Electronic Supplementary Material (ESI) for ChemComm.

Amide-functionalized pillar[5]arenes as novel type of macrocyclic receptors for the sensing of $H_2PO_4^-$ anion

L. S. Yakimova, D. N. Shurpik, and I. I. Stoikov*

Kazan Federal University, A.M. Butlerov Chemical Institute, 420008, Kremlevskaya Street, 18, Kazan, Russian Federation, ivan.stoikov@mail.ru

Electronic Supplementary Information (20 pages)

1. Materials and methods

^{1}H NMR spectra were recorded on the Bruker Avance-400 (400 MHz) spectrometer and ^{13}C and 2D NOESY NMR spectra were obtained on the impulse spectrometer Bruker Avance II (with 125 MHz and 500 MHz respectively). Chemical shifts were determined against the signals of residual protons of deuterated solvent (D_2O, $CDCl_3$). The concentration of sample solutions was 3-5 %.

Attenuated total internal reflectance IR spectra were recorded with Spectrum 400 (Perkin Elmer) Fourier spectrometer.

Elemental analysis was performed with Perkin Elmer 2400 Series II instrument.

Mass spectra (ESI) were recorded on an AmaZonX mass spectrometer (Bruker Daltonik GmbH, Germany). The drying gas was nitrogen at 300° C. The capillary voltage was 4.5 kV. The samples were dissolved in acetonitrile (concentration ~10^{-6} g ml^{-1})

Melting points were determined using the Boetius Block apparatus.

Additional control of the purity of compounds and monitoring of the reaction were carried out by thin-layer chromatography using Silica G, 200 μm plates, UV 254.

Most chemicals were purchased from Aldrich and used as received without additional purification. Organic solvents were purified in accordance with standard procedures.

2. Synthesis of the compounds A-C and 1-3

Initial pillar[5]arene **A** was obtained removal of methoxyl protections by literary method.[S1] Pillar[5]arene with ethoxycarbonyl fragments **B** was obtained by the reaction of compound **A** with ethyl bromoacetate.

*Pillar[5]arene (**A**).* Product yield: 91%. The decomposition was observed at 230°C without melting. ^{1}H NMR (CD_3COCD_3) δ_H, ppm: 3.66 (s, 10H, -$\underline{CH_2}$-), 6.64 (s, 10H, ArH), 7.99 (s, 10H, -$\underline{OH}$). MALDI-TOF MS $C_{35}H_{30}O_{10}$: calculated [M$^+$] m/z = 610.2, found $[M+Na]^+$ m/z = 633.1, $[M+K]^+$ m/z = 649.2.

*4,8,14,18,23,26,28,31,32,35-Deca-[(ethoxycarbonyl)methoxy]pillar[5]arene (**B**).* [S2] Product yield: 80%. Mp: 199 °C, 196.7 °C.[S3] ^{1}H NMR ($CDCl_3$) δ_H, ppm (*J*/Hz): 0.96 (m, 30H, -$CH_2\underline{CH_3}$), 3.86 (s, 10H, -$\underline{CH_2}$-), 4.09 (m, 20H, -$\underline{CH_2}CH_3$), 4.55 (dd, 20H, O-$\underline{CH_2}$C(O)-), 7.04 (s, 10H, ArH). MALDI-TOF MS: calculated [M$^+$] m/z = 1471.24, found $[M+Na]^+$ m/z = 1494.28.

*4,8,14,18,23,26,28,31,32,35- Deca-(carboxymethoxy)pillar[5]arene (**C**)* was synthesized according literature method.[S2] Product yield: 89%. Mp: 243 °C, 293 °C. ^{1}H NMR (DMSO-d_6) δ_H, ppm (*J*/Hz): 3.74 (s, 10H, -CH_2-), 4.41 (d, AB-system, 10H, $^2J_{HH}$= 16.0, O-$\underline{CH_2}$C(O)-OH), 4.70 (d, AB-system, 10H, $^2J_{HH}$= 16.0, O-$\underline{CH_2}$C(O)-OH), 7.10 (s, 10H, ArH), 12.94 (bs, 10H, -C(O)-$\underline{OH}$). ^{13}C NMR (DMSO-d_6) δ_H, ppm: 28.58, 65.08, 114.24, 128.07, 148.46, 170.47. MALDI-TOF MS: calculated [M$^+$] m/z = 1190.2, found $[M+Na]^+$ m/z = 1213.2.

General procedure of the synthesis of the compounds 1-3.

