

ESI for

Sugar-functionalized water-soluble pillar[5]arene and its host–guest interaction with fullerene

Hui Li,^a Qi Chen,^{*,a} Christian Schönbeck,^{a,b} Bao-Hang Han^{*,a}

^a *National Center for Nanoscience and Technology, Beijing 100190, China.*

Tel: +86 10 8254 5576; E-mail: hanbh@nanoctr.cn

^b *Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100*

Copenhagen, Denmark.

Contents

1. Computational details.....	3
2. NMR and MALDI-TOF Spectra of 3 and 4	5

1. Computational details

An MD simulation of a 1:1 complex in a $60\times60\times60$ Å³ periodic TIP3P water box was run by the NAMD code¹ using CHARMM force field parameters. No parameters are readily available for C₆₀ and a suitable set of parameters must be chosen. Since all carbons in C₆₀ are equivalent, the charges are set to 0 and the atom type is set to CG2RC0 with the associated non-bonded parameters from the Charmm General Force Field v.2b8.² The precise values of the parameters for the angles and dihedrals are not important in a conformationally restricted molecule like C₆₀ and the dihedral force constant is set to 0. The angle parameters are chosen as a weighted average of appropriate single and double bonds, resulting in an angle equilibrium value of 115.5 degrees with a force constant of 52 kcal mol⁻¹ rad⁻².² A proper choice of bond parameters are important as these determine the nucleus to nucleus diameter of C₆₀ which is 7.07 Å.³ The 6:6 and 6:5 bond lengths are 1.38 and 1.454 Å, respectively,⁴ giving an average of 1.42 Å for the single type of bonds that are present in the MD model. Likewise, the bond force constants are evaluated from the average Pauling bond order (0.36) and the force constants for single and double bonds (222.5 and 440 kcal mol⁻¹ Å⁻², respectively) to yield a bond force constant of 300 kcal mol⁻¹ Å⁻². These parameters result in a nucleus to nucleus diameter of 7.11 Å when the structure is minimized in vacuum and an average diameter of 7.10 Å when conducting an MD simulation in TIP3P water.

Atom types, charges and parameters for the atoms in the central pillararene moiety of **P5A-G** are based on the residues p-ethylphenol and methoxybenzene in the

Charmm General Force Field v.2b8.² For the chain containing the triazole ring and the sulfur atom, the atom types, charges and parameters were assigned by the Paramchem tool version 0.9.7 beta^{5,6} together with the Charmm General Force Field v.2b8. Large penalty scores (up to 117) were associated with many of the dihedral parameters that involve the sulfur atom, meaning that these parameters are of a poor quality. Since the MD simulations were not meant to provide any quantitative information about the system, these low-quality parameters were used as provided by the ParamChem tool. Atom types, charges and parameters for the glucose moiety is from the CHARMM36 all-atom carbohydrate force field.⁷

The initial coordinates of the central pillararene moiety is based on the crystal structure of dimethoxypillar[5]arene.⁸ Structures of the glucose-containing side chains were drawn and minimized in the Avogadro molecular editor before being attached to the pillararene structure in random orientations. The C₆₀ molecule was placed in front of one of the cavity openings of **P5AG**.

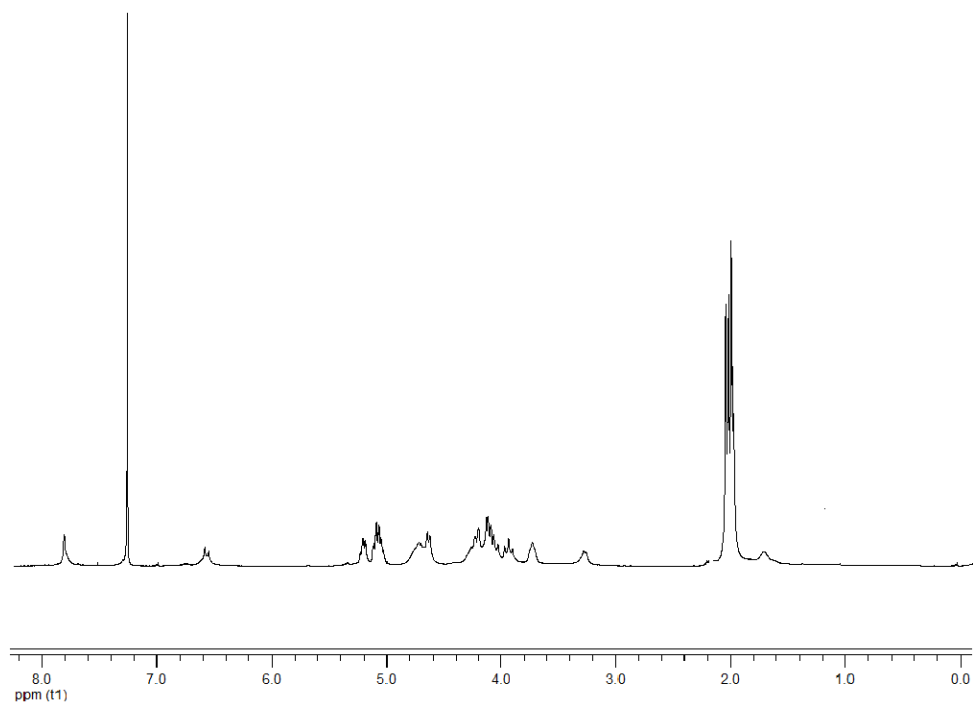
Simulations were run for 50 nanoseconds (ns) with a two femtosecond timestep in the NPT ensemble at 298 K and 1.013 bar. The van der Waals interactions were cut off at 12 Å with a switching function starting at 10 Å.

