Electronic Supplementary information

Crystal structure of a complex between β–glucopyranose and a macrocyclic receptor with dendritic multicharged water solubilizing chains

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1 Crystallography

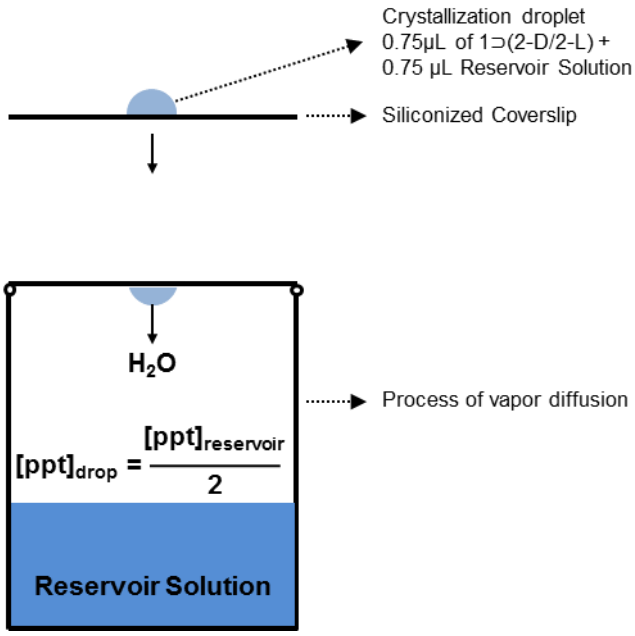
1.1 Crystallogenesis. The monocyclic anthracene-based receptor **1** was saturated with a 500 mM racemic mixture of **2** (D- and L-*β*-glucopyranose). The final concentration of **1⊃(2-D/2-L)** solution to start the crystallization screening was 10 mg/mL. Crystallization experiments were performed using the hanging drop vapour diffusion method[1] in 24-well Linbro-style plates. The initial screening for crystallization conditions were carried out using commercially available sparse matrix screens JBScreen Basic 1 to 4, from Jena Bioscience.[2,3] This ensured screening with an intentional bias towards conditions which have been proven successful in the crystallization of biological macromolecules. For each screening condition, hanging drops were prepared using 0.75 µL of **1⊃(2-D/2-L)** and 0.75 µL of the crystallization reagent on a silanized glass slide, which was then suspended over a reservoir solution. Crystals (see Figure S1) appeared from one out of the 96 crystallization reagents of this sparse matrix screen, after 5 days when the trays were incubated at 293 K. X-ray quality crystallogenesis was optimized by increasing the drop size by the equilibration of a mixture containing 1 µL of **1⊃(2-D/2-L)** and 1µL of a reservoir solution of 100 mM HEPES buffer [pH 7.5], 200mM $CaCl_2$ and 28% vol/vol polyethylene glycol 400) against 500 µL of the reservoir solution. Subsequent efforts were made to crystallize **1** with the single enantiomer **2**-D using the same crystallization reagent. However, no crystal was obtained.

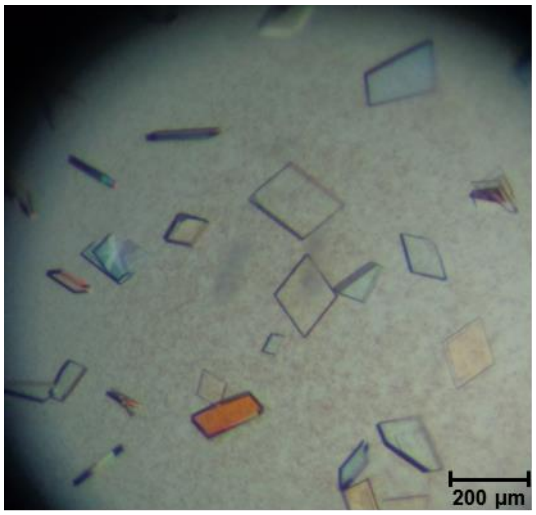
1.2 Data collection, structure determination and refinement. For low temperature diffraction measurements, the crystal was vitrified in a stream of cold nitrogen gas at 100 K. The mother liquor served as cryo-protectant for the crystal. X-ray diffraction data were collected at the French CRG beamline FIP (BM30A) at European Synchrotron Radiation Facility (ESRF), Grenoble using an ADSC quantum 315r detector at a wavelength of 0.8726 Å. The crystal diffracted to a maximum resolution of 1.08 Å. Diffraction data were processed and scaled using the *XDS package*.[4] The symmetry of the crystal is monoclinic with space group $P2_1/c$ (no.14), Z' = 2 and unit cell parameters: *a*, 44.59 Å; *b*, 51.64 Å; *c*, 38.96 Å, *β*, 107.10 (The X-ray data collection and refinement statistics are given in Table S1). The structure was solved by direct method using the charge-flipping program *Superflip*.[5] The phase set calculated allowed to identify most of the core atoms of the receptor and sugar molecules. The structure was refined by full-matrix least-squares method on F^2 with SHELXL-2014.[6] Due to moderate resolution of the data, observed disorder and most probably radiation induced damage the position of some atoms from side chains could not be established. For all non-hydrogen atoms attempts to introduce anisotropic displacement parameters were made. However, whenever the

