Thematic Section: Physicochemical Research. **Full Paper**
Subsection: Organic Chemistry.
The Reference Object Identifier – ROI: jbc-01/20-63-7-1
The Digital Object Identifier – DOI: 10.37952/ROI-jbc-01/20-63-7-1
Submitted on July 22, 2020.

The solvent nature influence on the self-assembly of monosubstituted pillar[5]arenes containing *N*-(aminoalkyl)amide fragment

© **Anastasia A. Nazarova**, **Alsu I. Gilyazeva**, and **Ivan I. Stoykov***+
A.M. Butlerov Institute of Chemistry. Kazan Federal University.
Kremlevskaya St., 18. Kazan, 420008. Tatarstan Republic. Russia.
Phone: +7 (843) 233-72-41. E-mail: ivan.stoikov@mail.ru

*Supervising author; +Corresponding author

Keywords*:* pillar[5]arenes, synthesis, supramolecular chemistry, self-assembly, aminolysis.

Abstract

Chemistry of macrocyclic compounds is one of the rapidly developing areas of modern organic chemistry. These macrocycles have become widespread due to the high availability of parents compounds, the possibility of synthesis of ligands based on them for highly selective recognition, ion-selective membranes, electrodes, sensors and nanocontainers for targeted drug delivery. Moreover, in the past few years, attention of researchers has again been riveted on mechanically interlocked molecules (rotaxanes and pseudorotaxans) and supramolecular polymers, which can be explained by their potential application as molecular machines and materials. Mechanically interlocked molecules are molecular architectures consisting from two or more components which mechanically bind due to their own topology. Supramolecular polymers are comprise ordered monomer units combined via non-covalent bonds (hydrogen bonds or electrostatic interactions). Thus, this manuscript presents an approach to the synthesis of monosubstituted pillar[5]arenes containing *N*-(aminoalkyl)amide fragments with various substituent lengths. The formation of self-inclusion complexes by synthesized macrocycles was established by one- and two-dimensional NMR spectroscopy. According to NMR data, only four carbon atoms of the alkyl fragment were included in the macrocyclic cavity regardless of the alkyl chain length. Formation of self-inclusion complexes becomes possible due to the intramolecular hydrogen bond between the NH protons and the oxygen atom of methoxyl fragment, which is confirmed by IR spectroscopy. It was shown by dynamic light scattering that the synthesized pillar[5]arenes in chloroform form aggregates with an average hydrodynamic diameter of 316-640 nm and polydispersity index from 0.18 to 0.20, while polydisperse systems are formed in dimethyl sulfoxide.

References

[1] J.F. Stoddart. Mechanically interlocked molecules (MIMs)-molecular shuttles, switches, and machines (Nobel Lecture). *Angew. Chem. Int. Ed*. **2017**. Vol.56. No.37. P.11094-11125. DOI: 10.1002/anie.201703216
[2] T. Ogoshi, D. Yamafuji, T. Aoki, K. Kitajima, T.-A. Yamagishi, Y. Hayashi, S. Kawauchi. High-yield diastereoselective synthesis of planar chiral [2]- and [3]rotaxanes constructed from per-ethylated pillar[5]arene and pyridinium derivatives. *Chem. Eur. J*. **2012**. Vol.18. No.24. P.7493-7500. DOI: 10.1002/chem.201200122
[3] T. Ogoshi, T. Aoki, R. Shiga, R. Iizuka, S. Ueda, D. Demachi, D. Yamafuji, H. Kayama, T. Yamagishi. Cyclic host liquids for facile and high-yield synthesis of [2]rotaxanes. *J. Am. Chem. Soc*. **2012**. Vol.134. No.50. P.20322-20325. DOI: 10.1021/ja310757p
[4] L. Carlucci, G. Ciani, D.M. Proserpio. Polycatenation, polythreading and polyknotting incoordination network chemistry. *Coordin. Chem. Rev*. **2003**. Vol.246. No.1-2. P.247-289. DOI: 10.1016/S0010-8545(03)00126-7
[5] E.A. Neal, S.M. Goldup. Chemical consequences of mechanical bonding in catenanes and rotaxanes: isomerism, modification, catalysis and molecular machines for synthesis. *Chem. Commun*. **2014**. Vol.50. No.40. P.5128-5142. DOI: 10.1039/C3CC47842D
[6] D.A. Leigh, V. Marcos, M.R. Wilson. Rotaxane catalysts. *ACS Catal*. **2014**. Vol.4. No.12. P.4490-4497. DOI: 10.1021/cs5013415
[7] V. Aucagne, K.D. Hänni, D.A. Leigh, P.J. Lusby, D.B. Walker. Catalytic "click" rotaxanes: a substoichiometric metal-template pathway to mechanically interlocked architectures. *J. Am. Chem. Soc*. **2006**. Vol.128. No.7. P.2186-2187. DOI: 10.1021/ja056903f

