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Electronic Supplementary Information (ESI)

IRMPD spectroscopy of metalated flavins: Structure and bonding of M^{q+}-lumichrome complexes (M^{q+}=Li^+-Cs^+, Ag^+, Mg^{2+})

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Figure S1. Laser power of FELIX operated at 10 Hz for recording the $Mg^{2+}LC_2$ spectrum (blue) and the other M^+LC spectra (red).

Figure S2. Comparison of the IRMPD spectrum of Li^+LC with linear IR absorption spectra of the $Li^+LC(O4)$ isomer calculated at different levels of theory using either GAUSSIAN or TURBOMOLE. The theoretical spectra are linearly scaled to match the position of the band at 1800 cm^{-1} and convoluted with a Gaussian line profile with a width of 20 cm^{-1} (FWHM).

Figure S3. Comparison of the IRMPD spectrum of Li^+LC to linear IR absorption spectra calculated for different isomers at the B3LYP/cc-pVDZ level. Binding free energies (G) are indicated in kJ/mol.

Figure S4. Plot of free energies of the O4 and O2 isomers of M^+LC (M=alkali atoms Li-Cs, filled blue circles), Ag^+LC (open blue circle), $Mg^{2+}LC_n$ (n=1 and 2, filled red squares), and H^+LC (green filled circles) and their difference as a function of the inverse ionic radius of the metal ion (Table 2). Also shown are plots of the NBO charges of M^{q+}.

Figure S5. Plot of selected structural parameters of the O4 and O2 isomers of M^+LC (M=alkali atoms Li-Cs, filled blue circles), Ag^+LC (open blue circle), $Mg^{2+}LC_n$ (n=1 and 2, filled red squares), and H^+LC (green filled circles) as a function of the inverse ionic radius of the metal ion (Table 3).

Figure S6. Plot of selected vibrational parameters (C=O stretch modes) of the O4 and O2 isomers of M^+LC (M=alkali atoms Li-Cs, filled blue circles), Ag^+LC (open blue circle), $Mg^{2+}LC_n$ (n=1 and 2, filled red squares), and H^+LC (green filled circles) as a function of the inverse ionic radius of the metal ion (Table 3).

Figure S7. Comparison of the IRMPD spectrum of Li^+LC to linear IR absorption spectra calculated for LC, iso-LC, and the O4 and O2 isomers of their Li^+ complexes at the B3LYP/cc-pVDZ level. Relative free energies (ΔG) and binding free energies (G) are indicated in kJ/mol.

Figure S8. Comparison of the IRMPD spectra of Li^+LC and Ag^+LC to linear IR absorption spectra calculated for the O4 isomers of Li^+LC and Ag^+LC at the B3LYP/cc-pVDZ level.

Figure S9. NBO charge distribution (in me) of LC evaluated at the B3LYP/cc-pVDZ level.

