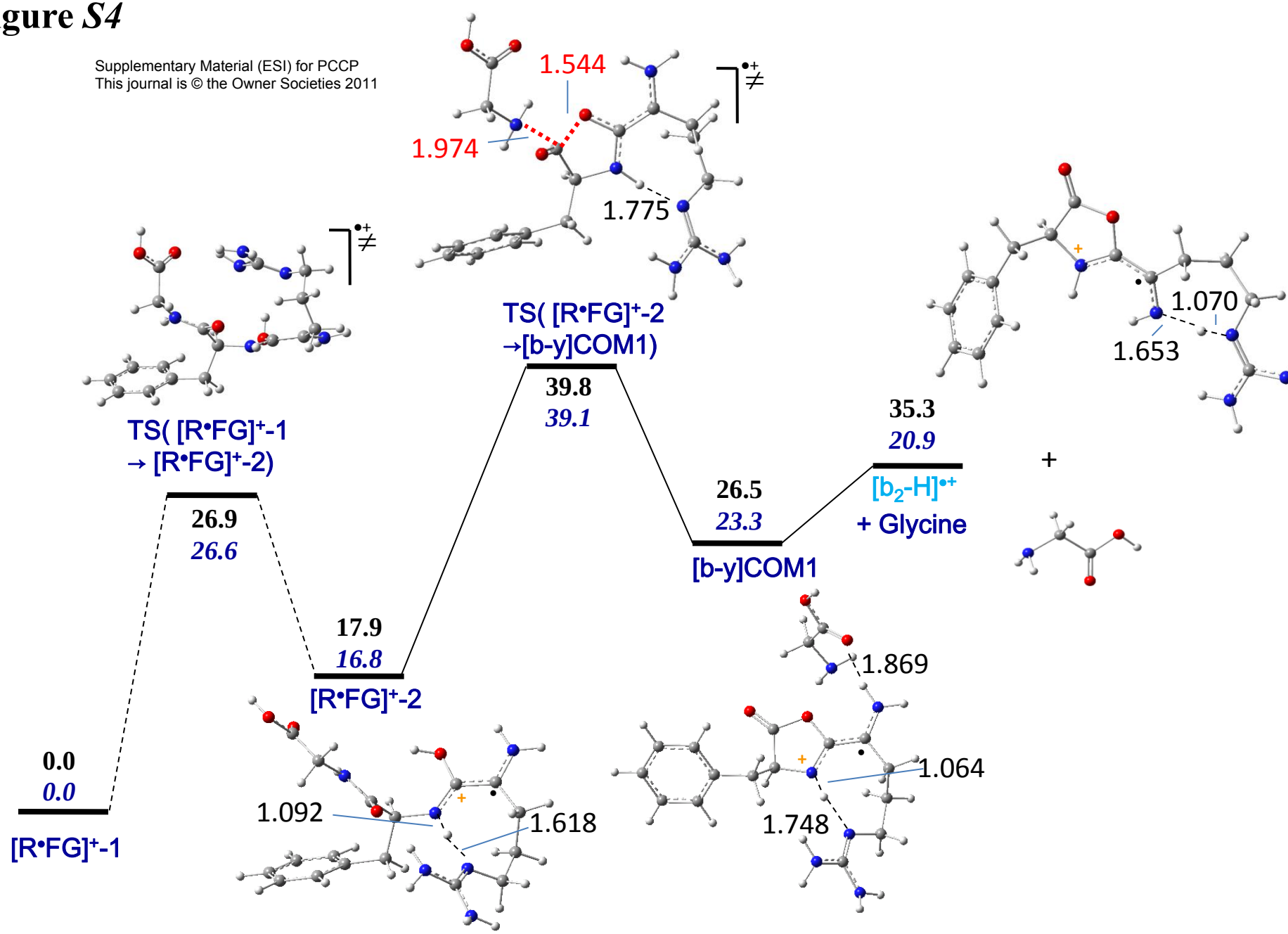
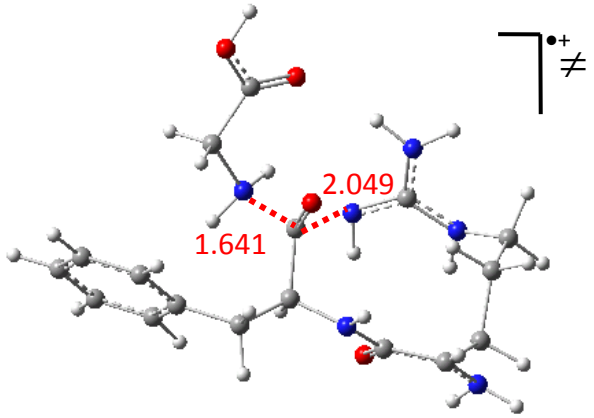


