ESI for "Theoretical and experimental investigation of the structural and spectroscopic properties of coumarin 343 fluoroionophores"

Conformer	ΔE (%)	$\theta_{2\text{-}1\text{-}16\text{-}N}$	$\theta_{1\text{-}16\text{-}N\text{-}17}$	$\theta_{16\text{-}N\text{-}17\text{-}18}$	$\theta_{1\text{-}16\text{-}N\text{-}19}$	$\theta_{16\text{-}N\text{-}19\text{-}20}$
		C343-dea-K^+				
a	2.5 (9)	-48.8	-18.2	118.8	174.8	85.6
b	2.6 (8)	48.9	18.3	-119.0	-174.7	-85.7
c	1.9 (11)	40.4	23.4	-124.8	-172.8	75.2
d	2.0 (11)	-48.1	-20.2	123.7	173.7	-78.5
e	0.0 (24)	-44.8	-29.0	-86.5	167.2	-109.7
f	0.6 (19)	44.7	28.8	87.3	-166.9	108.4
g	4.0 (5)	-45.8	-18.5	-114.5	167.1	76.8
h	4.1 (5)	51.0	12.8	121.6	-167.2	-81.6
i	4.5 (4)	-51.5	-22.4	-66.6	168.6	95.3
j	4.2 (4)	51.7	22.6	67.3	-168.6	-95.6
		C343-dea-Li^+				
a	0.0 (16)	42.2	23.8	95.9	-169.1	78.6
b	0.3 (14)	39.1	20.3	-123.1	-173.7	78.3
c	0.4 (14)	-41.3	-24.5	-96.3	168.7	-77.1
d	0.6 (12)	-38.3	-20.7	123.0	173.0	-78.1
e	0.8 (12)	38.6	18.0	-118.1	-174.9	-85.3
f	1.0 (11)	-38.0	-18.5	188.2	174.7	85.4
g	2.2 (6)	41.7	14.4	124.4	-166.3	-82.3
h	2.6 (6)	-41.7	-14.9	-123.5	166.2	81.8
i	3.1 (5)	42.9	24.2	62.2	-166.8	-94.8
j	3.3 (4)	-42.8	-24.0	-62.2	168.8	94.9
		C343-dea-Mg^{++}				
a	0.0 (30)	-33.5	-18.5	121.0	171.1	-76.9
b	0.4 (26)	34.1	18.0	-120.8	-171.5	77.0
c	1.5 (16)	-36.8	-21.4	-104.0	165.8	-76.3
d	1.9 (14)	37.5	21.3	103.0	-165.5	78.0
e	3.5 (7)	33.3	16.0	-115.7	-173.7	-87.7
f	3.6 (7)	-32.9	-15.8	115.7	173.6	87.7
		C343-dea-Ca^{++}				
a	0.0 (30)	34.8	18.0	-120.3	-171.5	77.1
b	0.5 (25)	-34.4	-18.4	120.8	171.3	-77.2
c	0.6 (24)	-38.7	-20.8	-102.2	166.5	-77.7
d	1.4 (17)	38.9	20.7	102.7	-165.9	78.8
e	8.3 (1)	34.5	15.1	-115.0	-174.2	-87.7
f	8.9 (1)	-34.5	-15.1	115.1	174.2	87.4
g	9.7 (1)	-37.6	165.4	84.6	-13.7	-128.0
h	9.8 (1)	-39.1	167.5	98.9	-21.6	-61.3

Table S1: Relative conformer energies (kJ/mol), MB population ratios (in parentheses) and selected torsion angles (in degrees) of C343-dea complexes with, K^+, Li^+, Mg^{++}, and Ca^{++} as determined at the IEFPCM/B3LYP/6-311G(d) level of approximation.

C343-dea	**q : C_2-H**	**q : C_4-H**	**Δq : C_2-H**	**Δq : C_4-H**
Free	0.188	-0.027	/	/
Li^+	0.193	-0.018	0.005	0.009
K^+	0.201	-0.005	0.013	0.022
Mg^{++}	0.214	0.007	0.026	0.034
Ca^{++}	0.203	0.002	0.015	0.029

Table S2: IEFPCM/B3LYP/6-311G(d) Mulliken charges, q, and differences of charges, Δq, (in a.u.) on the C_2 and C_4 atoms of the complexes with respect to the free C343-dea. The -CH units have been considered as a whole.

