Electronic Supporting Information (10 pages)

Phototransduction in a supramolecular cascade: a mimic for essential features of the vision process

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1. General methods and materials

All chemicals (geranylamine – **GA**, dopamine – **DA**, cucurbit[8]uril – CB8, 3-amino-1-adamantol), except **1** and cucurbit[7]uril (CB7), were commercially available from Sigma-Aldrich and used as received without further purification. The photoswitch **1** was available from a previous project[1] and CB7 was prepared by following a published procedure.[2] The water content of CB7 was determined to 27% by ^{1}H NMR spectroscopy, using malonic acid as internal standard.

^{1}H NMR measurements were done on a Bruker Advanced 500 MHz HPPR2 instrument. Deuterium oxide for NMR measurements (D_2O, 99.6 atom% D) was purchased from Eurisotope. The residual solvent peak (δ = 4.79 ppm) was used as reference signal for the ^{1}H NMR spectra. All measurements were done at room temperature and at pD 5.4. The pD was adjusted by addition of DCl or NaOD and corrected for isotope effects (pD = pH + 0.4).[3]

For the irradiation a TLC lamp (Vilber Lourmat-6.LC, 365 nm) or a 150 W xenon lamp (Oriel GmbH & Co. KG), equipped with a 550 nm optical long-pass filter, was employed.

The NMR titrations were made by consecutive additions of a stock solution of CB7 (4 mM) to a solution of DTE **1** (400 μM).

2. ^{1}H NMR spectra

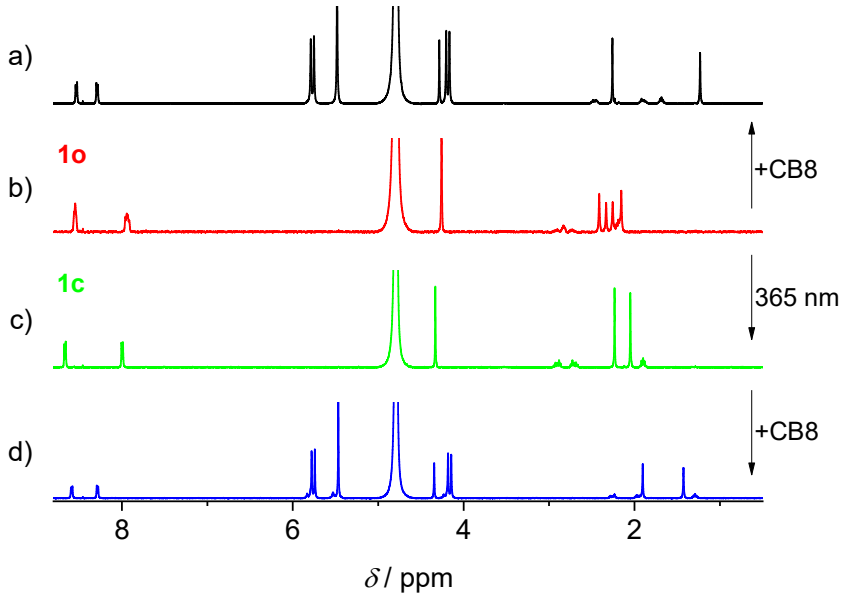

Figure S1. ^{1}H NMR spectra (all at pD 5.4 in D_2O) of a) **1o** in presence of CB8 (both at 200 µM); b) **1o** (200 µM); c) **1c** (200 µM; generated by irradiation of **1o** at 365 nm for 15 min); d) **1c** in the presence of CB8 (both at 200 µM).