References

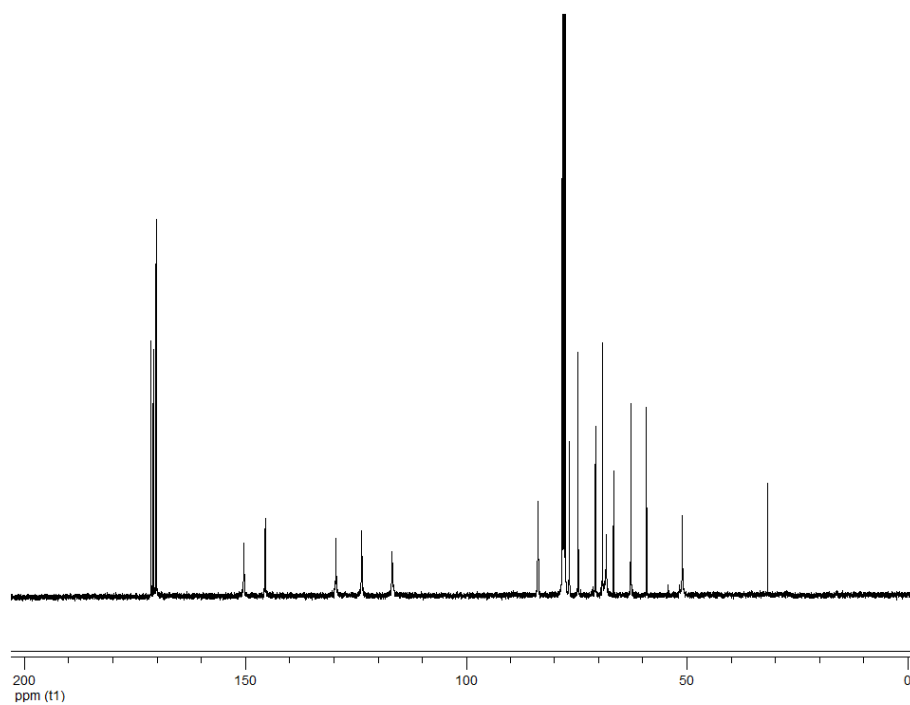
1 J. C. Phillips, R. Braun, W. Wang, J. Gumbart, E. Tajkhorshid, E. Villa, C. Chipot, R. D. Skeel, L. Kalé and K. Schulten, Scalable molecular dynamics with NAMD. *J. Comput. Chem.*, 2005, **26** (16), 1781–1802.

- 2 K. Vanommeslaeghe, E. Hatcher, C. Acharya, S. Kundu, S. Zhong, J. Shim, E. Darian, O. Guvench, P. Lopes, I. Vorobyov and A. D. Mackerell, CHARMM general force field: A force field for drug-like molecules compatible with the CHARMM all-atom additive biological force fields. *J. Comput. Chem.*, 2010, **31** (4), 671–690.
- 3 S. Liu, Y. J. Lu, M. M. Kappes and J. A. Ibers, The structure of the C₆₀ molecule: X-ray crystal structure determination of a twin at 110 K. *Science*, 1991, **254** (5030), 408–410.
- 4 L. Gross, F. Mohn, N. Moll, B. Schuler, A. Criado, E. Guitián, D. Pena, A. Gourdon and G. Meyer, Bond-order discrimination by atomic force microscopy. *Science*, 2012, **337** (6100), 1326–1329.
- 5 K. Vanommeslaeghe and A. D. MacKerell, Automation of the CHARMM general force field (CGenFF) I: Bond perception and atom typing. *J. Chem. Inf. Model.*, 2012, **52** (12), 3144–3154.
- 6 K. Vanommeslaeghe, E. P. Raman and A. D. MacKerell, Automation of the CHARMM general force field (CGenFF) II: Assignment of bonded parameters and partial atomic charges. *J. Chem. Inf. Model.*, 2012, **52** (12), 3155–3168.
- 7 O. Guvench, S. N. Greene, G. Kamath, J. W. Brady, R. M. Venable, R. W. Pastor and A. D. Mackerell, Additive empirical force field for hexopyranose monosaccharides. *J. Comput. Chem.*, 2008, **29** (15), 2543–2564.
- 8 T. Ogoshi, S. Kanai, S. Fujinami, T. A. Yamagishi and Y. Nakamoto, Para-bridged symmetrical pillar[5]arenes: Their lewis acid catalyzed synthesis and host–guest property. *J. Am. Chem. Soc.*, 2008, **130** (15), 5022–5023.

