Supplementary Materials

Metal–Assisted Complexation of Fluorogenic Dyes by Cucurbit[7]uril and Cucurbit[8]uril: A DFT Evaluation of the Key Factors Governing the Host–Guest Recognition

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Table S1. M062X/6−31G(d,p) calculated thermodynamic parameters in kcal mol^{-1}.

Reaction	ΔH	TΔS	ΔG[1]	ΔG[78]
CB[7] + TO^+ → CB[7]@TO^+	−64.0	−23.6	−40.5	−12.0
CB[7] + TfT^+ → CB[7]@TfT^+	−69.6	−22.1	−47.5	−12.3
CB[7] + NR^0 → CB[7]@NR^0	−28.1	−19.5	−8.6	1.3
CB[7] + NRH^+ → CB[7]@NRH^+	−65.5	−18.7	−46.7	−9.4
CB[8] + TO^+ → CB[8]@TO^+	−62.4	−21.9	−40.5	−11.1
CB[8] + TfT^+ → CB[8]@TfT^+	−61.9	−21.6	−40.3	−6.7
CB[8] + NR^0 → CB[8]@NR^0	−29.1	−21.1	−8.0	5.0
CB[8] + NRH^+ → CB[8]@NRH^+	−60.3	−20.6	−39.8	−1.5
Substitution				
CB[7]@TO^+ + Mg^{2+} → CB[7]@Mg^{2+} + TO^+	−245.9	10.2	−256.1	−35.9
CB[7]@TfT^+ + Mg^{2+} → CB[7]@Mg^{2+} + TfT^+	−240.3	8.8	−249.1	−35.6
CB[7]@NRH^+ + Mg^{2+} → CB[7]@Mg^{2+} + NRH^+	−244.5	5.4	−249.8	−38.5
CB[8]@TO^+ + Mg^{2+} → CB[8]@Mg^{2+} + TO^+	−243.1	7.5	−250.6	−34.5
CB[8]@TfT^+ + Mg^{2+} → CB[8]@Mg^{2+} + TfT^+	−236.7	7.1	−250.8	−38.9
CB[8]@NRH^+ + Mg^{2+} → CB[8]@Mg^{2+} + NRH^+	−245.2	6.1	−251.3	−44.1
CB[7]@TO^+ + $[Mg(H_2O)_6]^{2+}$ → CB[7]@$[Mg(H_2O)_6]^{2+}$ + TO^+	−92.4	2.2	−94.7	−15.6
CB[7]@Tft^+ + $[Mg(H_2O)_6]^{2+}$ → CB[7]@$[Mg(H_2O)_6]^{2+}$ + TfT^+	−86.8	0.8	−87.6	−15.3
CB[7]@NRH^+ + $[Mg(H_2O)_6]^{2+}$ → CB[7]@$[Mg(H_2O)_6]^{2+}$ + NRH^+	−91.0	−2.6	−88.4	−18.2
CB[8]@TO^+ + $[Mg(H_2O)_6]^{2+}$ → CB[8]@$[Mg(H_2O)_6]^{2+}$ + TO^+	−82.4	−3.9	−78.6	4.6
CB[8]@Tft^+ + $[Mg(H_2O)_6]^{2+}$ → CB[8]@$[Mg(H_2O)_6]^{2+}$ + TfT^+	−83.0	−4.2	−78.7	0.2
CB[8]@NRH^+ + $[Mg(H_2O)_6]^{2+}$ → CB[8]@$[Mg(H_2O)_6]^{2+}$ + NRH^+	−84.5	−5.2	−79.3	−5.0
Addition				
CB[7]@TO^+ + Mg^{2+} → CB[7]@TO^+@Mg^{2+}	−242.4	−11.5	−230.9	−32.0
CB[7]@TfT^+ + Mg^{2+} → CB[7]@TfT^+@Mg^{2+}	−243.2	−10.1	−233.1	−45.9