Conformers	ΔE (%)	$\theta_{2\text{-}1\text{-}16\text{-}N}$	$\theta_{1\text{-}16\text{-}N\text{-}17}$	$\theta_{16\text{-}N\text{-}17\text{-}18}$	$\theta_{1\text{-}16\text{-}N\text{-}19}$	$\theta_{16\text{-}N\text{-}19\text{-}20}$
C343-crown-Li^+						
a	0.0 (97)	139.0	-172.1	-78.1	-31.6	159.4
b	9.1 (2)	-141.4	176.8	71.9	39.8	-156.9
c	12.0 (1)	-141.9	175.9	72.4	38.5	-161.5
C343-crown-K^+						
a	0.0 (99)	139.0	-172.1	-78.1	-31.7	159.6
b	11.8 (1)	-141.9	175.9	72.4	38.5	-161.5
C343-crown-Mg^{++}						
a	0.0 (56)	155.9	170.6	-74.0	-62.9	165.7
b	1.1 (35)	-154.7	61.1	-164.1	-171.7	72.5
c	4.6 (9)	-154.7	-168.6	71.4	65.6	-164.5
C343-crown-Ca^{++}						
a	0.0 (54)	152.0	174.6	-74.6	-58.1	169.6
b	0.4 (46)	-153.2	59.4	-170.5	-173.0	69.5

Table S3: Relative conformer energies (kJ/mol), MB population ratios (in parentheses) and selected torsion angles (in degrees) of C343-crown complexes with Li^+, K^+, Mg^{++}, and Ca^{++} as determined at the IEFPCM/B3LYP/6-311G(d) level of approximation.

C343-crown	q : C_2-H	q : C_4-H	Δq : C_2-H	Δq : C_4-H
Free	0.233	-0.027	/	/
Li^+	0.208	-0.011	-0.025	0.016
K^+	0.208	-0.011	-0.025	0.016
Mg^{++}	0.241	0.019	0.008	0.045
Ca^{++}	0.238	0.016	0.005	0.043

Table S4: IEFPCM/B3LYP/6-311G(d) Mulliken charges, q, and differences of charges, Δq, (in a.u.) on the C_2 and C_4 atoms of the complexes with respect to the free C343-crown. The -CH units have been considered as a whole.

Conformers	ΔE (%)	$\theta_{2\text{-}1\text{-}16\text{-}N}$	$\theta_{1\text{-}16\text{-}N\text{-}17}$	$\theta_{16\text{-}N\text{-}17\text{-}18}$	$\theta_{1\text{-}16\text{-}N\text{-}19}$	$\theta_{16\text{-}N\text{-}19\text{-}20}$
C343-dibenzocrown-Li^+						
a	0.0 (100)	151.3	178.7	-63.4	-41.2	-174.9
C343-dibenzocrown-K^+						
a	0.0 (100)	151.2	178.7	-63.5	-41.2	-174.8
C343-dibenzocrown-Mg^{++}						
a	0.0 (97)	157.9	170.6	-75.3	-62.7	168.2
b	9.1 (3)	-158.2	64.9	-168.2	-168.9	70.3
C343-dibenzocrown-Ca^{++}						
a	0.0 (79)	156.5	172.9	-69.7	-59.1	175.8
b	3.2 (21)	-155.2	60.9	-174.1	-172.0	68.8

Table S5: Relative conformer energies (kJ/mol), MB population ratios (in parentheses) and selected torsion angles (in degrees) of C343-dibenzocrown complexes with Li^+, K^+, Mg^{++}, and Ca^{++} as determined at the IEFPCM/B3LYP/6-311G(d) level of approximation.

C343-dibenzocrown	q : C_2-H	q : C_4-H	Δq : C_2-H	Δq : C_4-H
Free	0.194	-0.022	/	/
Li^+	0.203	-0.006	0.009	0.016
K^+	0.203	-0.006	0.009	0.016
Mg^{++}	0.246	0.021	0.052	0.042
Ca^{++}	0.237	0.018	0.044	0.040

Table S6: IEFPCM/B3LYP/6-311G(d) Mulliken charges, q, and differences of charges, Δq, (in a.u.) on the C_2 and C_4 atoms of the complexes with respect to the free C343-dibenzocrown. The -CH units have been considered as a whole.