4,8,14,18,23,26,28,31,32,35-Deca-(carboxymetoxy)pillar[5]arene **C** (0.3 g, 0.252×10^{-3} mol) was placed into a round-bottom flask and $SOCl_2$ (10 ml, 0.084 mol) and catalytic amount of DMF were added. The mixture was refluxed for 18 h after which excess of $SOCl_2$ was removed under reduced pressure. The remainder was dried under reduced pressure for 2 h. The obtained residue was dissolved in 10 ml of dichloromethane. The resulting solution was added to a mixture of *n*-octylamine or *n*-decylamine or aniline (7.56×10^{-3} mol) and 5 ml (0.036 mol) of triethylamine in 20 ml dichloromethane over a period of 20 minutes. The mixture was stirred under argon at rt for 48 h. The reaction mixture was then washed with 2 M HCl (2 × 30 ml) and water (2 × 30 ml). The organic layer was separated and evaporated in vacuo. The residue was crystallized from 2-propanol. The precipitate obtained was dried under reduced pressure over phosphorus pentoxide.

4,8,14,18,23,26,28,31,32,35-Deca-[(phenylamidocarbonyl)methoxy]-pillar[5]arene (1). Yield: 0.37 g (76%). M.p.: 167°C. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K), δ (ppm), J/Hz: 3.83 (s, 10H, -CH_2-), 4.67 (d, AB-system, 10H, $^2J_{HH}$= 14.1 Hz, O-CH_2-C(O)N-), 4.91 (d, AB- system, 10H, $^2J_{HH}$= 14.1 Hz, O-CH_2-C(O)N-), 6.98 (t, 10H, $^3J_{HH}$= 7.7 Hz, -NH-$\underline{Ph}$), 7.17 (t, 20H, $^3J_{HH}$= 7.7 Hz, -NH-$\underline{Ph}$), 7.25 (s, 10H, ArH), 7.61 (d, 20H, $^3J_{HH}$= 7.7 Hz, -NH-$\underline{Ph}$), 10.10 (s, 10H, -$\underline{NH}$-Ph). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K), δ (ppm): 28.97, 67.95, 114.74, 119.51, 123.50, 128.26, 128.69, 138.51, 149.04, 167.02. IR (ν/cm^{-1}): 3291 (-$\underline{NH}$-C(O)-), 3059-2918 (Ar, -CH-, -CH_3-), 1676 (-NH-$\underline{C(O)}$-), 1195 (Ar-O-CH_2-). MS (MALDI-TOF): calc. [M$^+$] m/z = 1941.7, found $[M]^+$ m/z = 1943.3. Found (%): C, 70.83; H, 5.54; N, 7.47. Calc. for $C_{115}H_{100}N_{10}O_{20}$ (%): C, 71.12; H, 5.19; N, 7.21.

4,8,14,18,23,26,28,31,32,35-Deca-[(octylamidocarbonyl)methoxy]- pillar[5]arene (2). Yield: 0.41 g (90%). M.p.: 164°C. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K), δ (ppm), J/Hz: 0.83 (t, 30H, $^3J_{HH}$= 7.0 Hz, -CH_2-$\underline{CH_3}$), 1.22 (m, 120H, -NH-CH_2-$\underline{(CH_2)}_6$-CH_3), 3.06 (m, 20H, -NH-$\underline{CH_2}$-$(CH_2)_6$-CH_3), 3.72 (s, 10H, -$\underline{CH_2}$-), 4.36 (s, 20H, O-$\underline{CH_2}$-C(O)NH-), 6.89 (s, 10H, ArH), 7.84 (br. s, 10H, , -$\underline{NH}$-CH_2-$(CH_2)_6$-CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K), δ (ppm): 13.96, 22.18, 26.21, 28.80, 28.85, 31.44, 38.38, 67.09, 113.77, 127.53, 148.64,167.66. IR (ν/cm^{-1}): 3317 (-$\underline{NH}$-C(O)-), 2924(Ar), 2853-2811 (-CH-, -CH_3-), 1663 (-NH-$\underline{C(O)}$-), 1201 (Ar-O-CH_2-). MS (MALDI-

TOF): calc. [M$^+$] m/z = 2302.6, found [M+H]$^+$ m/z = 2304.4. Found (%): C, 69.97; H, 9.76; N, 5.80. Calc. for $C_{135}H_{220}N_{10}O_{20}$ (%): C, 70.40; H, 9.63; N, 6.08.

