Electronic Supplementary Information

Solution-mediated and single-crystal to single-crystal transformations of the cucurbit[6]uril host-guest complexes with dopamine

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Crystallization

The dopamine was purchased from Sigma Aldrich. **CB6** was synthesized according to a literature procedure [A. Day *et al*, *J. Org. Chem*., 2001, 66, 8094]. **CB6**·10H_2O (10 mg, 8.5 µmol) and $MgCl_2$·6H_2O (173 mg, 0.85 mmol) were dissolved in distilled water (1 ml) upon gentle heating. The solution of dopamine guest (2 equivalents) in 1 ml of water was layered over the solution of the macrocycle. The diffraction quality crystals of complexes **I** (prisms) and **II** (needles) were formed concomitantly after one day. After several days only crystals of complex **II** were present in the crystallization vial. The crystals of complex **II** undergo single-crystal to single-crystal desolvation when out of mother solution. Despite some cracking and higher mosaicity the dried crystals **III** gave a satisfactory diffraction pattern.

Single crystal X-ray diffraction

The crystals were selected under Paratone-N oil, mounted on the nylon loops and positioned in the cold stream on the diffractometer. Uniformity of the samples was checked by unit cell determination of several crystals for each sample. The X-ray data for complexes **I**-**III** were collected on a SuperNova Agilent diffractometer using Cu*Kα* radiation (λ = 1.54184 Å). The data were processed with *CrysAlisPro*.[1] Structures were solved by direct methods and refined using *SHELXL*.[2] The figures were prepared using *Chimera*.[3]

Crystal data for I: $(C_{36}H_{36}N_{24}O_{12})\cdot(C_8H_{12}NO_2)^{+}\cdot Cl^{-}\cdot 13.5(H_2O)$, *Mr* =1429.7, colorless prisms, orthorhombic, space group $P2_12_12_1$, *a* = 12.6209(6), *b* = 15.8200(4), *c* = 30.3571(1) Å, *V* = 6061.2(4) Å^3, *Z* = 4, ρ_{calc} = 1.57 g cm^{-3}, μ(CuKα) = 1.51 mm^{-1}, θ_{max} = 68.2°, 19840 reflections measured, 11066 unique, 1072 parameters, *R* = 0.094, *wR* = 0.256 (*R* = 0.113, *wR* = 0.281 for all data), GooF = 1.02. CCDC 1954457.

Crystal data for II: $(C_{36}H_{36}N_{24}O_{12})\cdot(C_8H_{12}NO_2)^{+}\cdot Cl^{-}\cdot 14(H_2O)$, *Mr* =1438.7, colorless needles, trigonal, space group *R*-3, *a* = 50.711(2), *c* = 12.5325(8) Å, *V* = 27911(3) Å^3, *Z* = 18, ρ_{calc} = 1.54 g cm^{-3}, μ(CuKα) = 1.49 mm^{-1}, θ_{max} = 70.1°, 33038 reflections measured, 11712 unique, 1096 parameters, *R* = 0.094, *wR* = 0.279 (*R* = 0.110, *wR* = 0.306 for all data), GooF = 1.10. CCDC 1954458.

Crystal data for III: $(C_{36}H_{36}N_{24}O_{12})\cdot(C_8H_{12}NO_2)^{+}\cdot Cl^{-}\cdot 7.333(H_2O)$, *Mr* = 1318.6, colorless needles, trigonal, space group *R*-3, *a* = 48.442(2), *c* = 12.4117(4) Å, *V* = 25223(3) Å^3, *Z* = 18, ρ_{calc} = 1.56 g cm^{-3}, μ(CuKα) = 1.50 mm^{-1}, θ_{max} = 68.3°, 59616 reflections measured, 10226 unique, 964 parameters, *R* = 0.116, *wR* = 0.319 (*R* = 0.138, *wR* = 0.342 for all data), GooF = 1.12. CCDC 1954459.

Thermal analysis

The TG measurements were performed using STA 449 F1 Jupiter analyzer (Netzsch) coupled with quadrupole mass spectrometry QMS 403C Aëolos (Netzsch) and FT-IR spectrofotometer TENSOR 27 (Bruker) in helium flow. The heating rate was equal to 5 K/min.

The differential scanning calorimetry (DSC) curves were recorded using a Netzsch DSC 204 F1 Phoenix apparatus in argon flow. Aluminium crucible with a hole in a lid was used. The heating rate was equal to 5 K/min.