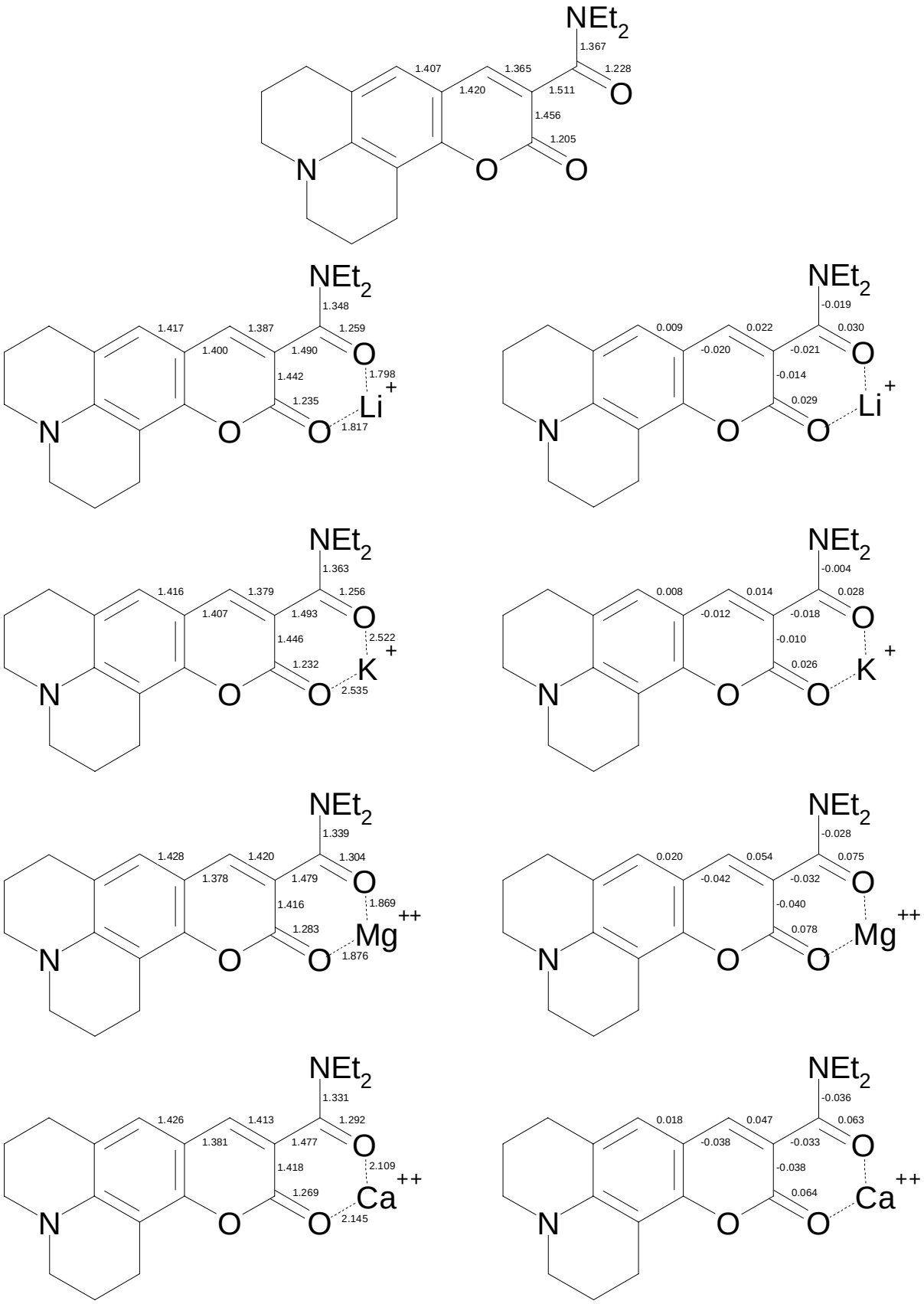


Figure S1: Selected bond lengths (Å) of C343-dea and its complexes. The structures on the left display the bond lengths of the complexes whereas these on the right the bond length variations with respect to C343-dea.