4,8,14,18,23,26,28,31,32,35-Deca-[(decylamidocarbonyl)methoxy]- pillar[5]arene (3). Yield: 0.48 g (74%). M.p.: 154°C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 298 K), δ (ppm), J/Hz: 0.62 (t, 30H, $^3J_{HH}$= 6.5 Hz, -CH$_2$-$\underline{CH_3}$), 1.15 (m, 160H, -NH-CH$_2$-($\underline{CH_2}$)$_8$-CH$_3$), 3.07 (m, 20H, -NH-$\underline{CH_2}$-(CH$_2$)$_8$-CH$_3$), 3.51 (s, 10H, -$\underline{CH_2}$-), 4.10(s, 20H, O-$\underline{CH_2}$-C(O)NH-), 6.62 (s, 10H, ArH), 8.03 (br. s, 10H, , -$\underline{NH}$-CH$_2$-(CH$_2$)$_6$-CH$_3$). ^{13}C NMR (100 MHz, DMSO-*d*$_6$, 298 K), δ (ppm): 14.24, 22.82, 27.18, 29.51, 29.88, 32.06, 39.52, 68.24, 115.19, 129.20, 149.81, 168.44. IR (ν/cm^{-1}): 3301 (-$\underline{NH}$-C(O)-), 2923-2854(-CH-, -CH$_3$-), 1662 (-NH-$\underline{C(O)}$-), 1213 (Ar-O-CH$_2$-). MS (MALDI-TOF): calc. [M$^+$] m/z = 2583.0, found [M$^+$] m/z = 2583.1. Found (%): C, 72.14; H, 9.97; N, 5.51. Calc. for $C_{155}H_{260}N_{10}O_{20}$ (%): C, 72.05; H, 10.14; N, 5.42;.

3. NMR, MALDI TOF MS, IR spectra of the compounds 1-3

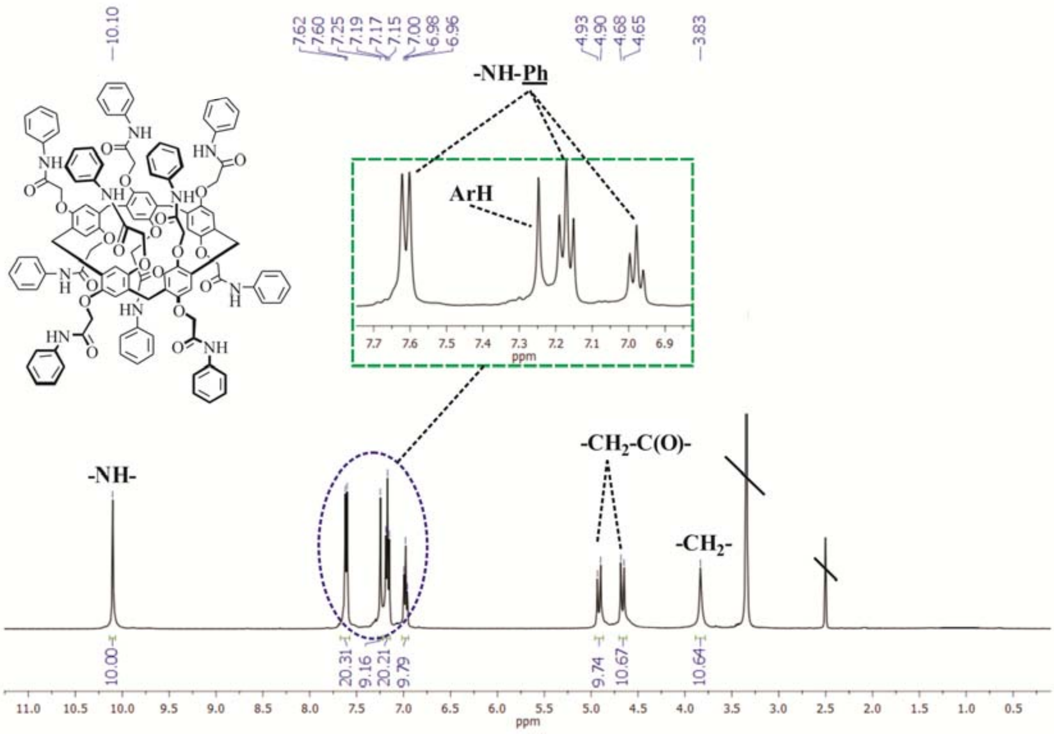

Fig. S1. ^{1}H NMR spectrum of 4,8,14,18,23,26,28,31,32,35-Deca-[(phenylamidocarbonyl)methoxy]-pillar[5]arene (1), DMSO- d_6, 298 K, 400 MHz