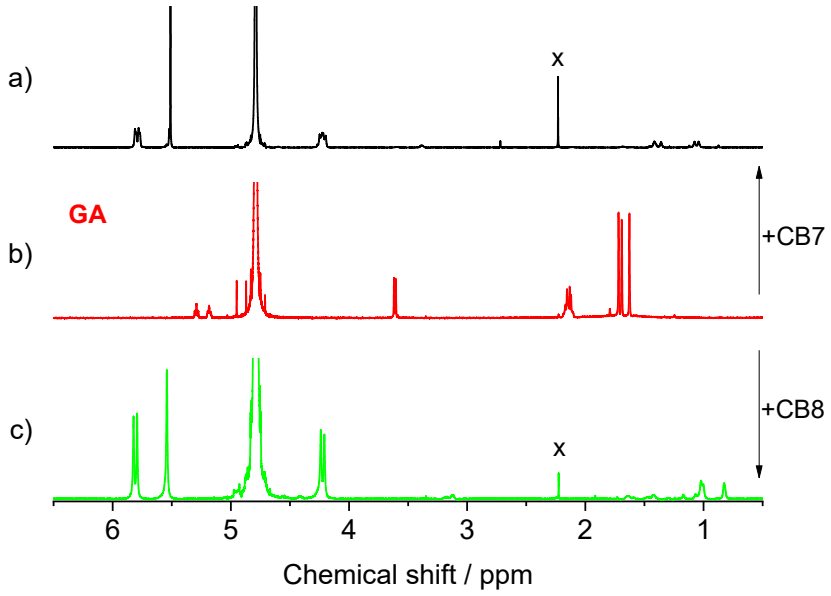

Figure S2. ^{1}H NMR spectra (all at pD 5.4 in D_2O) of a) **GA** in presence of CB7 (both at 500 µM); b) **GA** (500 µM); c) **GA** in presence of CB8 (both at 500 µM). x denotes a small solvent impurity (acetone).

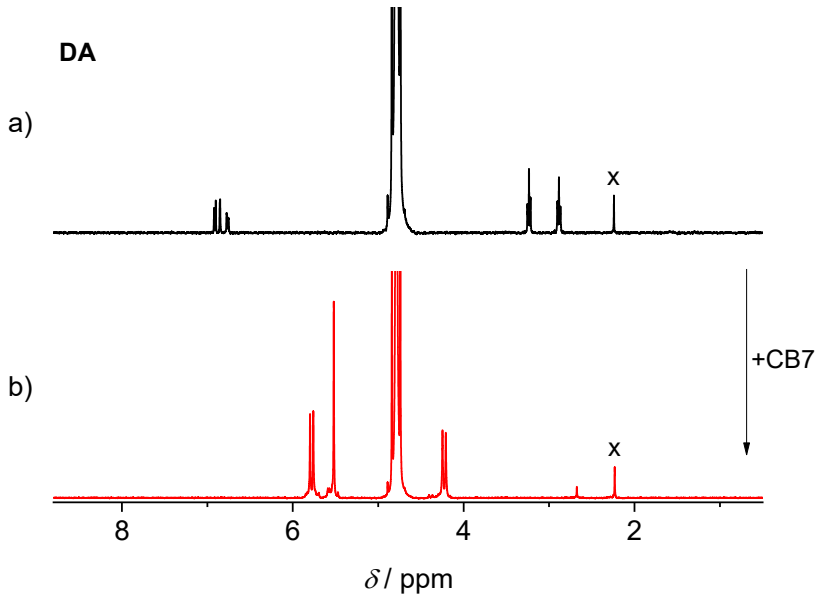

Figure S3. ^{1}H NMR spectra (all at pD 5.4 in D_2O) of a) **DA** (500 µM); b) **DA** in the presence of CB7 (both at 500 µM). x denotes a small solvent impurity (acetone).