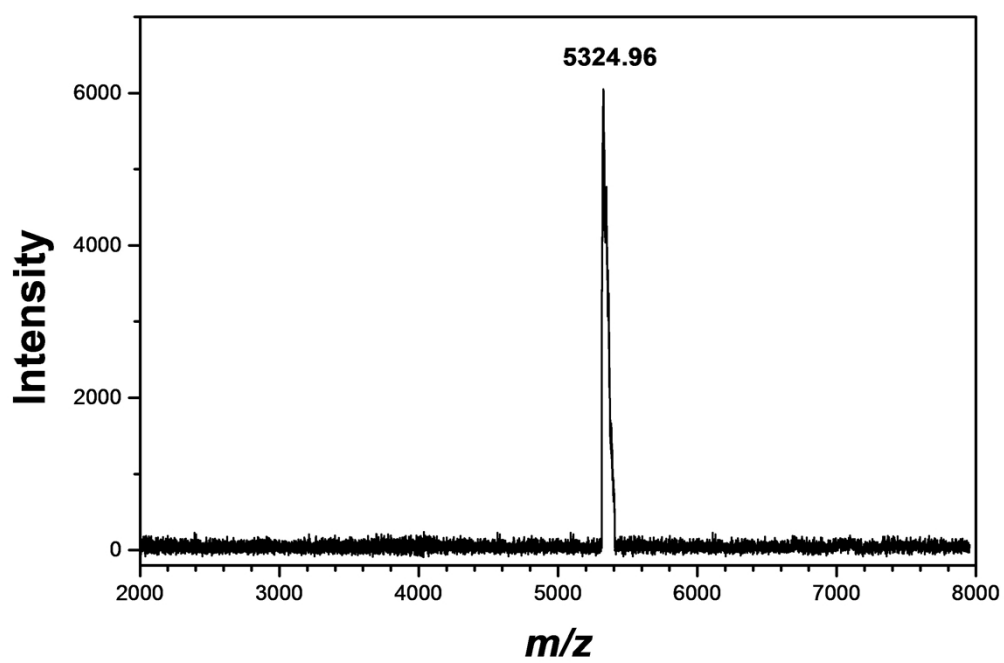
2. NMR and MALDI-TOF spectra of **3** and **4**