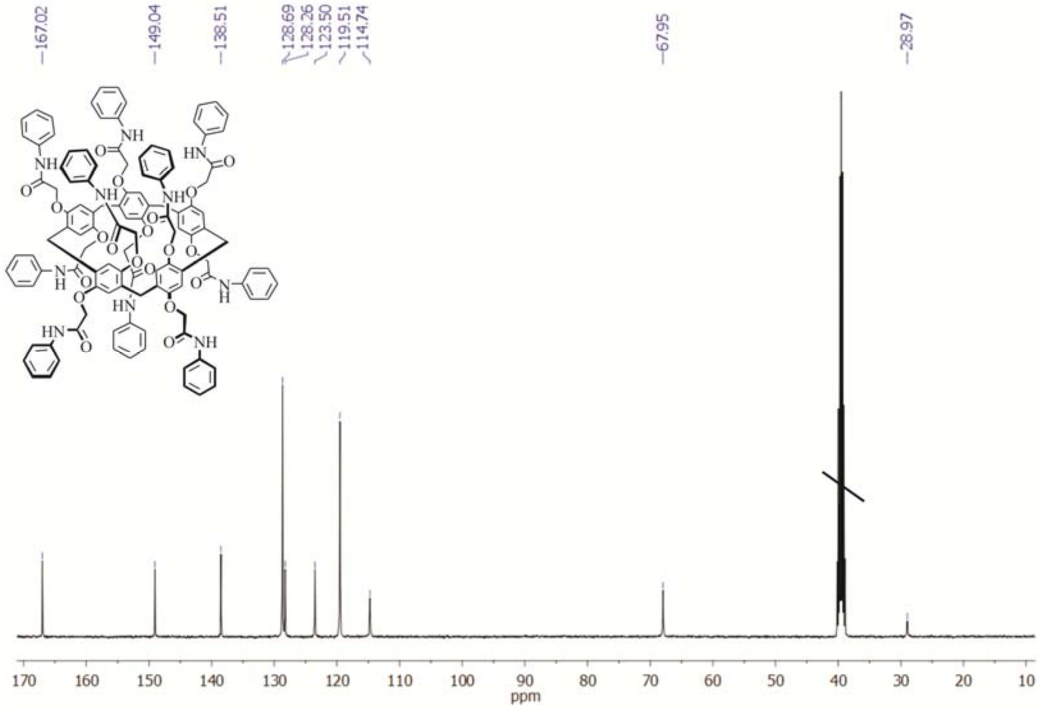

Fig. S2. ^{13}C NMR spectrum of 4,8,14,18,23,26,28,31,32,35-Deca-[(phenylamidocarbonyl)methoxy]-pillar[5]arene (**1**), DMSO- d_6, 298 K, 100 MHz