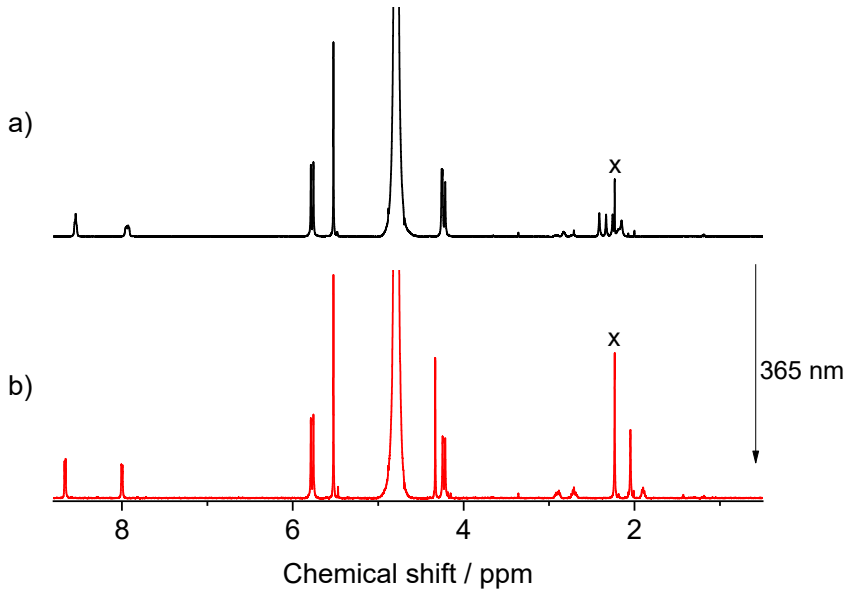

Figure S4. ^{1}H NMR spectra (all at pD 5.4 in D_2O) of a) **1o** (300 µM), **DA**, CB7 (both at 200 µM); b) mixture a) after irradiation at 365 nm for 15 min. No release of **DA** was observed. x denotes a small solvent impurity (acetone); note that in spectrum b) the solvent impurity overlaps with one of the signals of **1c**.

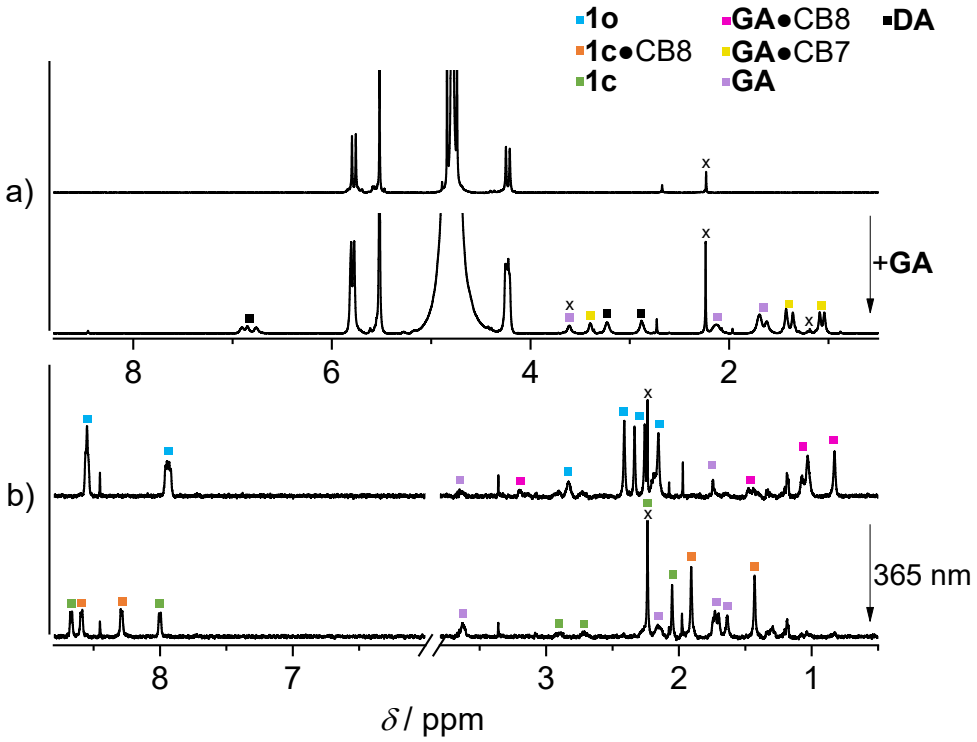

Figure S5. a) ^{1}H NMR spectra of **DA**, CB7 (both at 200 µM) and after addition of **GA** (200 µM); b) ^{1}H NMR spectra **1o** (300 µM) **GA** and CB8 (both at 200 µM) and after irradiation at 365 nm (yielding **1c**) for 15 min; all at pD 5.4 in D_2O. x denotes solvent impurities (acetone, diethylether).