ellipsoids have adopted unrealistic shape isotropic model was employed. FVAR and EADP instruction was used to force some of the isotropic temperature parameters to be equal. In order to model anisotropic displacement parameters RIGU instructions were used. If it was necessary geometry of molecules was improved using DFIX and AFIX66 SHELX instructions. The final cif file was checked using IUCR's checkcif algorithm. A - Level and B - level alerts were detected. These alerts are inherent to the data quality (weak intensities, moderate resolution), crystal composition (large asymmetric unit, large, heavily disordered parts, etc.) and decisions made during data refinement (*i.e.* isotropic displacement parameters for non-H atoms). All A and B alerts (except for data resolution) that remain concern the disordered solvent molecules and side chains of the receptor kept in the final model but not the receptors or sugar molecules themselves. After several attempts to model the disordered side chains, the SQUEEZE procedure was used to flatten the electron density map. Very disordered side chains and solvent molecules were removed. The total potential solvent accessible void volume given is 48898 $Å^3$ and the number of electron count per cell 16628. Interestingly, applying this procedure after removing the badly modeled side chains allowed to remove most of the restraints applied along the modeling and refinement process. The coordination environment of Ca10 looks chemically not sensible, but no extra electron density peaks are observed close to this Ca.

Atomic coordinates and structure factors for the crystal structure has been deposited in the Cambridge Crystallographic Data Centre (CCDC) with accession code 1482231. These data are available free of charge upon request (www.ccdc.cam.ac.uk/).

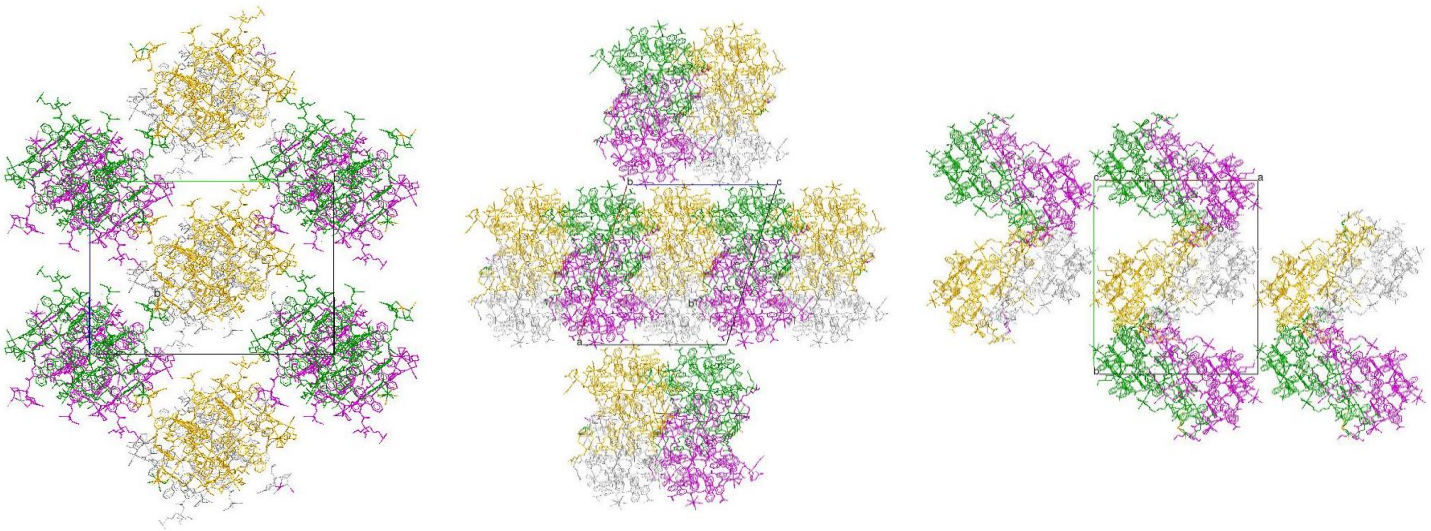
2 Supplementary Figures





(A) **(B)**

Figure S1: (A) Hanging drop vapor diffusion set up; (B) Crystals of **1⊃2** viewed under crossed polarizing microscope. The crystal colors that appear upon shining white light under crossed polarizers is a property called interference color. The differences in color reflect differences in crystal thickness



(A) (B) (C)

Figure S2: Crystal arrangement views along (A) the a axis; (B) the b axis; (C) the c axis. The clusters are colored by symmetry operations. This image was prepared with Mercury3.6 (https://www.ccdc.cam.ac.uk/)

3 Supplementary Table

Table S1: Summary of data collection and atomic model refinement statistics.

CCDC Number	CCDC 1482231
Chemical formula	$C_{798}H_{638}N_{72}O_{322}Ca_{17}$
Z	2
Space group	$P2_1/c$
Unit cell (Å and °)	a=44.593(9) b=51.642(10) c=38.959(8) ß=107.10(3)
Cell Volume ($Å^3$)	85753(32)
Index ranges	h = -40→40, k = -47→47, l = -35→35
Completeness to theta = 23.595°	99.0%
Reflections collected	461296
Reflections observed [I > 2 σ (I)]	69293
R_{int}	0.0362
Data/parameters/restrains	4261/44
Goodness-of-fit on F^2	1.801
Highest residual peak Deepest hole	0.58 -0.690
Final R indices [I>2sigma(I)]	R1 = 0.1428 wR2 = 0.4199
R indices (all data)	R1 = 0.1832 wR2 = 0.4574

4 References

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