

Anthocyanin Color Stabilization by Host-Guest Complexation with *p*-Sulfonatocalix[n]arenes

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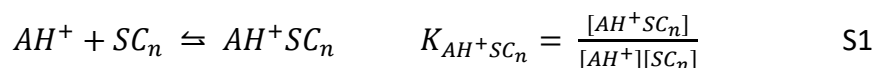
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Calculation of the association constants

Equation 1 and 2 were used to calculate the host-guest association constants in complexes with 1:1 stoichiometries, these equations require an excess of the host in comparison with the guest. Following we present the deduction of such equations:

When flavylum cation guest (AH^+) is the sole species in solution (commonly at pH=1) the interaction with the host (SC_n) is described as follow:



The mass balance for the species containing the guest.

$$C_0 = [AH^+] + [AH^+SC_n] = [AH^+](1 + K_{AH^+SC_n}[SC_n]) \quad S2$$

The molar fraction of the species is calculated:

$$\chi_{AH^+} = \frac{[AH^+]}{C_0} = \frac{1}{1 + K_{AH^+SC_n}[SC_n]} \quad S3$$

$$\chi_{AH^+SC_n} = \frac{[AH^+SC_n]}{C_0} = \frac{K_{AH^+SC_n}[SC_n]}{1 + K_{AH^+SC_n}[SC_n]} \quad S4$$

As the absorbance follows the Lambert-Beer law, we can express it as follow:

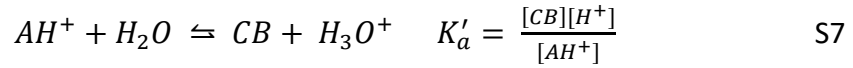
$$A_\lambda = C_0(\epsilon_{AH^+}\chi_{AH^+} + \epsilon_{AH^+SC_n}\chi_{AH^+SC_n}) \quad S5$$

And then, introducing the parameter $r_{AH^+SC_n}$:

$$r_{AH^+SC_n} = \frac{\epsilon_{AH^+SC_n}}{\epsilon_{AH^+}} \quad S6$$

Being ε_{AH^+} and $\varepsilon_{AH^+SC_n}$ the molar absorption coefficient of the free flavylum and the complexed respectively. Including the mole fraction in Eq. S5, we have equation 1, presented in the main text, where the parameters $r_{AH^+SC_n}$ and $K_{AH^+SC_n}$ are fitted with the experimental data.

On the other hand, Equation 2 is deduced taking in account the possible interaction of the conjugate base (CB) species with the macrocycle.



The mass balance would be:

$$\begin{aligned} C_0 &= [AH^+] + [AH^+SC_n] + [CB] + [CBSC_n] \\ &= [AH^+](1 + K_{AH^+SC_n}[SC_n] + \frac{(1 + K_{CBSC_n}[SC_n])K'_a}{[H^+]}) \end{aligned} \quad S9$$

And the mole fraction calculated as:

$$\chi_{AH^+} = \frac{[H^+]}{(1 + K_{AH^+SC_n}[SC_n])[H^+] + (1 + K_{CBSC_n}[SC_n])K'_a} = \frac{[H^+]}{D} \quad S10$$

$$\chi_{AH^+SC_n} = \frac{K_{AH^+SC_n}[SC_n][H^+]}{D} \quad S11$$

$$\chi_{CB} = \frac{K'_a}{D} \quad S12$$

$$\chi_{CBSC_n} = \frac{K_{CBSC_n}K'_a[SC_n]}{D} \quad S13$$

The Lambert-Beer law, can be expressed as:

$$A_\lambda = C_0(\varepsilon_{AH^+}\chi_{AH^+} + \varepsilon_{AH^+SC_n}\chi_{AH^+SC_n} + \varepsilon_{CB}\chi_{CB} + \varepsilon_{CBSC_n}\chi_{CBSC_n}) \quad S14$$

And then, introducing the parameters r_{CB} and r_{CBSC_n} :

$$r_{CB} = \frac{\varepsilon_{CB}}{\varepsilon_{AH^+}} \quad r_{CBSC_n} = \frac{\varepsilon_{CBSC_n}}{\varepsilon_{AH^+}} \quad S15$$