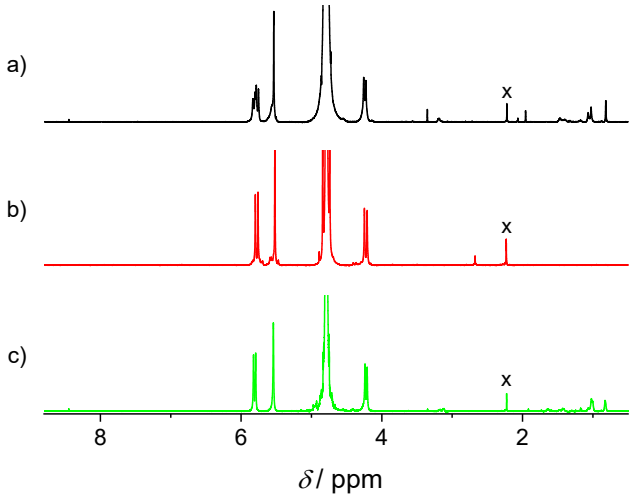

Figure S6. ^{1}H NMR spectra (all at pD 5.4 in D_2O) of a) **GA**, CB8, **DA**, and CB7 (all at 200 µM); b) **DA** in presence of CB7 (both at 500 µM); c) **GA** in presence of CB8 (both at 500 µM). x denotes a small solvent impurity (acetone).

3. NMR titration for binding of 1o and 1c by CB7

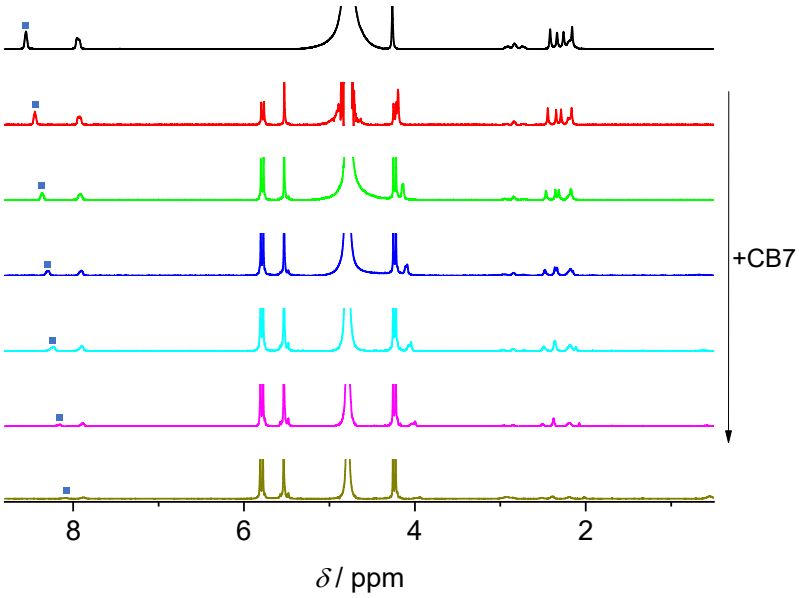

Figure S7. Selected ^{1}H NMR spectra (all at pD 5.4 in D_2O) for the titration of **1o** (400 μM) upon consecutive additions of a stock solution of CB7 (4 mM).