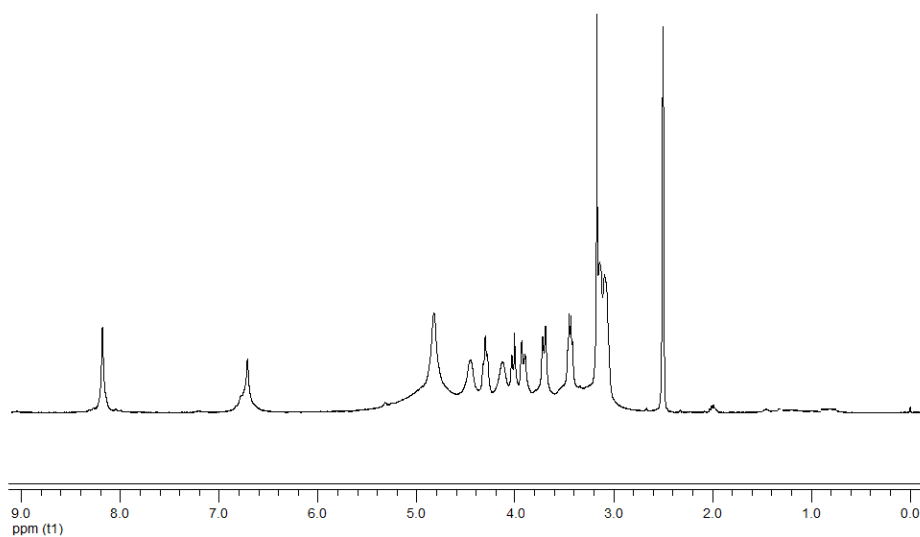
^1H NMR spectrum of **3**



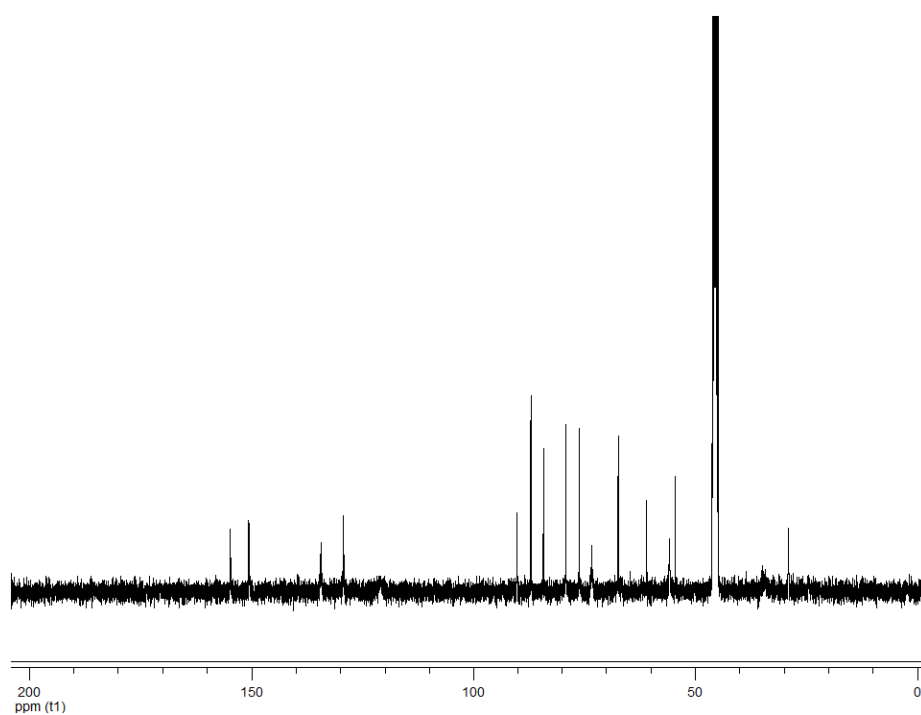
^{13}C NMR spectrum of **3**



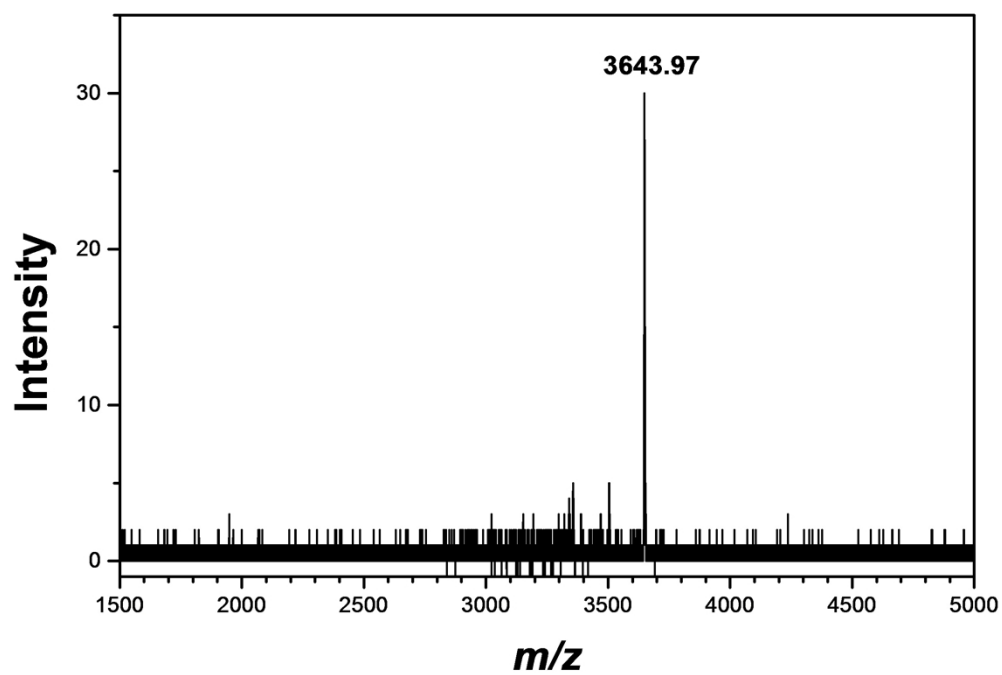
MS spectrum of **3**



^1H NMR spectrum of **4**



^{13}C NMR spectrum of **4**



MS spectrum of **4**