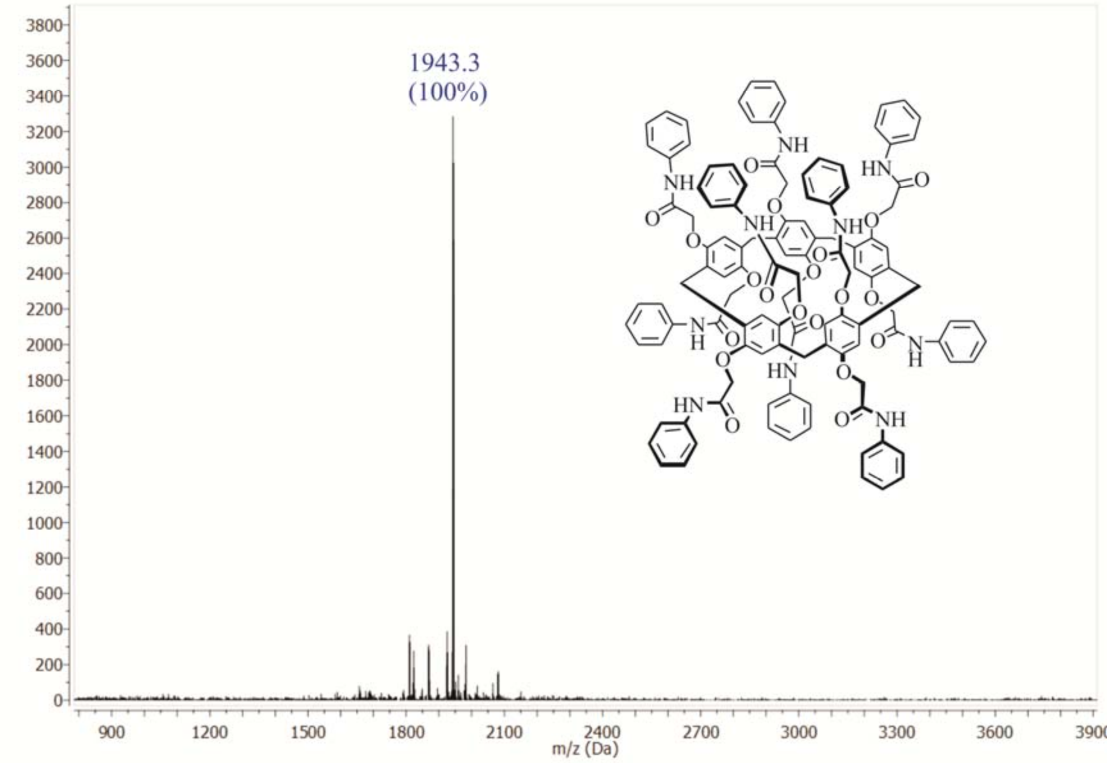

Fig. S3. Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of 4,8,14,18,23,26,28,31,32,35-Deca-[(phenylamidocarbonyl)methoxy]-pillar[5]arene (**1**).

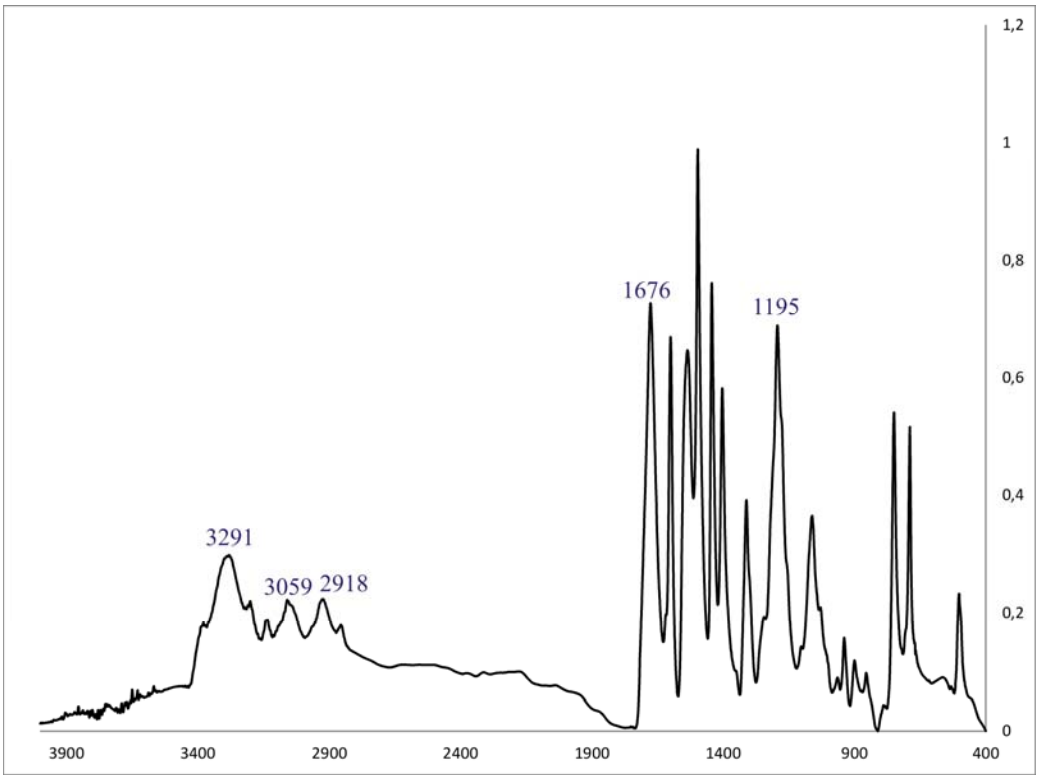

Fig. S4. IR spectrum of 4,8,14,18,23,26,28,31,32,35-Deca-[(phenylamidocarbonyl)methoxy]-pillar[5]arene (**1**).