$CB[7]@NRH^+ + Mg^{2+} \rightarrow CB[7]@NRH^+@Mg^{2+}$	−236.9	−12.9	−224.1	−35.5
$CB[8]@TO^+ + Mg^{2+} \rightarrow CB[8]@TO^+@Mg^{2+}$	−235.3	−10.4	−224.9	−34.1
$CB[8]@TfT^+ + Mg^{2+} \rightarrow CB[8]@TfT^+@Mg^{2+}$	−229.9	−13.0	−216.9	−43.1
$CB[8]@NRH^+ + Mg^{2+} \rightarrow CB[8]@NRH^+@Mg^{2+}$	−235.4	−13.4	−222.0	−31.0
$CB[7]@TO^+ + [Mg(H_2O)_6]^{2+} \rightarrow CB[7]@TO^+@[Mg(H_2O)_6]^{2+}$	−28.3	−15.9	−12.4	−1.0
$CB[7]@TfT^+ + [Mg(H_2O)_6]^{2+} \rightarrow CB[7]@TfT^+@[Mg(H_2O)_6]^{2+}$	−51.1	−23.9	−27.1	−7.0
$CB[7]@NRH^+ + [Mg(H_2O)_6]^{2+} \rightarrow CB[7]@NRH^+@[Mg(H_2O)_6]^{2+}$	−45.5	−20.0	−25.5	−6.4
$CB[8]@TO^+ + [Mg(H_2O)_6]^{2+} \rightarrow CB[8]@TO^+@[Mg(H_2O)_6]^{2+}$	−52.0	−20.3	−31.7	−10.1
$CB[8]@TfT^+ + [Mg(H_2O)_6]^{2+} \rightarrow CB[8]@TfT^+@[Mg(H_2O)_6]^{2+}$	−67.8	−22.0	−45.8	−12.6
$CB[8]@NRH^+ + [Mg(H_2O)_6]^{2+} \rightarrow CB[8]@NRH^+@[Mg(H_2O)_6]^{2+}$	−69.1	−24.8	−44.3	−14.1

Table S2. Gibbs energies of CB@dye formation in a gas phase (ΔG^1) and aqueous solution (ΔG^{78}) in kcal mol^{-1}.

Reaction	ΔG^1	ΔG^{78}
$CB[7] + TO^+ \rightarrow CB[7]@TO^+$	−37.4	−5.0
$CB[7] + TfT^+ \rightarrow CB[7]@TfT^+$	−44.7	−5.5
$CB[7] + NRH^+ \rightarrow CB[7]@NRH^+$	−43.9	−3.0
$CB[7] + NR^0 \rightarrow CB[7]@NR$	−7.0	7.5
$CB[8] + TO^+ \rightarrow CB[8]@TO^+$	−38.1	−4.9
$CB[8] + TfT^+ \rightarrow CB[8]@TfT^+$	−38.7	−1.4
$CB[8] + NRH^+ \rightarrow CB[8]@NRH^+$	−37.7	4.6
$CB[8] + NR^0 \rightarrow CB[8]@NR^0$	−6.1	11.9

Table S3. Gibbs energies of CB@dye formation in a gas phase (ΔG^1) and aqueous solution (ΔG^{78}) in kcal mol^{-1}, where the initial CB[7]@8W is considered.

Reaction	ΔG^1	ΔG^{78}
$CB[7] + TO^+ \rightarrow CB[7]@TO^+$	−9.1	−8.2
$CB[7] + TfT^+ \rightarrow CB[7]@TfT^+$	−16.5	−8.7
$CB[7] + NRH^+ \rightarrow CB[7]@NRH^+$	−15.7	−6.2
$CB[7] + NR^0 \rightarrow CB[7]@NR$	21.3	4.3

Table S4. Gibbs energies of $CB@M^{n+}$ formation through substitution of the dye molecule in a gas phase (ΔG^1) and aqueous solution (ΔG^{78}) in kcal mol^{-1}.

Substitution	ΔG^1	ΔG^{78}
$CB[7]@TO^+ + Mg^{2+} \rightarrow CB[7]@Mg^{2+} + TO^+$	−249.9	−33.0
$CB[7]@NRH^+ + Mg^{2+} \rightarrow CB[7]@Mg^{2+} + NRH^+$	−238.0	−35.0
$CB[7]@TfT^+ + Mg^{2+} \rightarrow CB[7]@Mg^{2+} + TfT^+$	−242.6	−32.5
$CB[7]@TfT^+ + Ga^{3+} \rightarrow CB[7]@Ga^{3+} + TfT^+$	−704.3	−240.4
$CB[8]@TO^+ + Mg^{2+} \rightarrow CB[8]@Mg^{2+} + TO^+$	−244.3	−30.6
$CB[8]@TfT^+ + Mg^{2+} \rightarrow CB[8]@Mg^{2+} + TfT^+$	−243.8	−34.1
$CB[8]@NRH^+ + Mg^{2+} \rightarrow CB[8]@Mg^{2+} + NRH^+$	−244.8	−40.2