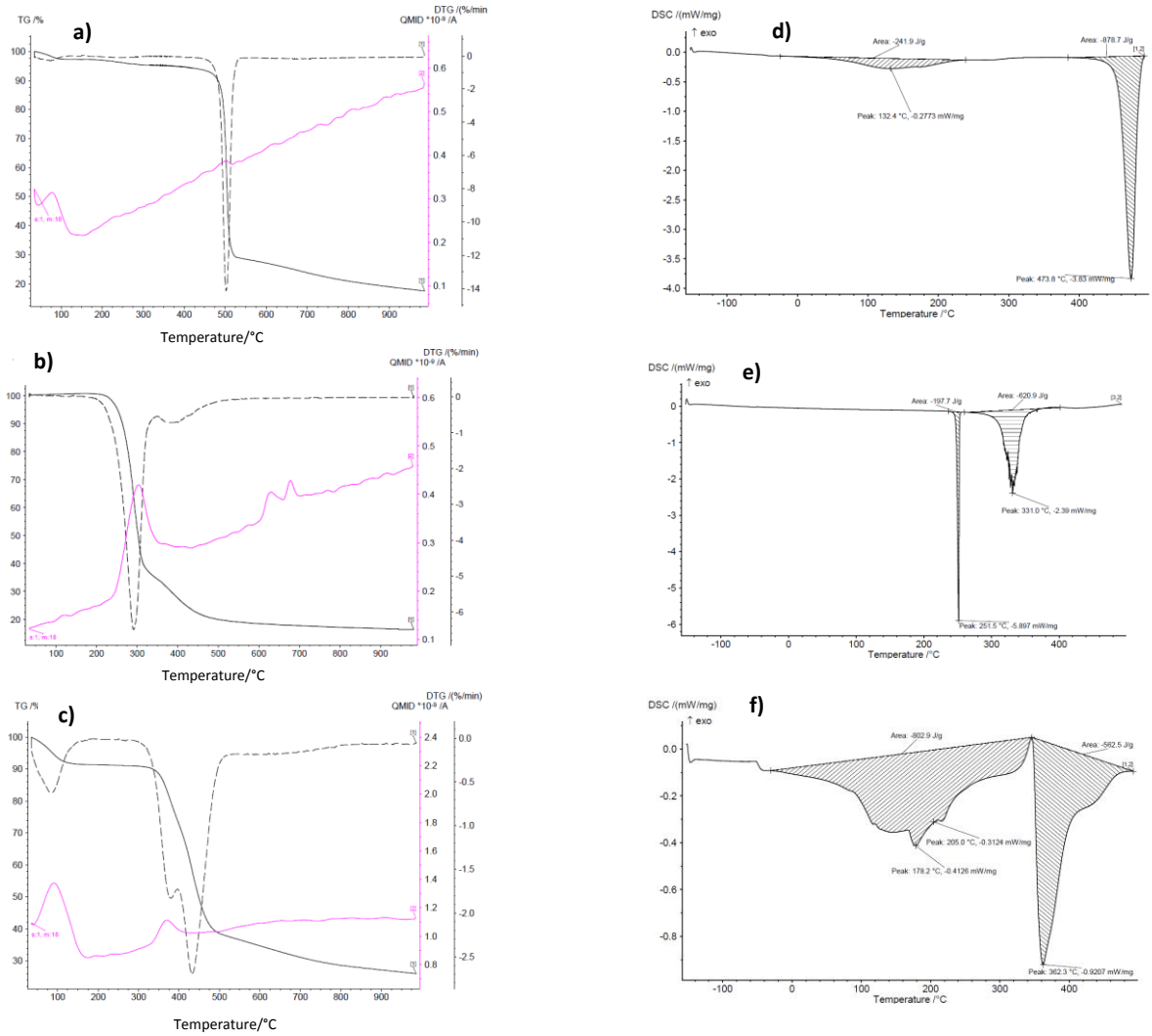

Fig. ESI-1 TG and DSC curves of cucurbit[6]uril (a and d), dopamine (b and e) and cucurbit[6]uril-dopamine complex III (c and f). The crystals of complex III were dried for 24 hours in air at ambient conditions prior to measurements.

[1] Agilent Technologies, CrysAlisPro, Version 1.171.36.32.
[2] G. M. Sheldrick, *Acta Cryst*., **2008**, 64A, 112.
[3] E. F. Pettersen, T. D. Goddard, C C. Huang, G. S. Couch, D. M. Greenblatt, E. C. Meng, T. E. Ferrin, *J. Comput. Chem*., **2004**, 25(13), 1605.