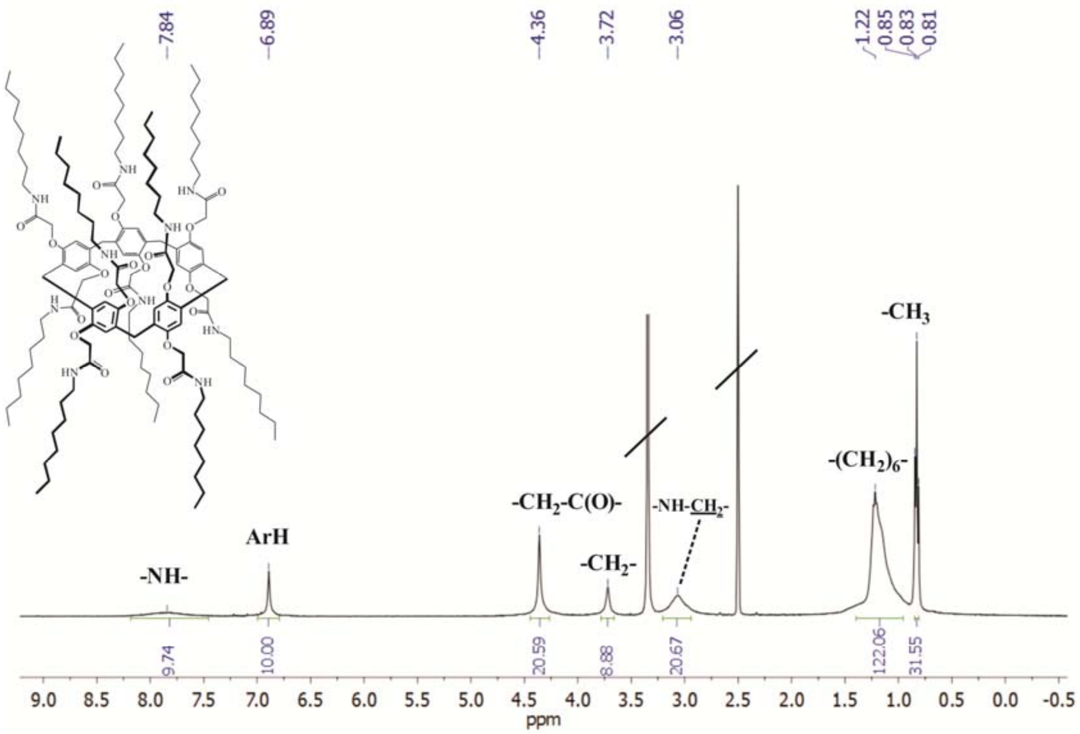

Fig. S5. ^{1}H NMR spectrum of 4,8,14,18,23,26,28,31,32,35-Deca-[(octylamidocarbonyl)methoxy]- pillar[5]arene (**2**), DMSO- d_6, 298 K, 400 MHz