CB[7]@TO^{+}+ [Mg(H$_2$O)$_6$]$^{2+}$ → CB[7]@[Mg(H$_2$O)$_6$]$^{2+}$ + TO^{+}	−88.2	−10.0
CB[7]@NRH^{+}+ [Mg(H$_2$O)$_6$]$^{2+}$ → CB[7]@[Mg(H$_2$O)$_6$]$^{2+}$ + NRH^{+}	−81.7	−12.0
CB[7]@Tft^{+}+ [Mg(H$_2$O)$_6$]$^{2+}$ → CB[7]@[Mg(H$_2$O)$_6$]$^{2+}$ + TfT^{+}	−80.9	−9.5
CB[7]@TfT^{+}+ [Ga(H$_2$O)$_6$]$^{3+}$ → CB[7]@[Ga(H$_2$O)$_6$]$^{3+}$ + TfT^{+}	−224.4	−28.3
CB[7]@TfT^{+}+ [Ga(OH)$_4$(H$_2$O)$_2$]$^{-}$ → CB[7]@[Ga(OH)$_4$(H$_2$O)$_2$]$^{-}$ + TfT^{+}	12.3	−6.5
CB[8]@TO^{+}+ [Mg(H$_2$O)$_6$]$^{2+}$ → CB[8]@[Mg(H$_2$O)$_6$]$^{2+}$ + TO^{+}	−74.3	8.5
CB[8]@Tft^{+}+ [Mg(H$_2$O)$_6$]$^{2+}$ → CB[8]@[Mg(H$_2$O)$_6$]$^{2+}$ + TfT^{+}	−73.7	5.0
CB[8]@NRH^{+}+ [Mg(H$_2$O)$_6$]$^{2+}$ → CB[8]@[Mg(H$_2$O)$_6$]$^{2+}$ + NRH^{+}	−74.7	−1.0

Table S5. Gibbs energies of CB@dye@M^{n+} formation through addition of metal cation in a gas phase (ΔG^{1}) and aqueous solution (ΔG^{78}) in kcal mol^{-1}.

Addition	ΔG^{1}	ΔG^{78}
CB[7]@TO^{+}+ Mg^{2+} → CB[7]@TO^{+}@Mg^{2+}	−223.0	−24.0
CB[7]@NRH^{+}+ Mg^{2+} → CB[7]@NRH^{+}@Mg^{2+}	−215.6	−26.4
CB[7]@TfT^{+}+ Mg^{2+} → CB[7]@TfT^{+}@Mg^{2+}	−224.7	−36.5
CB[7]@TfT^{+}+ Ga^{3+} → CB[7]@TfT^{+}@Ga^{3+}	−703.0	−274.3
CB[8]@TO^{+}+ Mg^{2+} → CB[8]@TO^{+}@Mg^{2+}	−216.7	−25.5
CB[8]@TfT^{+}+ Mg^{2+} → CB[8]@TfT^{+}@Mg^{2+}	−207.3	−32.1
CB[8]@NRH^{+}+ Mg^{2+} → CB[8]@NRH^{+}@Mg^{2+}	−212.7	−20.9
CB[7]@TO^{+}+ [Mg(H$_2$O)$_6$]$^{2+}$ → CB[7]@TO^{+}@[Mg(H$_2$O)$_6$]$^{2+}$	−8.6	4.9
CB[7]@NRH^{+}+ [Mg(H$_2$O)$_6$]$^{2+}$ → CB[7]@NRH^{+}@[Mg(H$_2$O)$_6$]$^{2+}$	−20.7	0.8
CB[7]@TfT^{+}+ [Mg(H$_2$O)$_6$]$^{2+}$ → CB[7]@TfT^{+}@[Mg(H$_2$O)$_6$]$^{2+}$	−19.7	2.9
CB[7]@TfT^{+}+ [Ga(H$_2$O)$_6$]$^{3+}$ → CB[7]@TfT^{+}@[Ga(H$_2$O)$_6$]$^{3+}$	−125.2	−14.1
CB[7]@TfT^{+}+ [Ga(OH)$_4$(H$_2$O)$_2$]$^{-}$ → CB[7]@TfT^{+}@[Ga(OH)$_4$(H$_2$O)$_2$]$^{-}$	−49.8	4.3
CB[8]@TO^{+}+ [Mg(H$_2$O)$_6$]$^{2+}$ → CB[8]@TO^{+}@[Mg(H$_2$O)$_6$]$^{2+}$	−25.2	−1.1
CB[8]@TfT^{+}+ [Mg(H$_2$O)$_6$]$^{2+}$ → CB[8]@TfT^{+}@[Mg(H$_2$O)$_6$]$^{2+}$	−38.4	−2.5
CB[8]@NRH^{+}+ [Mg(H$_2$O)$_6$]$^{2+}$ → CB[8]@NRH^{+}@[Mg(H$_2$O)$_6$]$^{2+}$	−36.5	−3.8