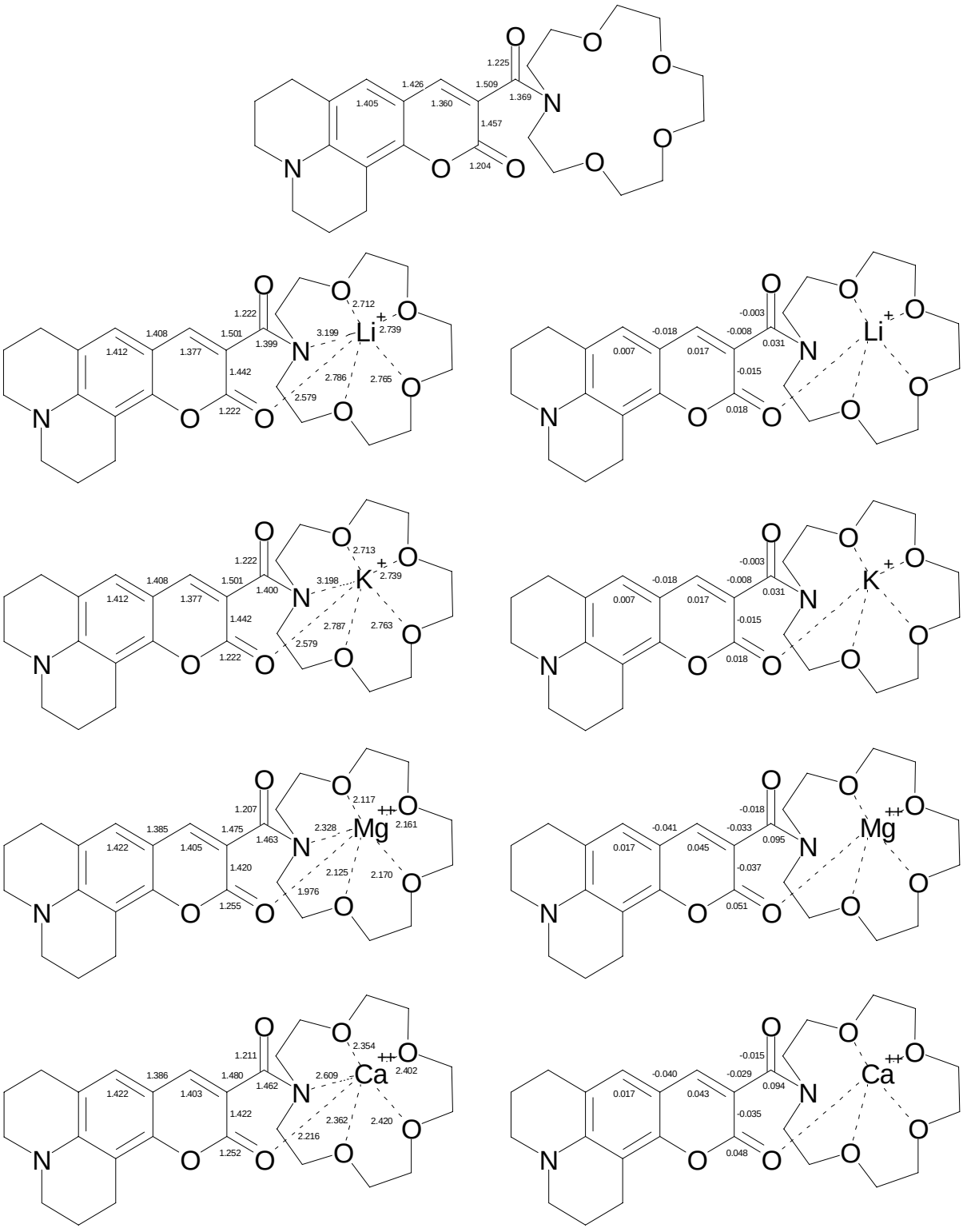
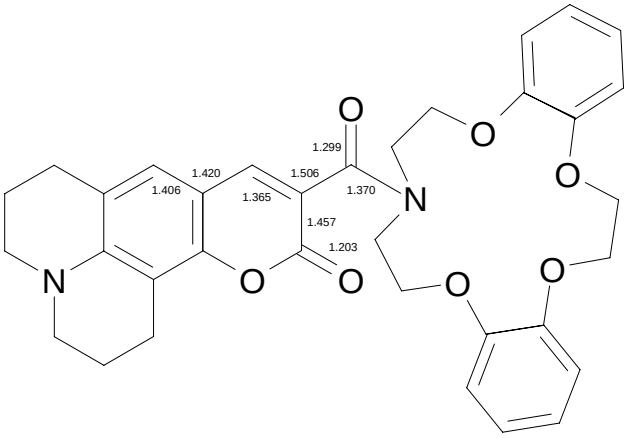