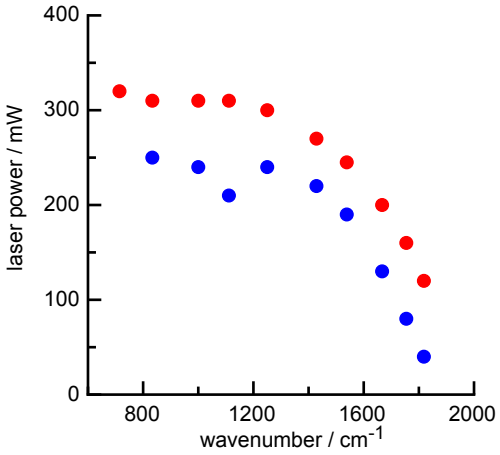

400
300
200
100
0
laser power / mW
800
1200
1600
2000
wavenumber / cm-1

Figure S1

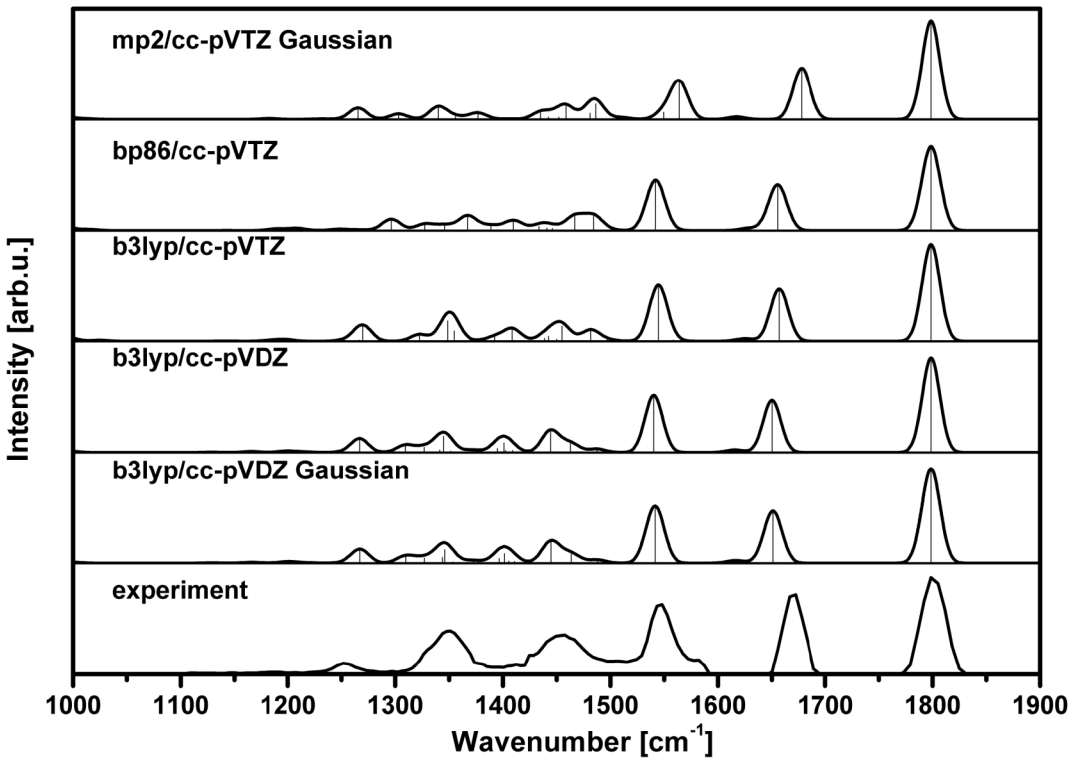
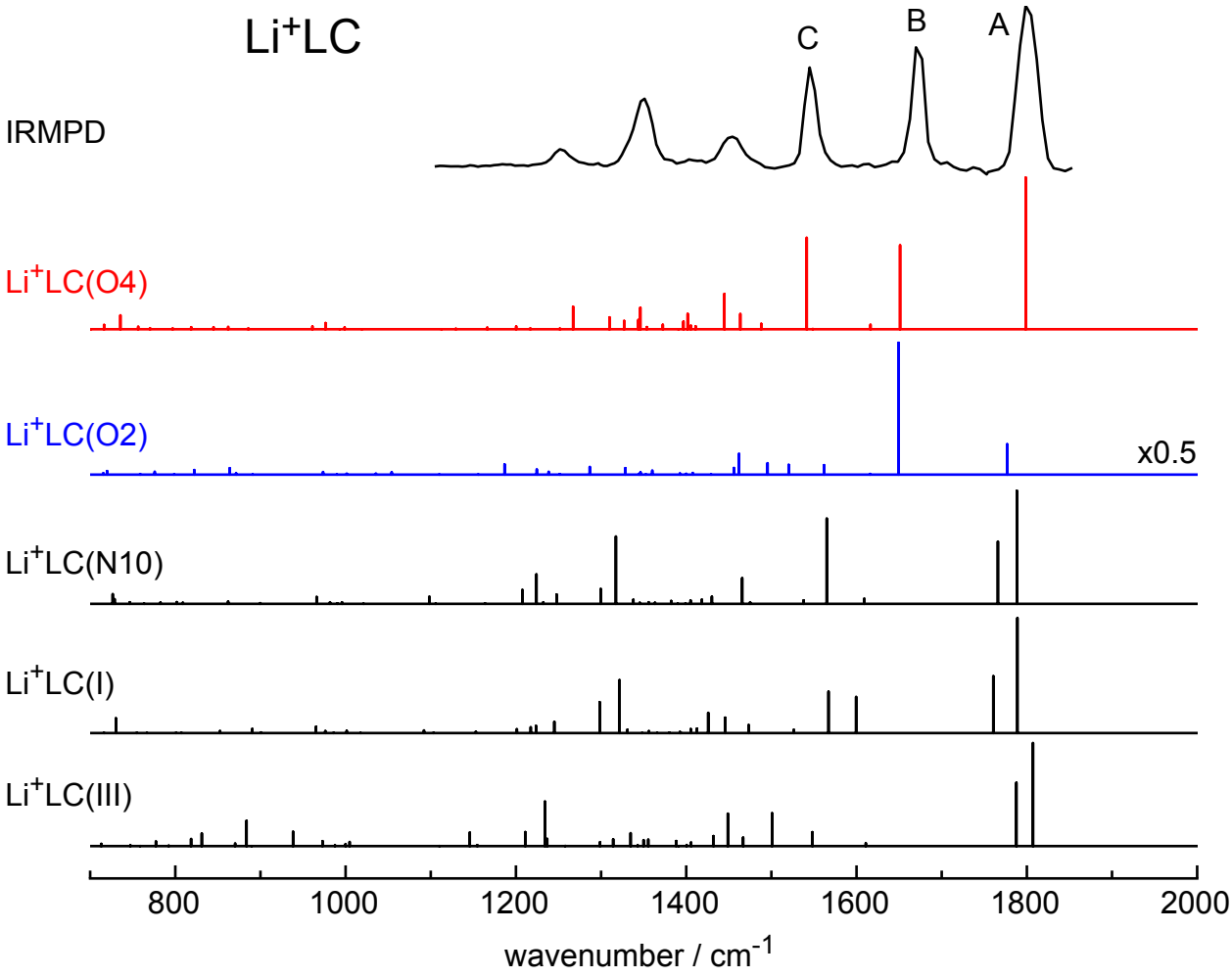