Being ε_{CB} and ε_{CBSC_n} the molar absorption coefficient of the free CB species and the complexed respectively. Including the mole fraction in Eq. S14, we have equation 2, where the parameters r_{CBSC_n} and K_{CBSC_n} are fitted with the experimental data, while the r_{CB} can be obtained from the initial absorbance when $[SC_n]=0$.

$$A_{\lambda(SC_n=0)} = A_0\left(\frac{[H^+] + r_{CB}}{[H^+] + K'_a}\right) \quad S16$$

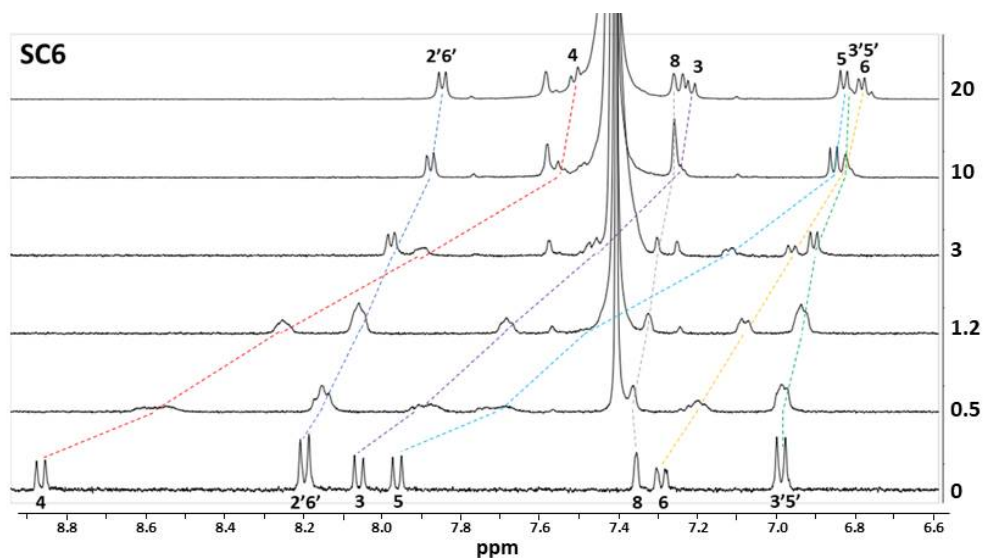


Figure S1. ^1H NMR spectra variations of 4'7OH (6.1×10^{-3} M) solution upon titration with increasing concentrations of the host: 0, 0.5, 1.2, 3, 10, and 20 equivalents of SC6.