Figure S2: Selected bond lengths (Å) of C343-crown and its complexes. The structures on the left display the bond lengths of the complexes whereas those on the right the bond length variations with respect to C343-crown.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O
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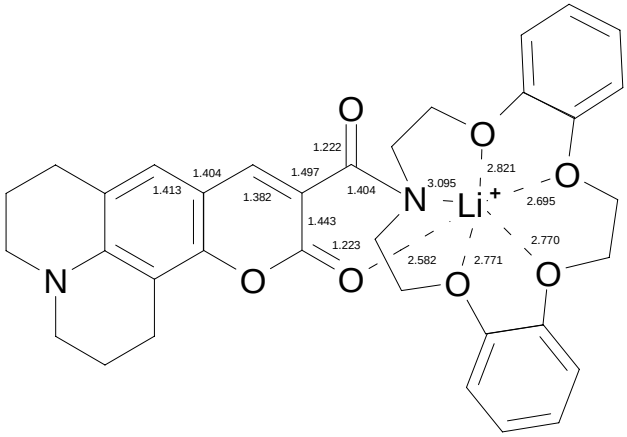
O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2.771
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O
O
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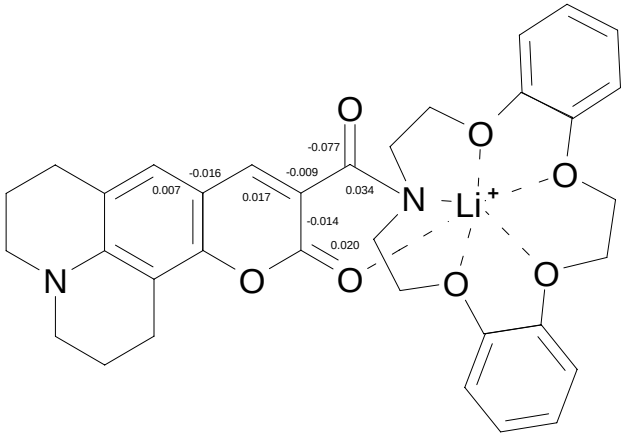
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Li+
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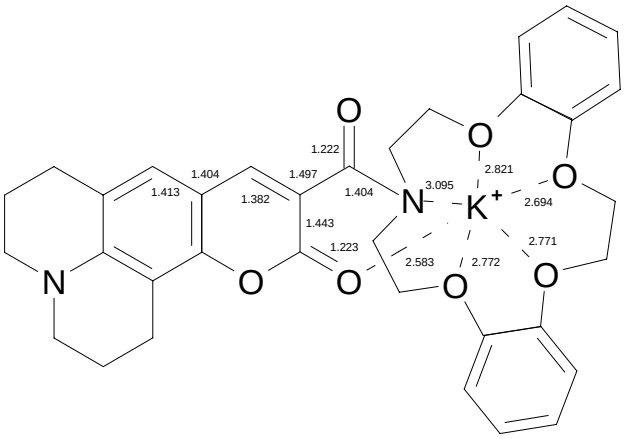
O
O
O
O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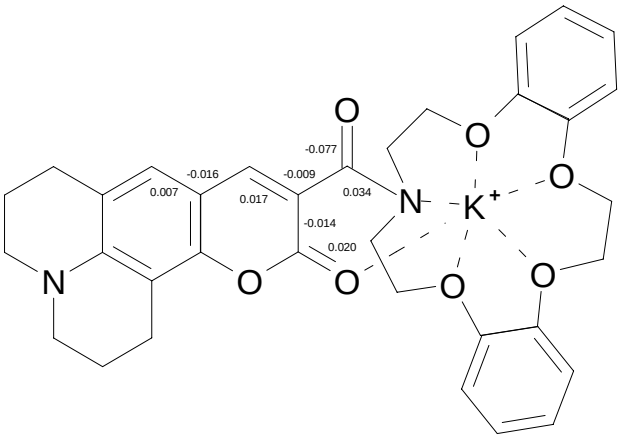
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K+
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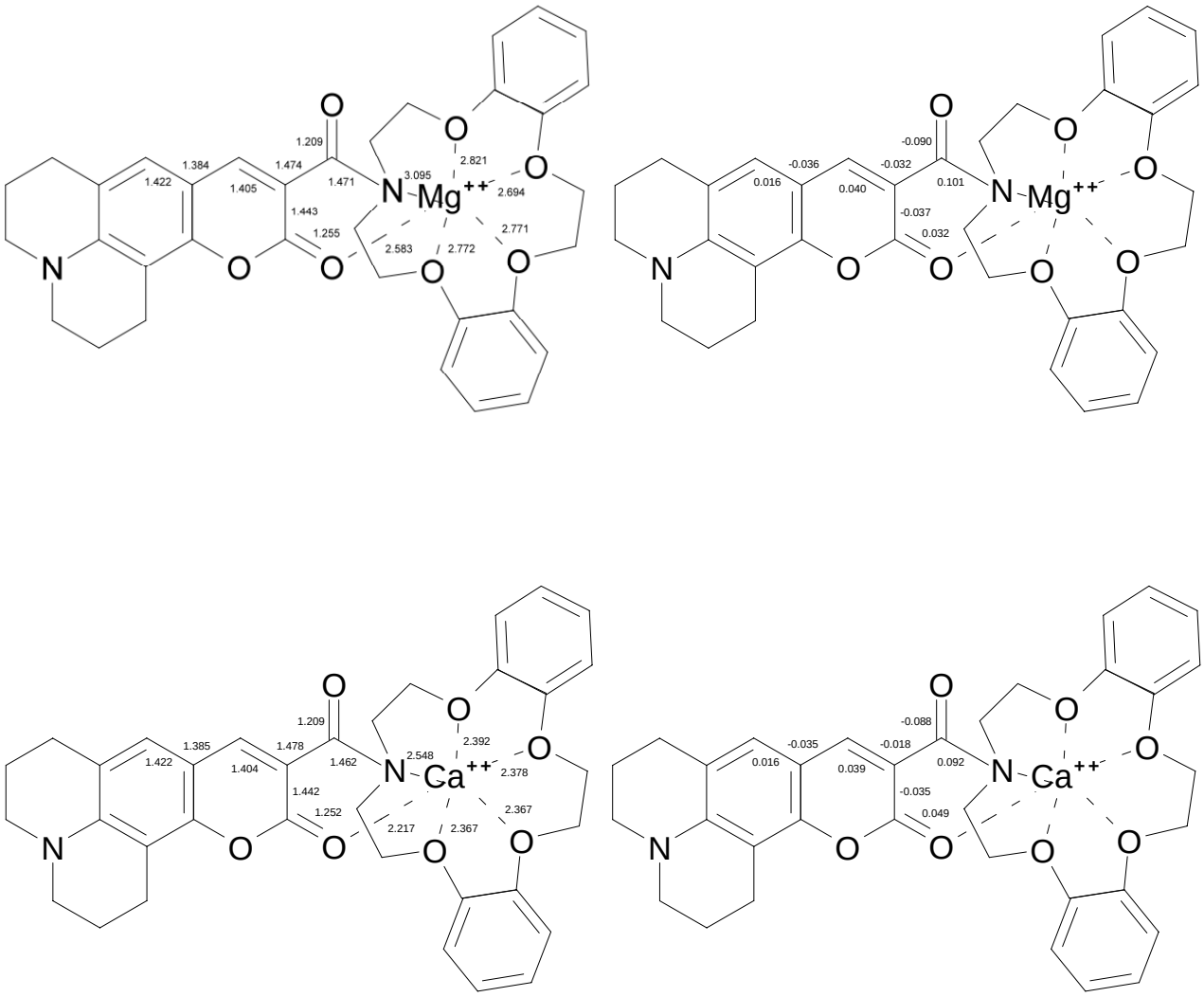