mp2/cc-pVTZ Gaussian
bp86/cc-pVTZ
b3lyp/cc-pVTZ
b3lyp/cc-pVDZ
b3lyp/cc-pVDZ Gaussian
experiment
Intensity [arb.u.]
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
Wavenumber [cm-1]

Figure S2


Li+LC
IRMPD
C
B
A
Li+LC(O4)
Li+LC(O2)
x0.5
Li+LC(N10)
Li+LC(I)
Li+LC(III)
800
1000
1200
1400
1600
1800
2000
wavenumber / cm-1

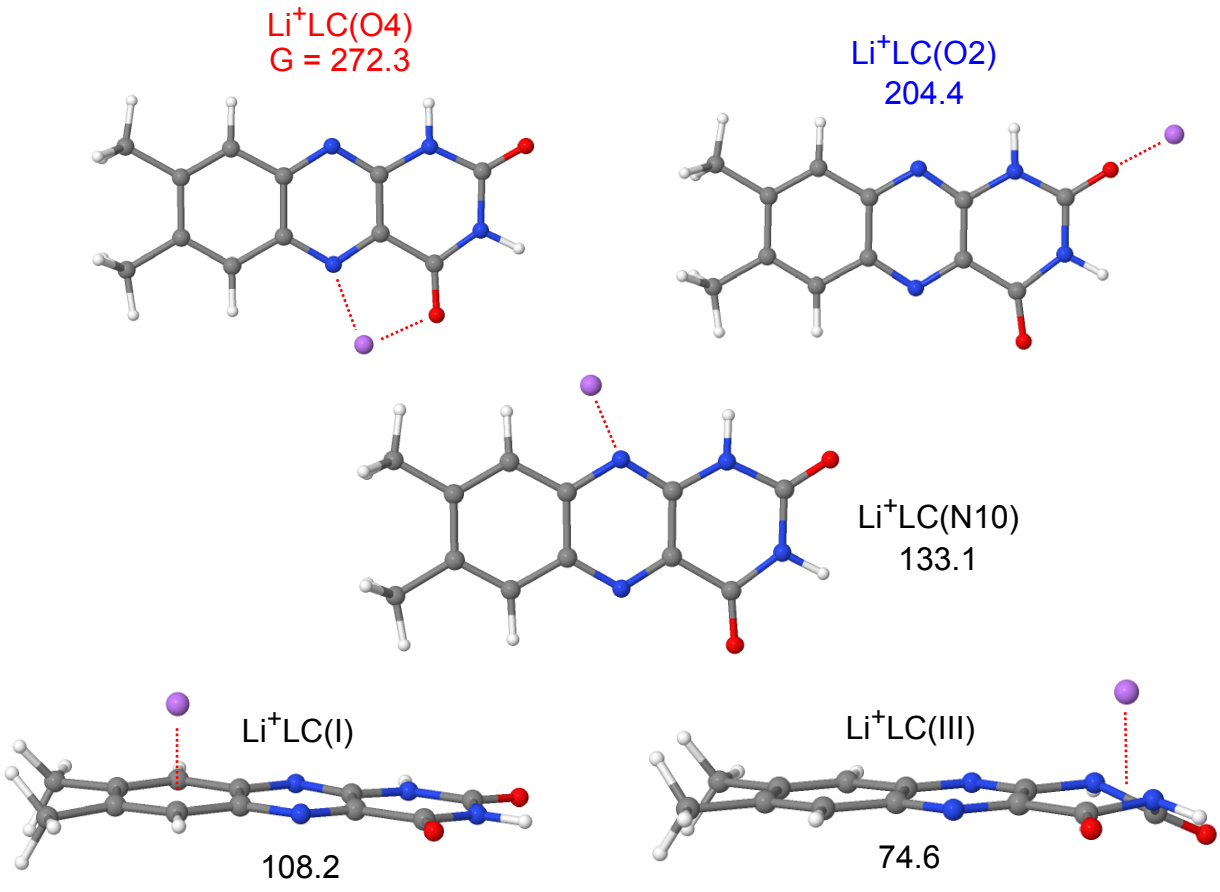

Li+LC(O4)
G = 272.3
Li+LC(O2)
204.4
Li+LC(N10)
133.1
Li+LC(I)
108.2
Li+LC(III)
74.6

Figure S3

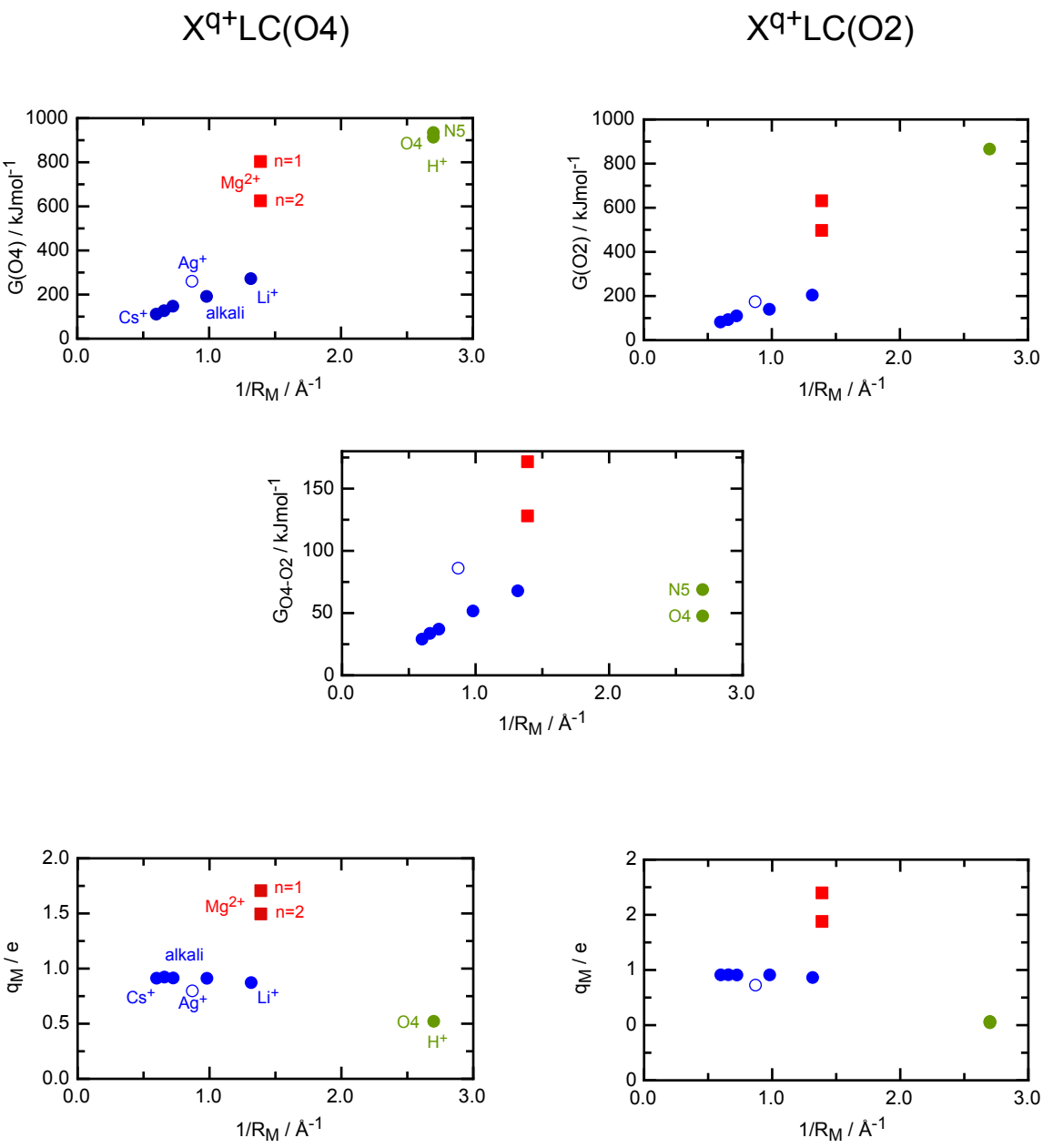

X^q+LC(O4)
X^q+LC(O2)
G(O4) / kJmol-1
G(O2) / kJmol-1
GO4-O2 / kJmol-1
qM / e
1/RM / Å-1
n=1
n=2
Mg2+
Ag+
Li+
Cs+
alkali
O4
N5
H+

