

Supporting Information

Kinetics of the reversible inclusion of flavopereirine in cucurbit[7]uril

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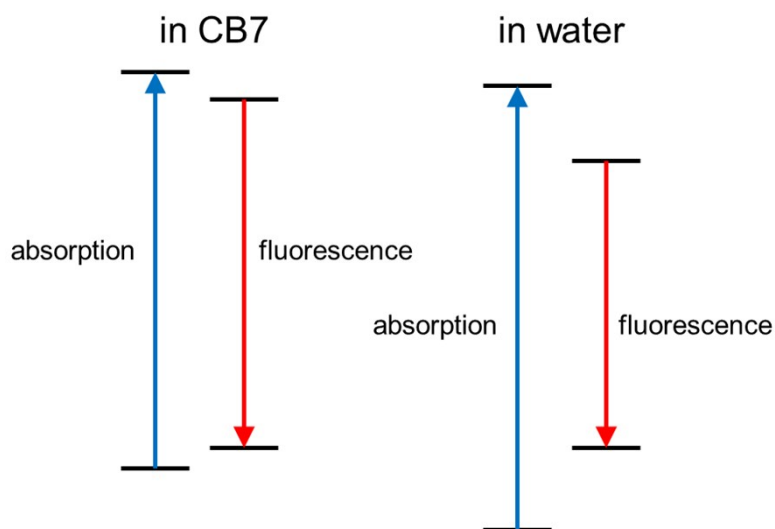


Figure S1 Effect of the local environment on the absorption and fluorescence of flavopereirine

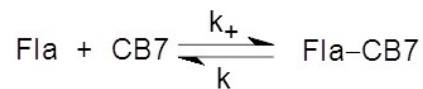
Figure S1 illustrates why the absorption spectrum is red-shifted and the fluorescence spectrum is blue-shifted upon encapsulation of flavopereirine in the apolar cavity of CB7. Quantum chemical calculations for related compounds have shown that the electron density on the nitrogen of the pyrrole ring decreases upon excitation to the lowest singlet-excited state (S_1).¹ Such an effect weakens the hydrogen bonding and van der Waals interactions of flavopereirine with water in the lowest singlet-excited state (S_1) compared to that in the ground state (S_0). Therefore, the energy of S_1 state diminishes to a smaller extent than the energy of the ground state when the flavopereirine is moved from CB7 cavity into water. As a result, the S_1 – S_0 energy gap observed by absorption becomes larger in water than in CB7. After photon absorption, vibrational relaxation and reorganisation of the microenvironment occur. These processes lead to more substantial energy gain when flavopereirine is located in water. Weaker interactions with the apolar CB7 cavity allow less significant energy diminution upon reaching the relaxed S_1 state. Similarly, the state obtained immediately after fluorescence emission can lose more energy in the course of the structural changes in the local environment when flavopereirine interacts with water instead of CB7. Thus, the photon emitted by water-solvated flavopereirine has lower energy than that originating from CB7 complex.

Reference

1. A. Dias, A. P. Varela, M. D. G. Miguel, A. L. Macanita and R. S. Becker, *J. Phys. Chem.*, 1992, 96, 10290-10296.

Analysis of the stopped-flow results on the reversible binding of flavopereirine in CB7

Flavopereirine (Fla) produces a 1:1 inclusion complex (Fla–CB7) with cucurbit[7]uril (CB7).



The changes of the concentrations of the components are defined by the following differential equations:

$$\frac{d[\text{Fla} - \text{CB7}]}{dt} = k_+ [\text{Fla}][\text{CB7}] - k_- [\text{Fla} - \text{CB7}] \quad (\text{S1})$$

$$-\frac{d[\text{Fla}]}{dt} = k_+ [\text{Fla}][\text{CB7}] - k_- [\text{Fla} - \text{CB7}] \quad (\text{S2})$$

$$-\frac{d[\text{CB7}]}{dt} = k_+ [\text{Fla}][\text{CB7}] - k_- [\text{Fla} - \text{CB7}] \quad (\text{S3})$$

where k_+ and k_- are the rate constants for the inclusion and dissociation, respectively. The overall fluorescence intensity at the wavelength of detection (I) is the sum of the emission intensities originating from excited Fla and Fla–CB7. As we use very dilute solutions, the fluorescence intensities are directly proportional to the fluorophor concentrations.

$$I = I(\text{Fla})[\text{Fla}] + I(\text{Fla} - \text{CB7})[\text{Fla} - \text{CB7}] \quad (\text{S4})$$

where $I(\text{Fla})$ and $I(\text{Fla} - \text{CB7})$ denote the parameters proportional to the fluorescence efficiency of Fla and Fla–CB7 at the wavelength of detection.

Starting with the initial estimates of k_+ and k_- , eqs S1–S3 were solved numerically using the total concentrations of Fla and CB7 as initial concentrations, while $[\text{Fla} - \text{CB7}] = 0$ M was taken for the concentration of the inclusion complex at $t = 0$ s. Then, the fluorescence intensity (I) was calculated on the basis of eq S4 and the iterations were repeated until the best

fit was achieved. The k_+ , $I(Fla_0)$ and $I(Fla-CB7)$ parameters were fitted, whereas k_- value determined by independent experiments were kept constant in the regression analysis.

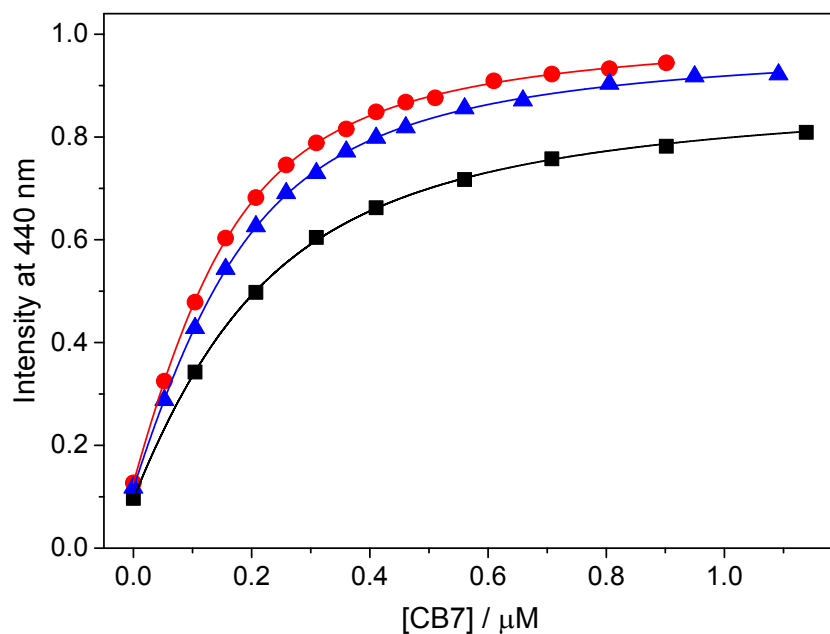


Figure S2 Fluorescence intensity alteration at 440 nm as a function of CB7 concentration in 0.16 μM Fla aqueous solution at 333 (●), 340 (▲), and 355 K (■). Excitation was performed at 355 nm. The lines represent the fitted functions.