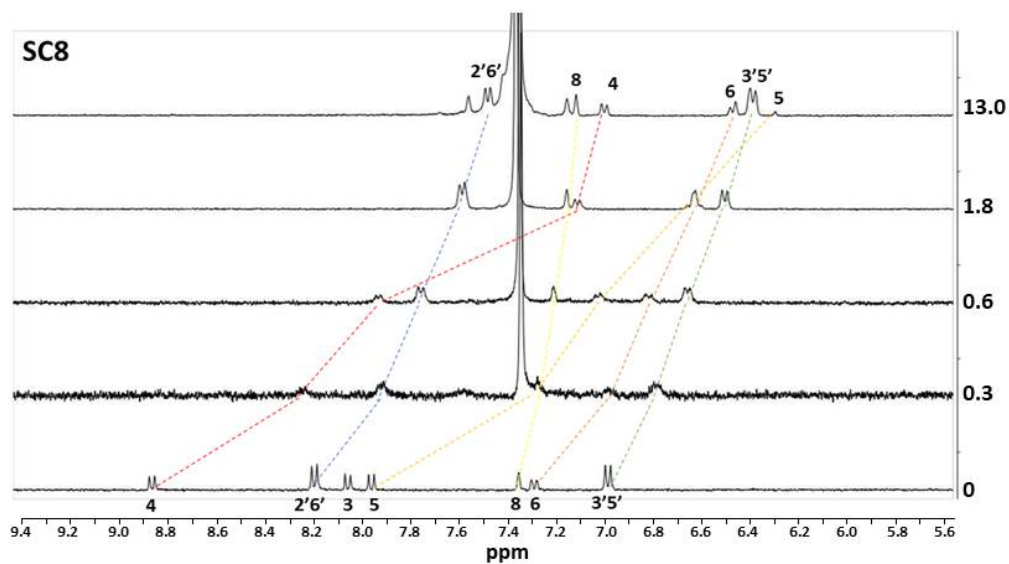


Figure S2. ^1H NMR spectra variations of 4'7OH (6.1×10^{-3} M) solution upon titration with increasing concentrations of the host: 0, 0.3, 0.6, 1.8, and 13 equivalents of SC8.

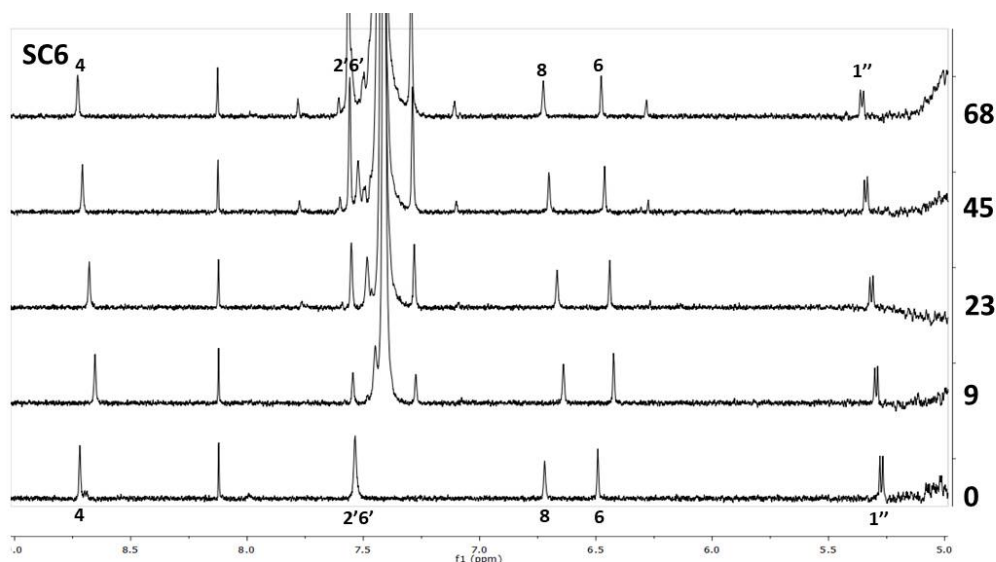


Figure S3. ^1H NMR spectra variations of Oenin (2.2×10^{-4} M) solution upon titration with increasing concentrations of the host: 0, 9, 23, 45 and 68 equivalents of SC6.