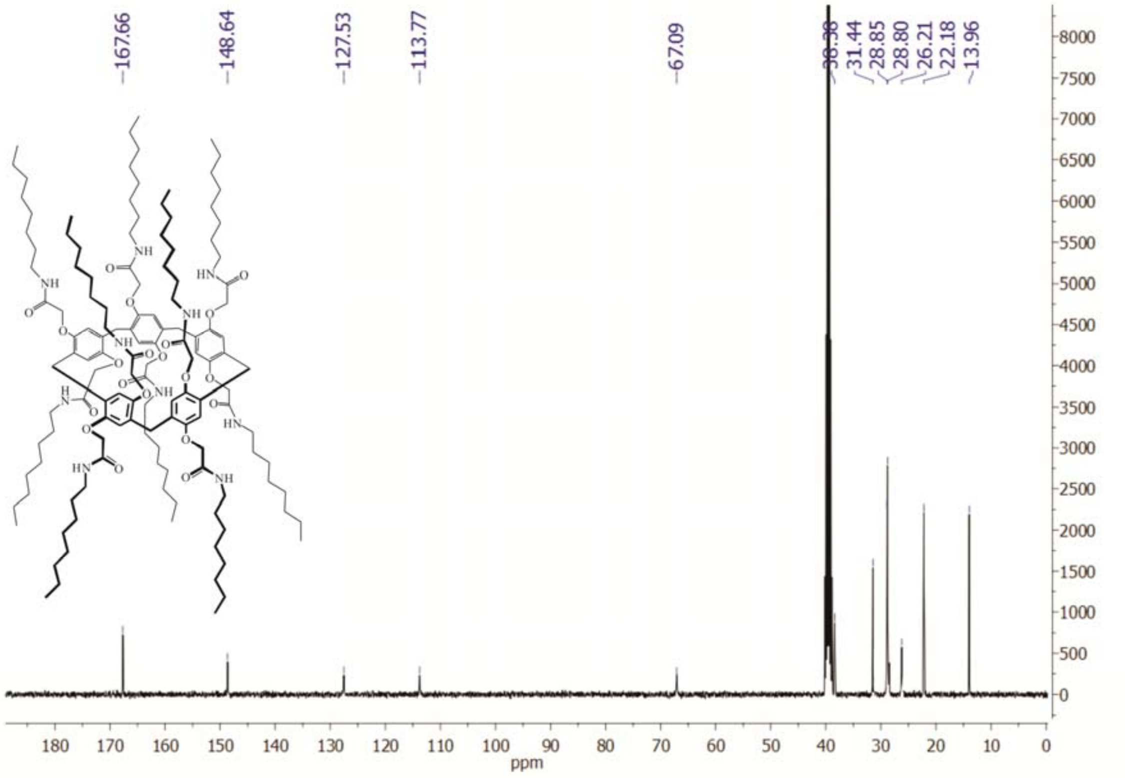

Fig. S6. ^{13}C NMR spectrum of 4,8,14,18,23,26,28,31,32,35-Deca-[(octylamidocarbonyl)methoxy]- pillar[5]arene (**2**), DMSO-d_6, 298 K, 100 MHz

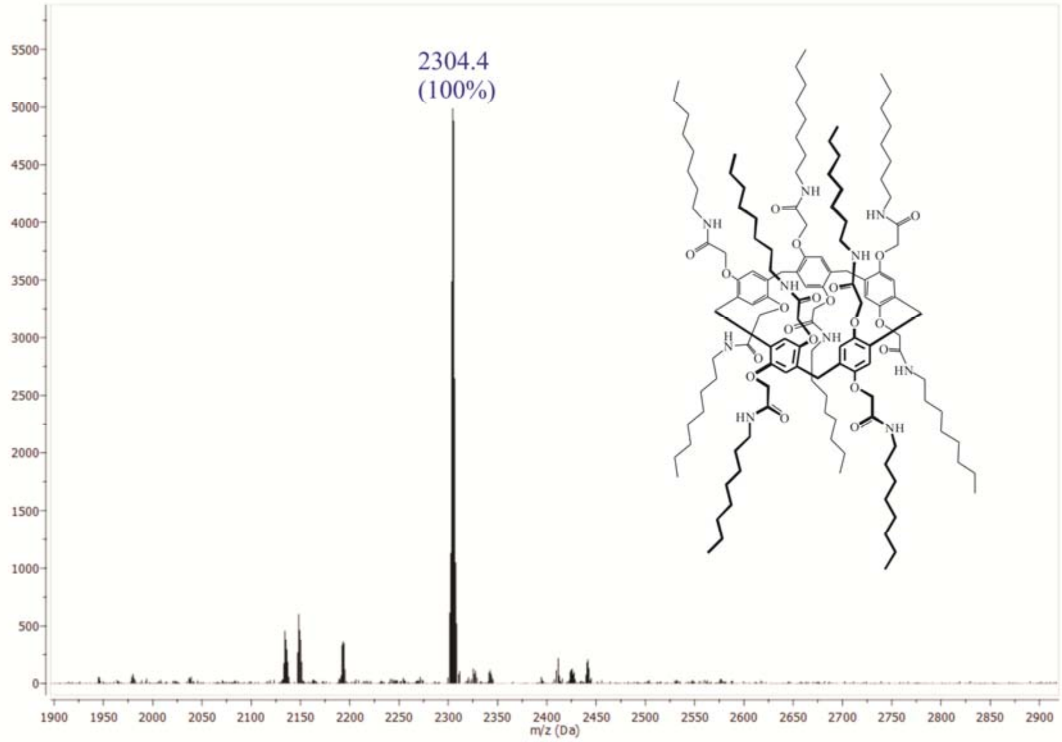

Fig. S7. Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of 4,8,14,18,23,26,28,31,32,35-Deca-[(octylamidocarbonyl)methoxy]- pillar[5]arene (**2**).