Figure *S5*

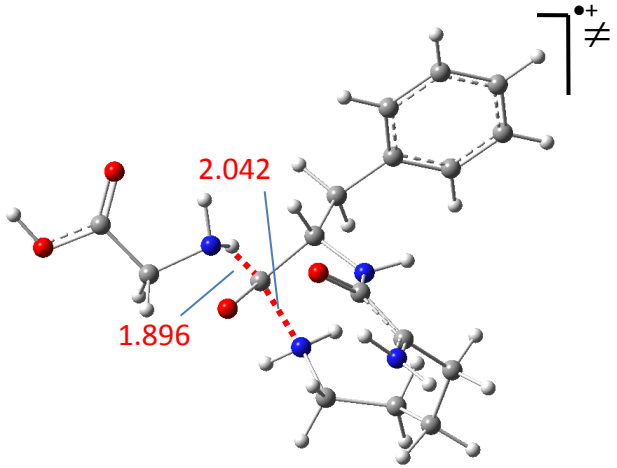
Supplementary Material (ESI) for PCCP



TS (side-chain attack to form $[b_2\text{-H}]^{\bullet+}$ from $[RFG]^{\bullet+}$)

49.2

52.2



TS (side-chain attack to form $[b_2\text{-H}]^{\bullet+}$ from $[KFG]^{\bullet+}$)

57.2

55.4

Figure S6

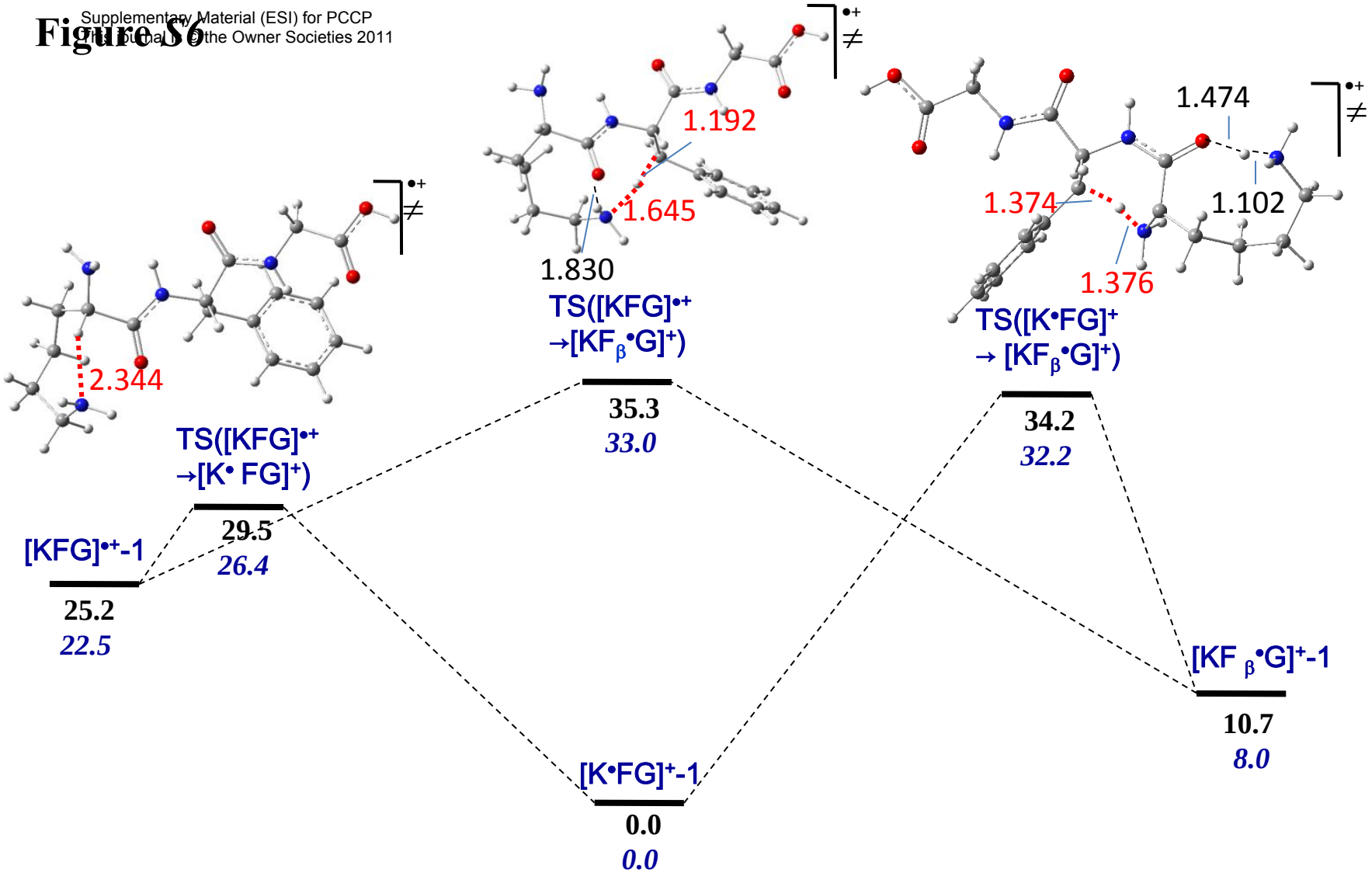

2.344
TS([KFG]•+ →[K• FG]+)
[KFG]•+-1
25.2
22.5
29.5
26.4
1.192
1.645
1.830
TS([KFG]•+ →[KFβ•G]+)
35.3
33.0
[K•FG]+-1
0.0
0.0
1.474
1.374
1.102
1.376
TS([K•FG]+ → [KFβ•G]+)
34.2
32.2
[KFβ•G]+-1
10.7
8.0

Figure *S7*

Supplementary Material (ESI) for PCCP