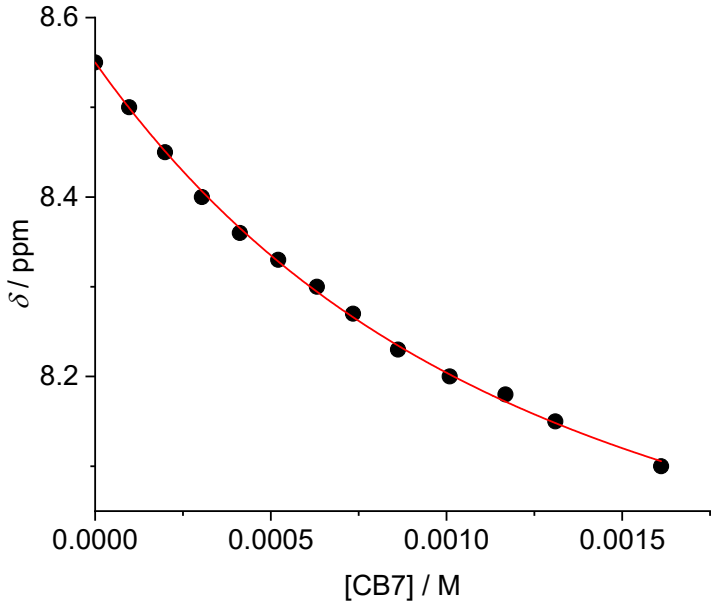

Figure S8. Fitting of the titration curve of **1o** with CB7 according to a 1:1 binding model.

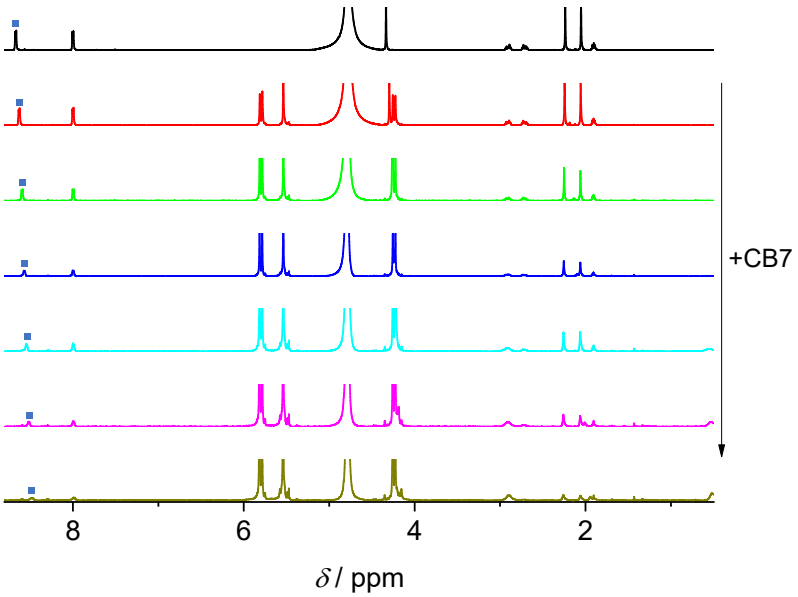

Figure S9. Selected ^{1}H NMR spectra (all at pD 5.4 in D_2O) for the titration of **1c** (400 μM) upon consecutive additions of a CB7 stock solution (4 mM).

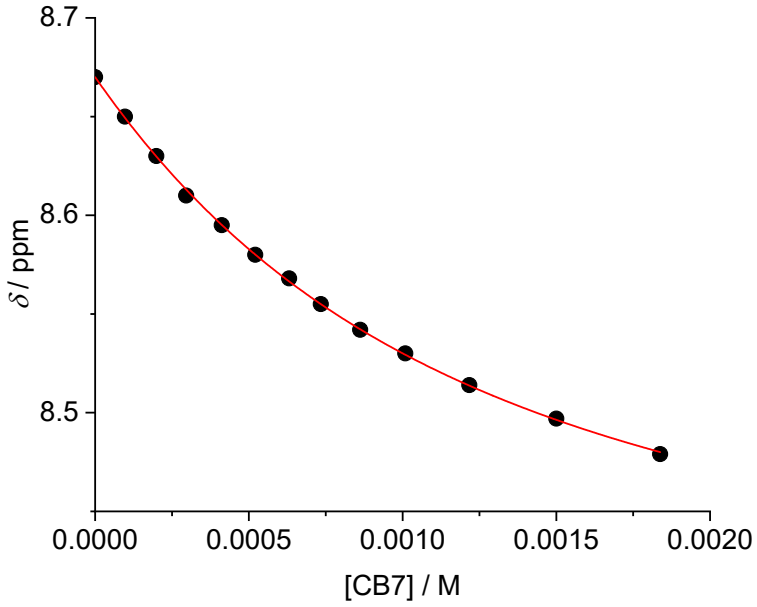

Figure S10. Fitting of the titration curve of **1c** with CB7 according to a 1:1 binding model.