Figure S3: Selected bond lengths (Å) of C343-dibenzocrown and its complexes. The structures on the left display the bond lengths of the complexes those on the right the bond length variations with respect to C343-dibenzocrown.

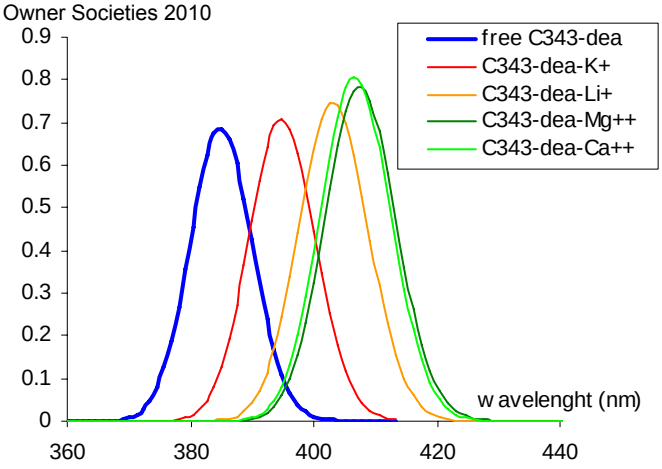


Figure S4: UV-visible absorption spectrum (FWMH = 0.25eV) for the free C343-dea and its complexes.

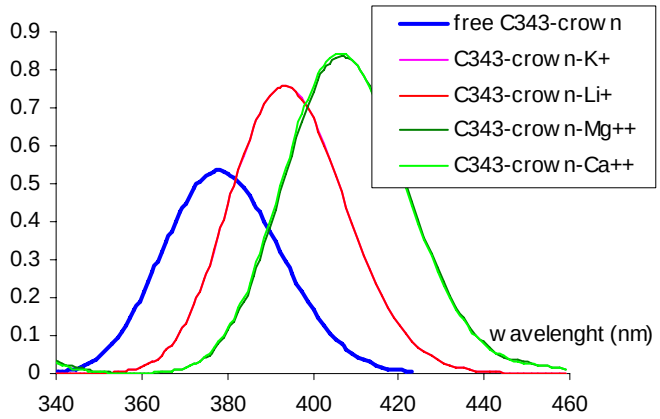


Figure S5: UV-visible absorption spectrum (FWMH = 0.25eV) for C343-crown and its complexes.

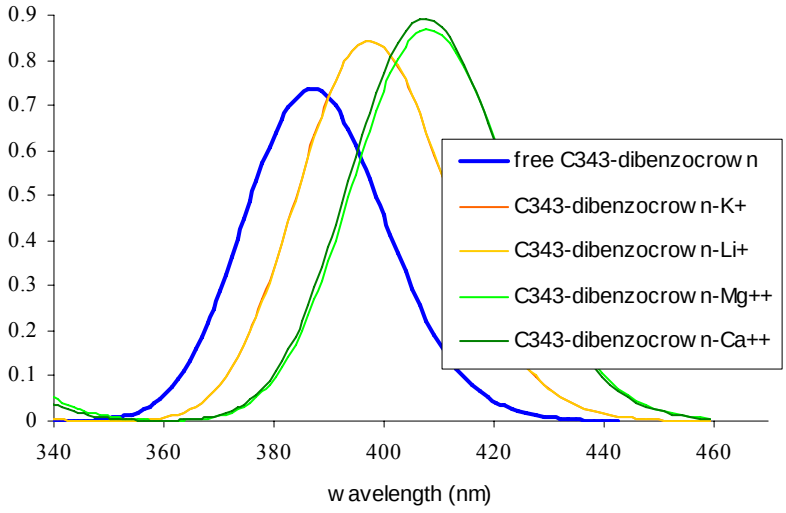
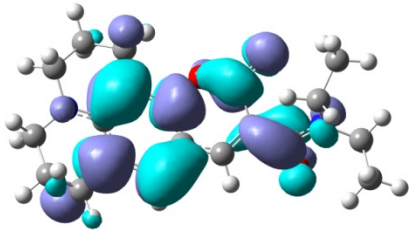


Figure S6: UV-visible absorption spectrum (FWMH = 0.25eV) for C343-benzocrown and its complexes.

C343-dea **ΔE(H-L) = 3.51 eV**



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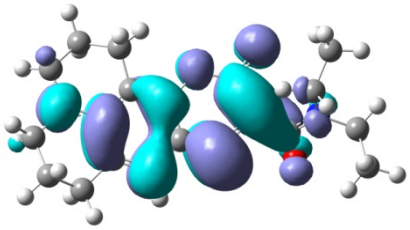

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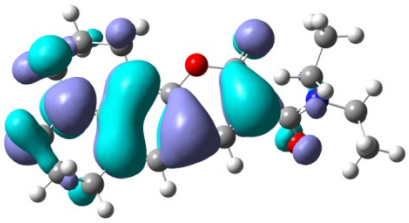