Figure S4

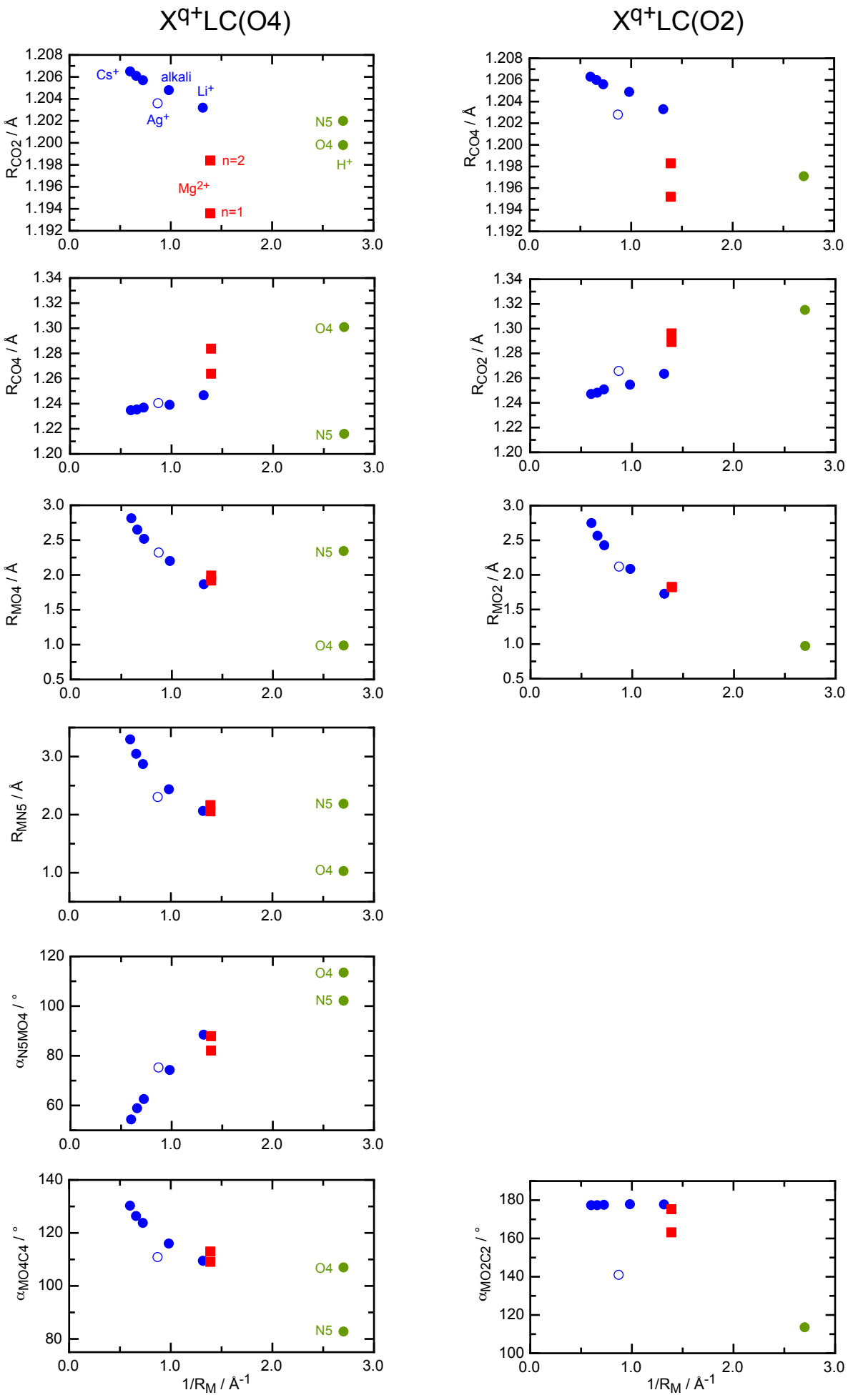

X^q+LC(O4)
X^q+LC(O2)
R_CO2 / Å
R_CO4 / Å
R_MO4 / Å
R_MO2 / Å
R_MN5 / Å
α_N5MO4 / °
α_MO4C4 / °
α_MO2C2 / °
1/R_M / Å^-1
Cs+
alkali
Li+
Ag+
Mg2+
n=2
n=1
N5
O4
H+

