Electronic Supplementary Information

Solid-state assembly of carboxylic acid substituted pillar[5]arene and its host-guest complex with tetracaine

Oksana Danylyuk and Volodymyr Sashuk

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

e-mail: odanylyuk@ichf.edu.pl, vsashuk@ichf.edu.pl

Tetracaine hydrochloride was purchased from Sigma-Aldrich. Carboxylic acid substituted pillar[5]arene has been synthesized according to literature procedure.[1]

^{1}H NMR spectra for host, guest and host-guest complex were recorded on a Varian (400 MHz) instrument.

ES-MS spectrum for host-guest complex was recorded on a SYNAPT G2-S HDMS spectrometer.

Crystallization of complex 1. 5 mg of carboxylic acid PA5 was dissolved in 1 ml of 1:1 water-ethanol mixture under gentle heating. The diffraction quality crystals grew upon slow cooling of the solution.

Crystallization of complex 2. 5 mg of carboxylic acid PA5 and four-fold excess of tetracaine hydrochloride (5mg) were dissolved in 1 ml of 1:1 water-ethanol mixture under gentle heating. The diffraction quality crystals grew upon slow cooling of the solution.

Crystallography. The crystals were selected under inert oil, mounted on the nylon loops and positioned in the cold stream on the diffractometer. The X-ray data for both complexes were collected at 100 K on a SuperNova Agilent diffractometer using Cu$K\alpha$ radiation (λ = 1.54184 Å). The data were processed with *CrysAlisPro*.[2] Structures were solved by direct methods and refined using *SHELXL-2013*.[3] The figures were prepared using *X-Seed*[4]/ *POV-Ray*[5] and *Chimera*[6]. In the structure 1 some of the pillar[5]arene substituents, one of the ethanol molecules included into host cavity, and water molecules have been modelled as disordered

over two positions. The crystals of complex 2 were of poor diffraction quality, with the number of 'observed' reflections being quite low (38% of all data). There is severe disorder of one of the tetracaine molecules included inside host cavity, this tetracaine was modelled as disordered over 2 positions with the 52 and 48 % occupancies. The soft restraints, such as SAME, SIMU and DELU have been used to get reasonable geometry and anisotropic parameters of tetracaine guests. Some of the pillar[5]arene substituents and water molecules have also been treated as disordered. The poor quality of crystals and refinement procedure account for reasonably high values of *R* factors in the structure 2, although gross atom-atom connectivities have been established.

ES-MS spectrum

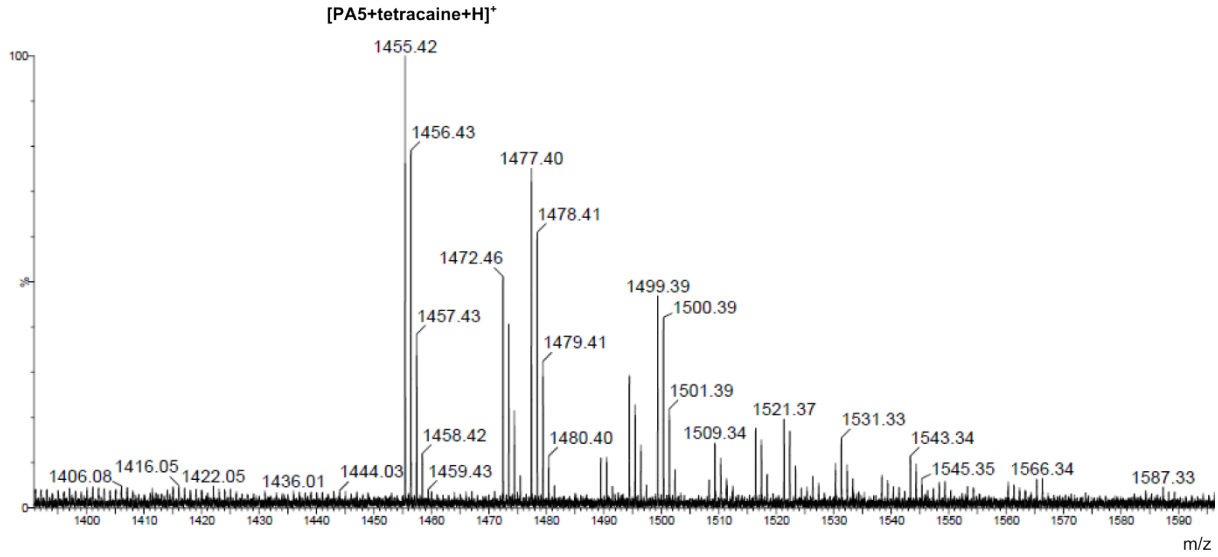

Fig 1. ES-MS spectrum for PA5-tetracaine host-guest complex in methanol. HRMS (ES): *m/z*: calcd for $C_{70}H_{75}N_2O_{32}$: 1455.4303; found: 1455.4254.

[1] T. Ogoshi, S. Kanai , S. Fujinami , T. Yamagishi, Y. Nakamoto, *J. Am. Chem. Soc*., **2008**, *130(15)*, 5022; C. Li, X. Shu, J. Li, S. Che, K. Han, M. Xu, B. Hu, Y. Yu, X. Jia, *J. Org. Chem*., **2011**, *76(20)*, 8458.

[2] Agilent Technologies, *CrysAlisPro*, Version 1.171.36.32.

[3] G.M. Sheldrick, *Acta Cryst*. A64, **2008**, 112.

[4] L. J. Barbour, *J. Supramol. Chem.* **2001**, *1*, 189.

[5] *POV-Ray*, version 3.6; Persistence of Vision Pty. Ltd., Persistence of Vision Raytracer, **2004**; available at http://www.povray.org/

[6] 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**, *13*, 1605.