4. Speciation simulation

The algorithm used to simulate the speciation of the multicomponent system containing two hosts (CB7 and CB8) and 3 guests (DTE **1o**/**1c**, **GA**, and **DA**) was based on a system of 5 equations constructed from the mass balance and equilibrium expressions. This system of equations was then numerically solved using the Newton-Raphson algorithm implemented in a conventional spreadsheet software to calculate the equilibrium concentrations of all species from the binding constants and initial concentrations.

Considering the formation of 1:1 complexes, the following binding equilibria applies in a multicomponent mixture containing two hosts (H_1 and H_2) and three guests (G_1, G_2, and G_3).

$$H_1 + G_1 \overset{K_{11}}{\rightleftharpoons} H_1G_1 \qquad H_2 + G_1 \overset{K_{21}}{\rightleftharpoons} H_2G_1$$

$$H_1 + G_2 \overset{K_{12}}{\rightleftharpoons} H_1G_2 \qquad H_2 + G_2 \overset{K_{22}}{\rightleftharpoons} H_2G_2$$

$$H_1 + G_3 \overset{K_{13}}{\rightleftharpoons} H_1G_3 \qquad H_2 + G_3 \overset{K_{23}}{\rightleftharpoons} H_2G_3$$

Scheme S1. Binding equilibria established in a multicomponent mixture containing two hosts and three guests.

$$[H_1]_0 = [H_1] + [H_1G_1] + [H_1G_2] + [H_1G_3] \qquad (S1)$$

$$[H_2]_0 = [H_2] + [H_2G_1] + [H_2G_2] + [H_2G_3] \qquad (S2)$$

$$[G_1]_0 = [G_1] + [H_1G_1] + [H_2G_1] \qquad (S3)$$

$$[G_2]_0 = [G_2] + [H_1G_2] + [H_2G_2] \qquad (S4)$$

$$[G_3]_0 = [G_3] + [H_1G_3] + [H_2G_3] \qquad (S5)$$

Replacing the concentrations of the complexes by the product of the respective binding constant with the equilibrium concentrations of free host and guest (*i.e.*, $[H_iG_j]= K_{ij}[H_i][G_j]$) leads to a system of five equations and five unknowns:

$$[H_1] + K_{11}[H_1][G_1] + K_{12}[H_1][G_2] + K_{13}[H_1][G_3] - [H_1]_0 = 0 \qquad (S6)$$

$$[H_2] + K_{21}[H_2][G_1] + K_{22}[H_2][G_2] + K_{23}[H_2][G_3] - [H_2]_0 = 0 \qquad (S7)$$

$$[G_1] + K_{11}[H_1][G_1] + K_{21}[H_2][G_1] - [G_1]_0 = 0 \qquad (S8)$$

$$[G_2] + K_{12}[H_1][G_2] + K_{22}[H_2][G_2] - [G_2]_0 = 0 \qquad (S9)$$

$$[G_3] + K_{13}[H_1][G_3] + K_{23}[H_2][G_3] - [G_3]_0 = 0 \qquad (S10)$$

The solutions of this system of equations provides the equilibrium concentrations of all free species that can be inserted in the equilibrium equations (*i.e.*, $[H_iG_j]= K_{ij}[H_i][G_j]$) to calculate the concentration of the complexes and construct the speciation plots.

5. References

[1] P. Máximo, M. Colaço, S. R. Pauleta, P. J. Costa, U. Pischel, A. J. Parola and N. Basílio, *Org. Chem. Front.,* **2022**, *9*, 4238-4249.

[2] C. Márquez, F. Huang and W. M. Nau, *IEEE Trans. Nanobiosci.*, **2004**, *3*, 39-45.

[3] P. K. Glasoe and F. A. Long, *J. Phys. Chem*., **1960**, *64*, 188-190.