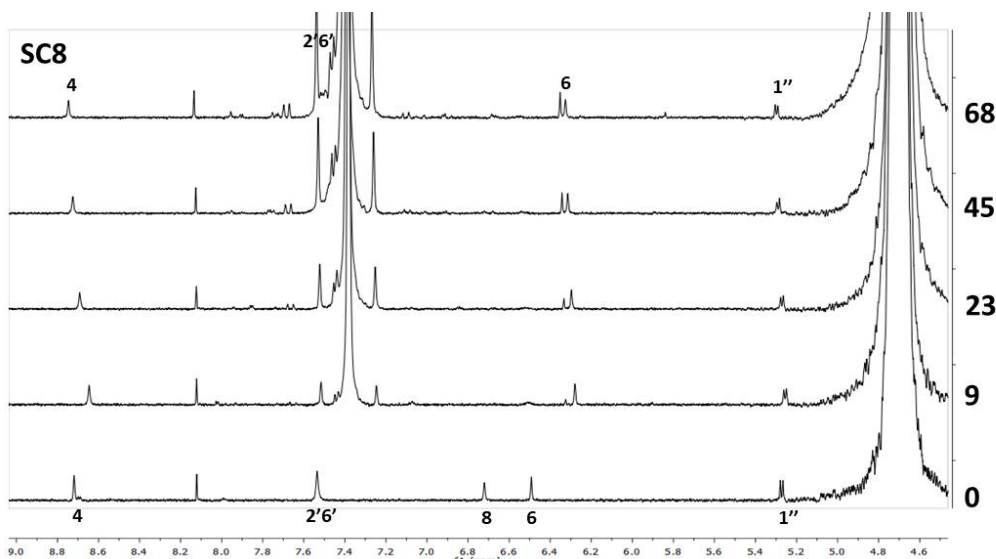


Figure S4. ^1H NMR spectra variations of Oenin (2.2×10^{-4} M) solution upon titration with increasing concentrations of the host: 0, 9, 23, 45 and 68 equivalents of SC8.

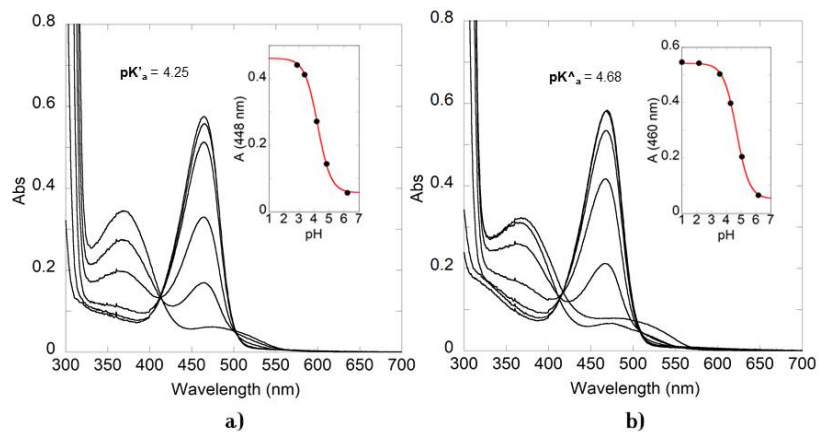


Figure S5. UV-Vis spectral variations of equilibrated solutions of 4'7-DHF 1.15×10^{-5} M obtained after direct pH jumps from pH=1 to higher pH values (citrate buffer 0.01M). a) in presence of SC6 64 mM and b) SC8 28 mM. The insets show the fitting for the calculation of pK'_a .

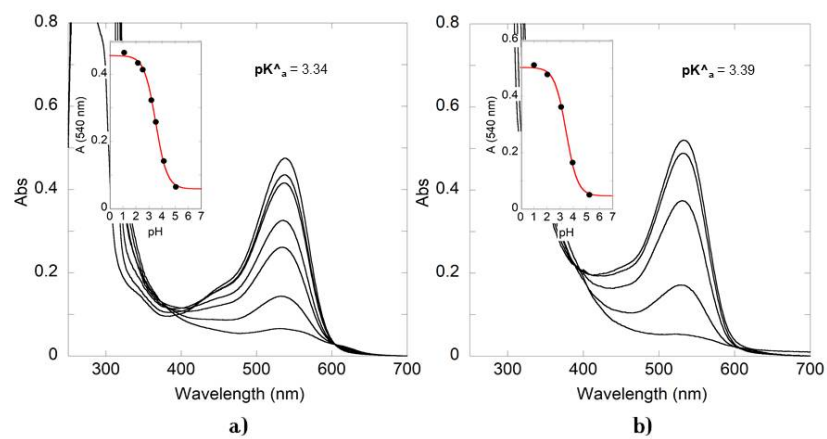


Figure S6. UV-Vis spectral variations of pseudo-equilibrated solutions of Oenin 1.7×10^{-5} M obtained after direct pH jumps from pH=1 to higher pH values (citrate buffer 0.01M). a) in presence of SC4 40 mM and b) SC6 32 mM. The insets show the fitting for the calculation of pK^a_a .