Figure S5

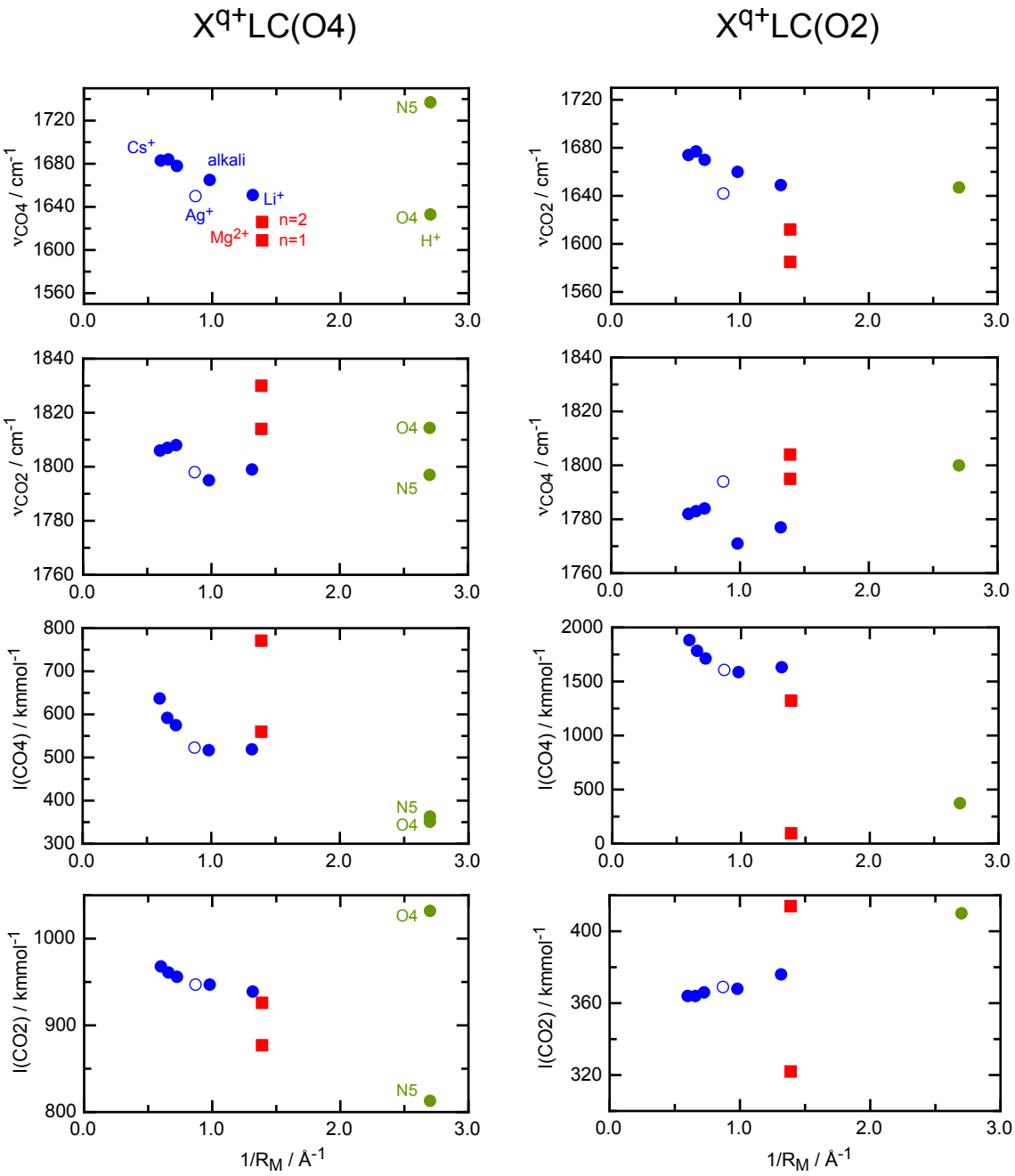

X^q+LC(O4)
X^q+LC(O2)
ν_CO4 / cm^-1
ν_CO2 / cm^-1
I(CO4) / kmmol^-1
I(CO2) / kmmol^-1
1/R_M / Å^-1
Cs+
alkali
Ag+
Li+
Mg2+
n=2
n=1
N5
O4
H+