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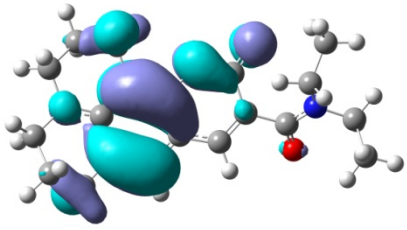

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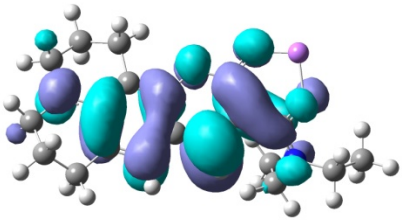
C343-dea-Li^+ $\Delta E(H-L) = 3.30$ eV



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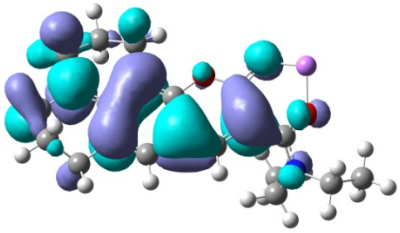

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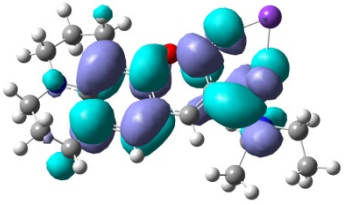
C343-dea-K^+ $\Delta E(H-L) = 3.40$ eV



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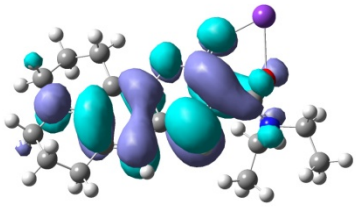

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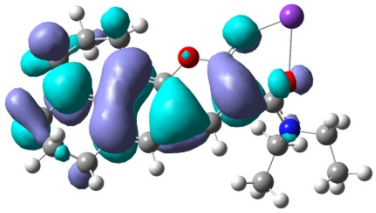

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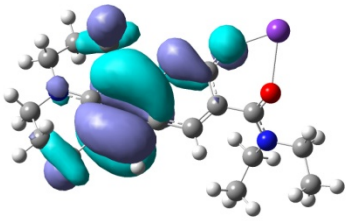
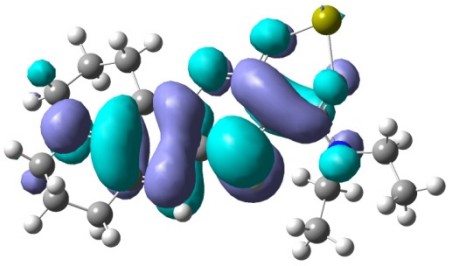


_____HOMO-1

C343-dea-Ca^{++} ΔE(H-L) = 3.26 eV



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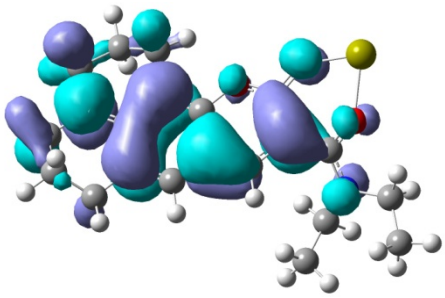

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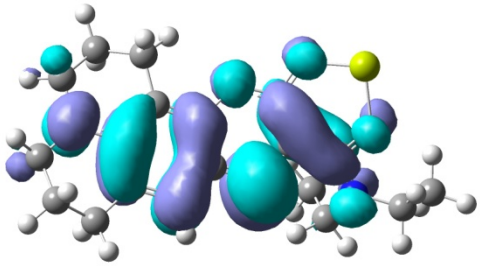
C343-dea-Mg^{++} ΔE(H-L) = 3.22 eV



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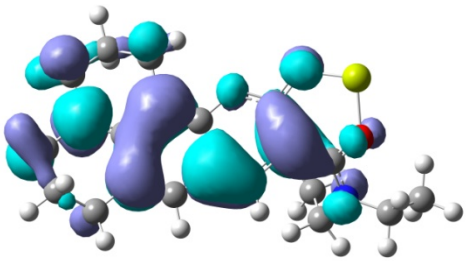

_____HOMO

Figure S7: Frontier orbitales of C343-dea and its complexes