Preference-oral
Smart recognition by macrocyclic hosts

Valery V. Gorbatchuk,* Marat A. Ziganshin, Karina V. Gataullina, Askar K. Gatiatulin
Institute of Chemistry, Kazan Federal University, Kazan, Russia
**Valery.Gorbatchuk@kpfu.ru*

Abstract

Smart properties of solid calixarenes and other hosts were observed boosting their selectivity and clathrate stability. Absolute selectivity of host response to guest inclusion and release was found, which goes far beyond the capability of ordinary key-to-lock mechanism. While current concept of molecular recognition is based on the preferential binding of complementary species, the present work uses specific cooperative properties of host crystals such as their memory of previously bound guest, pseudopolymorphism of host-guest clathrates with more than one step of guest inclusion, favorable hydration effect on binding of hydrophobic guests by hydrophilic hosts, and effect of clathrate preparation history on guest inclusion capacity and clathrate stability. Thus, small guest molecules having no more than one functional group capable of H-bonding or donor-acceptor interactions can be discriminated even from their close homologues.

A true recognition was found in a two-step formation of benzene clathrate with tert-butylthiacalix[4]arene derivative both on vapor sorption isotherm and in kinetic response of mass-sensitive sensor. This experiment is extremely selective being capable to detect benzene qualitatively and quantitatively in mixtures with any other compounds. Inclusion cooperativity of glassy calixarenes makes possible also a visual detection of organic vapors in mixtures giving a response to a very small step in guest concentration [1,2].

An observed ability of several calixarenes to remember evolved guests does not have any precedents by selectivity. This memory can be read in simultaneous TG/DSC experiment as an exothermic effect of host collapse from loose to dense phase without mass change. The memory parameters (enthalpy and temperature of polymorphic transition) strongly depend on the guest structure. This smart property persists also for guest mixtures [2]. In some cases, such memory effect can be found only after a solid-phase guest exchange in calixarene clathrates [3]. When combined, these effects give a controlled polymorphism of calixarenes with long-chain substituents with H-bonding capability [2].

The procedure of clathrate preparation by guest exchange is rather selective itself and gives a surge in guest inclusion capacity and clathrate stability both for calixarenes and beta-cyclodextrin [4]. This may produce clathrates that cannot be formed by host-guest interaction in binary systems. The highest clathrate stability was found for calixarene capable of special anti-sieve effect, so that larger guests can be bound, while smaller ones are excluded [5].

References

[1] K. V. Gataullina, M. A. Ziganshin, I. I. Stoikov, A. T. Gubaidullin, V. V. Gorbatchuk, *Phys. Chem. Chem. Phys.* **2015**, *17*, 15887

[2] K. V. Gataullina, M. A. Ziganshin, I. I. Stoikov, A. E. Klimovitskii, A. T. Gubaidullin, K. Suwińska, V. V. Gorbatchuk, Cryst. Growth & Design **2017**, DOI: 10.1021/acs.cgd.7b00463

[3] G. D. Safina, M.A. Ziganshin, A.T. Gubaidullin, V.V. Gorbatchuk, *Org. Biomol. Chem.* **2013**, *11*, 1318

[4] S. F. Galyaltdinov, M. A. Ziganshin, A. B. Drapailo, V. V. Gorbatchuk, *J. Phys. Chem. B* **2012**, *116*, 11379

[5] V. V. Gorbatchuk, A. K. Gatiatulin, M. A. Ziganshin, A.T.Gubaidullin, L.S.Yakimova, *J. Phys. Chem. B* **2013**, *117*, 14544

[6] S. F. Galyaltdinov, M. A. Ziganshin, A. T. Gubaidullin, S. G. Vyshnevsky, O. I. Kalchenko, V. V. Gorbatchuk, *CrystEngComm* **2014**, 3781-3787.