Figure S6

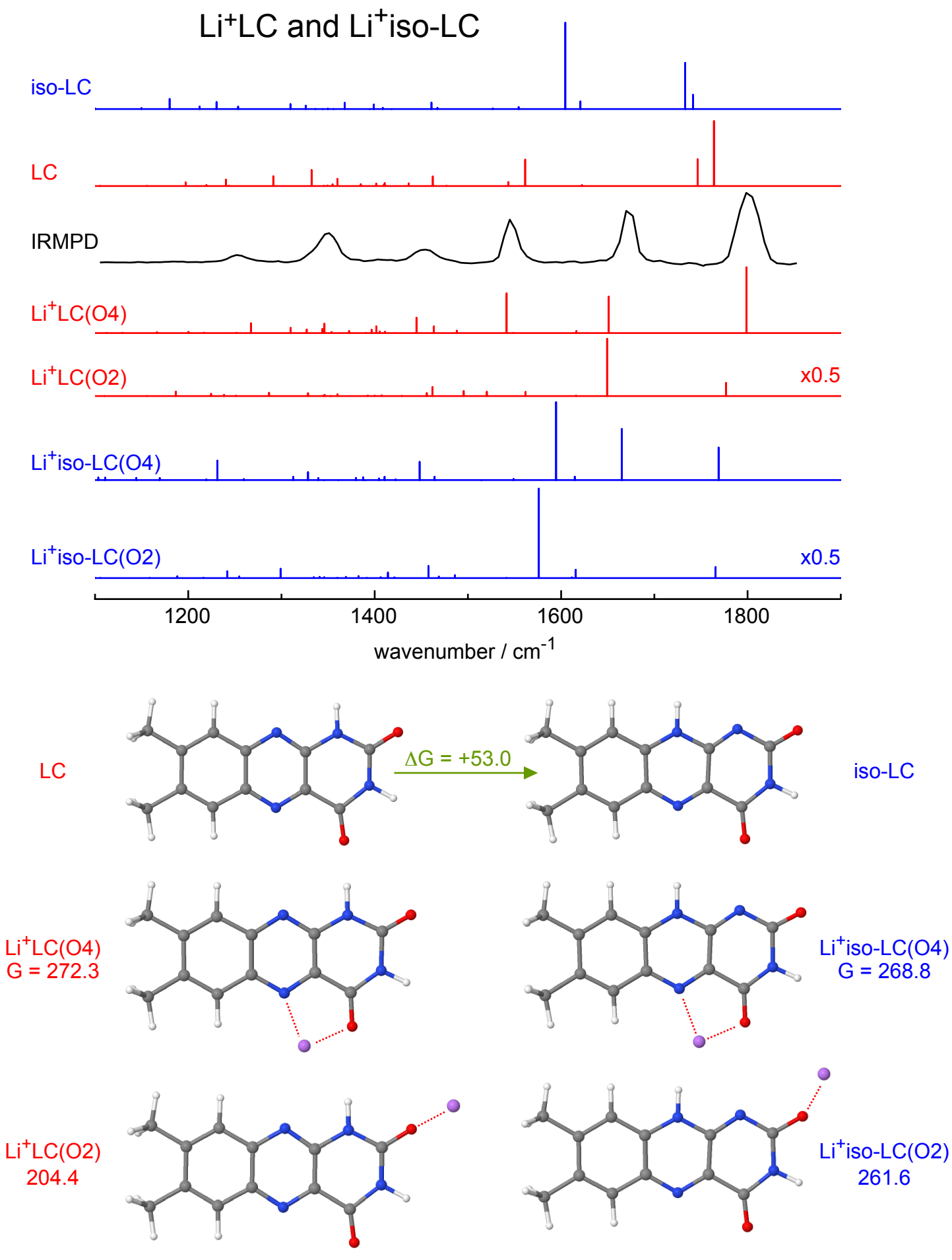

Li+LC and Li+iso-LC
iso-LC
LC
IRMPD
Li+LC(O4)
Li+LC(O2)
x0.5
Li+iso-LC(O4)
Li+iso-LC(O2)
x0.5
1200
1400
1600
1800
wavenumber / cm-1
LC
ΔG = +53.0
iso-LC
Li+LC(O4)
G = 272.3
Li+iso-LC(O4)
G = 268.8