[8] E. DeIonno, H.-R. Tseng, D.D. Harvey, J.F. Stoddart, J.R. Heath. Infrared spectroscopic characterization of [2]rotaxane molecular switch tunnel junction devices. *J. Phys. Chem. B*. **2006**. Vol.110. No.15. P.7609-7612. DOI: 10.1021/jp0607723
[9] X. Ma, H. Tian. Bright functional rotaxanes. *Chem. Soc. Rev*. **2010**. Vol.39. No.1. P.70-80. DOI: 10.1039/B901710K
[10] T. Ogoshi, S. Kanai, S. Fujinami, T.-A. Yamagishi, Y. Nakamoto. Para-bridged symmetrical pillar[5]arenes: their Lewis acid catalyzed synthesis and host–guest property. *J. Am. Chem. Soc*. **2008**. Vol.130. No.15. P.5022-5023. DOI: 10.1021/ja711260m
[11] D.-X. Chen, Y.-L. Sun, Y. Zhang, J.-Y. Cui, F.-Z. Shen, Y.-W. Yang. Supramolecular self-assembly and photophysical properties of pillar[5]arene-stabilized CdTe quantum dots mediated by viologens. *RSC Adv*. **2013**. Vol.3. No.17. P.5765-5768. DOI: 10.1039/C3RA40436F
[12] Y.-L. Sun, Y.-W. Yang, D.-X. Chen, G. Wang, Y. Zhou, C.-Y. Wang, J. F. Stoddart. Mechanized silica nanoparticles based on pillar[5]arenes for on-command cargo release. *Small*. **2013**. Vol.9. No.19. P.3224-3229. DOI: 10.1002/smll.201300445
[13] Y. Yao, M. Xue, X. Chi, Y. Ma, J. He, Z. Abliz, F. Huang. A new water-soluble pillar[5]arene: synthesis and application in the preparation of gold nanoparticles. *Chem. Commun*. **2012**. Vol.48. No.52. P.6505-6507. DOI: 10.1039/C2CC31962D
[14] Y. Zhang, B. Shi, H. Li, W. Qu, G. Gao, Q. Lin, H. Yao, T. Wei. Copillar[5]arene-based supramolecular polymer gels. *Polym. Chem*. **2014**. Vol.5. No.16. P.4722-4725. DOI: 10.1039/C4PY00186A
[15] L. Gao, Z. Zhang, S. Dong, M. Xue. Formation of a copillar[5]arene based supramolecular polymer in solution and in the solid state. *Macromol. Rapid Commun*. **2014**. Vol.35. No.10. P.987-991. DOI: 10.1002/marc.201400048
[16] Y. Chen, M. He, B. Li, L. Wang, H. Meier, D. Cao. A monophosphoryl copillar[5]arene: synthesis and host–guest complexation with alkanols. *RSC Adv*. **2013**. Vol.3. No.44. P.21405-21408. DOI: 10.1039/C3RA43744B
[17] Y. Chen, D. Cao, L. Wang, M. He, L. Zhou, D. Shollmeyer, H. Meier. Monoester copillar[5]arenes: synthesis, unusual self-inclusion behavior, and molecular recognition. *Chem. Eur. J*. **2013**. Vol.19. No.22. P.7064-7070. DOI: 10.1039/C3RA43744B
[18] E. Krieg, M.M.C. Bastings, P. Besenius, B. Rybtchinski. Supramolecular polymers in aqueous media. *Chem. Rev*. **2016**. Vol.116. No.4. P.2414-2477. DOI: 10.1021/acs.chemrev.5b00369
[19] T.L. Price, H.W. Gibson. Supramolecular pseudorotaxane polymers from biscryptands and bisparaquats. *J. Am. Chem. Soc*. **2018**. Vol.140. No.12. P.4455-4465. DOI: 10.1021/jacs.8b01480
[20] D.N. Shurpik, and I.I. Stoikov. Synthesis of the new monomeric fragments for the construction of paracyclophanes. *Butlerov Communications.* **2017**. Vol.51. No.8. P.76-83. DOI: 10.37952/ROI-jbc-01/17-51-8-76
[21] A.A. Nazarova, L.S. Yakimova, V.V. Klochkov, I.I. Stoikov. Monoaminophosphorylated pillar[5]arenes as hosts for alkaneamines. *New J. Chem*. **2017**. Vol.41. No.4. P.1820-1826. DOI: 10.1039/C6NJ03345H
[22] T. Ogoshi, K. Demachi, K. Kitajima, T.-A. Yamagishi. Monofunctionalized pillar[5]arenes: synthesis and supramolecular structure. *Chem. Commun*. **2011**. Vol.47. No.25. P.7164-7166. DOI: 10.1039/C1CC12333E
[23] A.A. Nazarova, L.S. Yakimova, P.L. Padnya, V.G. Evtugyn, Y.N. Osin, P.J. Cragg, I.I. Stoikov. Monosubstituted pillar[5]arene functionalized with (amino)phosphonate fragments are "smart" building blocks for constructing nanosized structures with some s-and p-metal cations in the organic phase. *New J. Chem*. **2019**. Vol.43. No.36. P.14450-14458. DOI: 10.1039/C9NJ03539G
[24] H. Zhu, J. Liu, B. Shi, H. Wang, Z. Mao, T. Shan, F. Huang. Pillararene-based host−guest recognition facilitated magnetic separation and enrichment of cell membrane proteins. *Mater. Chem. Front*. **2018**. Vol.2. No.8. P.1475-1480. DOI: 10.1039/C8QM00141C
[25] Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma, F. Huang. Formation of linear supramolecular polymers that is driven by C-H···π interactions in solution and in the solid state. *Angew. Chem. Int. Ed*. **2011**. Vol.50. No.6. P.1397-1401. DOI: 10.1002/anie.201006693
[26] C. Li. Pillararene-based supramolecular polymers: from molecular recognition to polymeric aggregates. *Chem. Commun*. **2014**. Vol.50. No.83. P.12420-12433. DOI: 10.1039/C4CC03170A
[27] L. Yang, X. Tan, Z. Wang, X. Zhang. Supramolecular polymers: historical development, preparation, characterization, and functions. *Chem. Rev*. **2015**. Vol.115. No.15. P.7196-7239. DOI: 10.1021/cr500633b