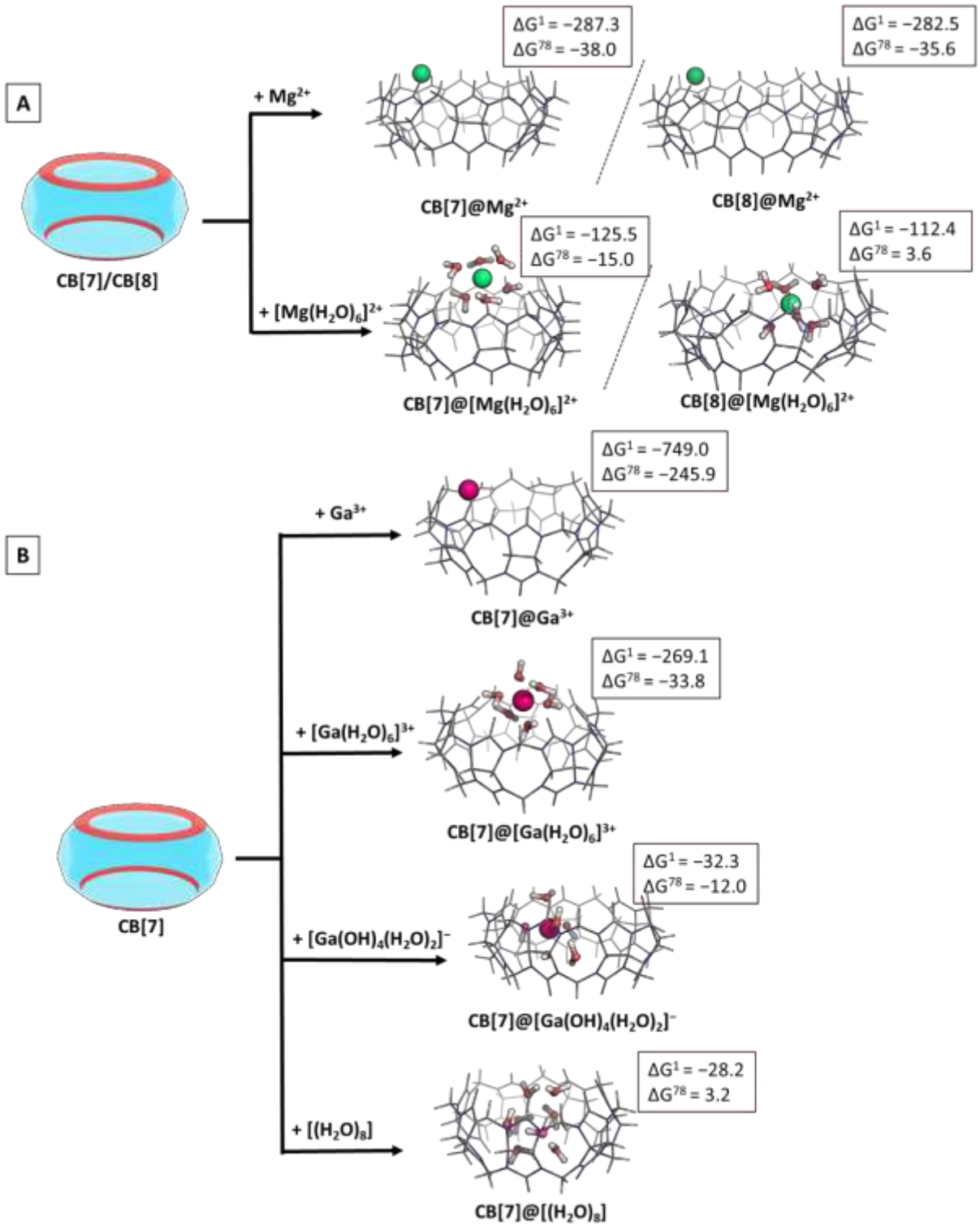

Figure S1. M062X/6−31G(d,p) optimized structures of the CB[7/8] complexes with bare (non−hydrated) and hydrated Mg^{2+} (A) cations, Ga^{3+} (B) cations and eight water molecules (B) in the gas phase; ΔG^{ε} values in kcal mol^{-1} for the complex formation in gas phase ($\varepsilon = 1$), and water ($\varepsilon = 78$) at the M062X/6−31+G(d,p)//M062X/6−31G(d,p) level of theory.