Li+LC(O2)
204.4
Li+iso-LC(O2)
261.6

Figure S7

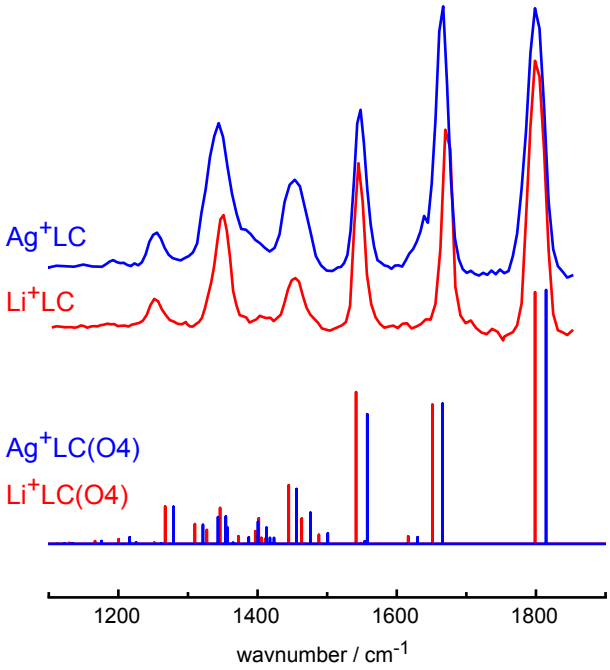


Figure S8

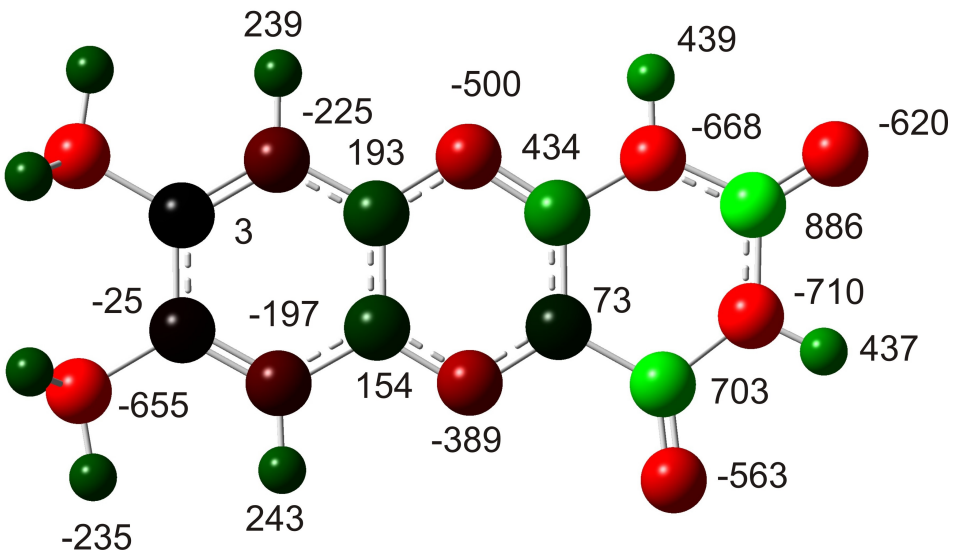

239
439
-500
-225
-668
-620
193
434
3
886
-25
-197
73
-710
437
154
703
-655
-389
-563
243
-235

Figure S9