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Electronic Supplementary Information (ESI)

1. Formalism for the determination of the association constant of a 1:n complex from absorption and fluorescence

The typical equilibria in supramolecular chemistry are defined by:

$$H+nG \rightleftharpoons C$$
,

where *H* is the host, *G* the guest and *C* the 1:n complex.

The general expression for equilibrium constant is:

$$K = \frac{\left[C\right]}{\left[H\right]\left[G\right]^{n}}.$$
(1)

The mass balance for the total concentration of the host H, $[H]_0$, is

$$[H]_{0} = [H] + [C] = [H] + K[H][G]^{n}$$
(2)

Combining the mass balance eqn (2) and the definition of the equilibrium constant in eqn (1), we obtain:

$$\left[H\right] = \frac{\left[H\right]_0}{1 + K\left[G\right]^n} \approx \frac{\left[H\right]_0}{1 + K\left[G\right]_0^n} \tag{3}$$

Considering that G is in excess, the concentration of free G, [G], is approximately equal to its total concentration, $[G]_0$.

Assuming that the guest *G* does not absorb (or emit), but that *H* and *C* absorb and can be fluorescent, with molar absorption coefficients at the excitation wavelength and fluorescence quantum yields ε_H , ε_C , Φ_H and Φ_C , respectively, the observed fluorescence intensity can be usually be described by:

$$F = \alpha \Big(\varepsilon_H \Phi_H f_H \big[H \big] + \varepsilon_C \Phi_C f_C \big[C \big] \Big), \tag{4}$$

Combining eqn (1) and eqn (3), eqn (4) becomes

$$F = \alpha \left[H \right]_0 \frac{\varepsilon_H \Phi_H f_H + \varepsilon_C \Phi_C f_C K \left[G \right]_0^n}{1 + K \left[G \right]_0^n} \,. \tag{5}$$

In the absence of the guest ([G] = 0), the fluorescence is defined by:

$$F_0 = \alpha \varepsilon_H \Phi_H f_H \left[H \right]_0, \tag{6}$$

assuming that the total concentration of host is constant, $[H]_0$, we get

$$\frac{F}{F_0} = \frac{1 + RK[G]^n}{1 + K[G]^n},\tag{7}$$

with

$$R = \frac{\varepsilon_C \Phi_C f_C}{\varepsilon_H \Phi_H f_H}.$$
(8)

We can manipulate eqn (7) to obtain:

$$\frac{F}{F_0} - 1 = \frac{(R-1)K[G]^n}{1 + K[G]^n}$$
(9)

and, finally, a linearized form

$$\frac{1}{\frac{F}{F_0} - 1} = \frac{1}{\left(R - 1\right) K \left[G\right]^n} + \frac{1}{R - 1},$$
(10)

or, equivalently,

$$\frac{1}{[G]^n} = \frac{(R-1)K}{\frac{F}{F_0} - 1} - K \tag{11}$$

In this way, a graphical representation of $1/[G]^n$ versus $1/\left(\frac{F}{F_0}-1\right)$ allows obtaining *K* (and *R*).

All the above equations are equally valid if we substitute the absorbance A for the fluorescence F. In this case: $R = \frac{\varepsilon_C}{\varepsilon_H}$.

2. Application of the formalism to calixarene-anion complexation

Eqn (11) is used to plot absorbance and fluorescence data for the system Phurea 5 - NO_3^- in CH₂Cl₂. The plots shown in Figs. 1 and 2 correspond to n = 1 and n = 2, respectively. The fits are satisfactory for n = 1 but unsatisfactory for n = 2, supporting the existence of 1:1 complexes.



Figure 1: Linear regression of 1/[G] versus *X*, where *X* represents $1/((A/A_0)-1)$ (full circles) and $1/((F/F_0)-1)$ (empty circles), [*G*] is the concentration of NO₃⁻ in CH₂Cl₂, and *A* and *F* refer to the values of absorbance and fluorescence intensity of Phurea 5, respectively.



Figure 2: Linear regression of $1/[G]^2$ versus *X*, where *X* represents $1/((A/A_0)-1)$ (full circles) and $1/((F/F_0)-1)$ (empty circles), [*G*] is the concentration of NO₃⁻ in CH₂Cl₂, and *A* and *F* refer to the values of absorbance and fluorescence intensity of Phurea 5, respectively.