Supporting Information

A Fluorescence Perspective on the Differential Interaction of Riboflavin and Flavin Adenine Dinucleotide with Cucurbit[7]uril

Sharmistha Dutta Choudhury, Jyotirmayee Mohanty, Achikanath C. Bhasikuttan and Haridas Pal**

Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, INDIA

Note S1

Following Scheme 2,

$K_1 = [B]/[A], \Rightarrow [B] = [A]K_1$ (1)

$K_1' = [B']/[A] \Rightarrow [B'] = [A] K_1'$ (2)

$K_2 = [BH]/[AH] \Rightarrow [BH] = [AH] K_2$ (3)

$K_2' = [B'H]/[AH] \Rightarrow [B'H] = [AH] K_2'$ (4)

Further, $K_B = [BH]/[B][H] \Rightarrow [BH] = K_B[B][H]$ (5)

$K_A = [AH]/[A][H] \Rightarrow [AH] = K_A[A][H]$ (6)

$K_{B'} = [B'H]/[B'][H] \Rightarrow [B'H] = K_B[B'][H]$ (7)

Also from Scheme 2, $K_B K_1 = K_2 K_A$ (8)

and $K_A K_2' = K_1' K_{B'}$ (9)

From eq. 8 and 9, it follows that for $K_B > K_A$, $K_2 > K_1$ and for $K_{B'} > K_A$, $K_2' > K_1'$ (10)

For all the above equations, [A] = $RF_{lactam, A}$, [B] = $RF_{lactim, B}$, [B′] = $RF_{lactim, B'}$ and [H] = [CB7]

The observed binding constant is given as,

$$K_{obs} = \frac{[BH]+[AH]+[B'H]}{([B]+[A]+[B'])[H]} \tag{11}$$

$$\Rightarrow K_{obs} = \frac{K_B[B][H]+K_A[A][H]+K_{B'}[B'][H]}{([B]+[A]+[B'])[H]}$$

$$\text{Or } K_{obs} = \frac{K_B K_1 + K_A + K_{B'}K_1'}{K_1 + 1 + K_1'} \tag{12}$$

Alternatively using eqs. 3 and 4,

$$K_{obs} = \frac{(K_2 + 1 + K_2')K_A}{K_1 + 1 + K_1'} \tag{13}$$

Since from eq. 10, $K_2 + K_2' > K_1 + K_1'$, so it follows that $K_{obs} > K_A$.

In other words, the preferential binding of CB7 with the lactim forms, leads to a larger conversion between the complexed lactam form to the complexed lactim forms ([AH] to [BH] and [B′H]), and the observed binding constant is thus expected to be larger than the binding constant for the pure lactam form.