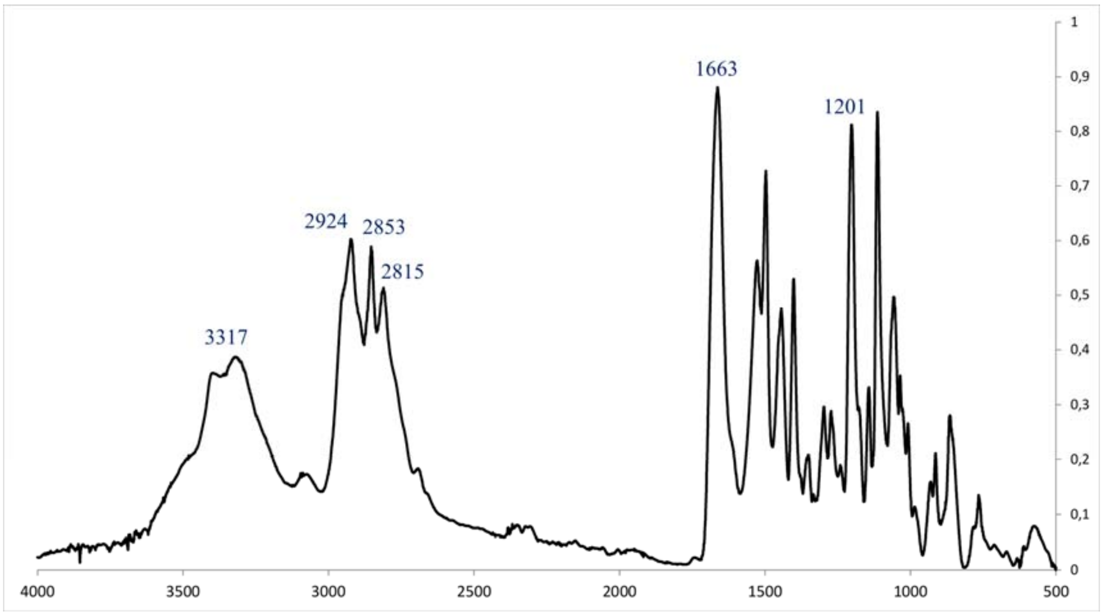

Fig. S8. IR spectrum of 4,8,14,18,23,26,28,31,32,35-Deca-[(octylamidocarbonyl)methoxy]- pillar[5]arene (**2**).

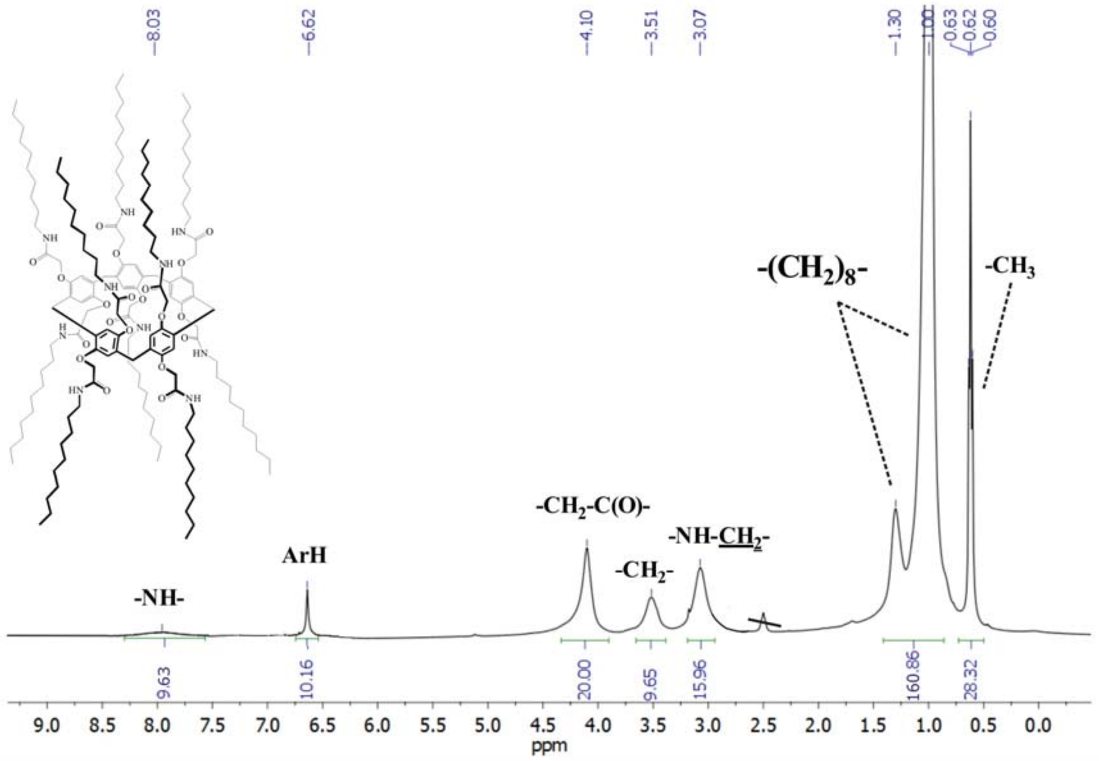

Fig. S9. ^{1}H NMR spectrum of 4,8,14,18,23,26,28,31,32,35-Deca-[(decylamidocarbonyl)methoxy]- pillar[5]arene (**3**), DMSO-d$_6$, 298 K, 400 MHz

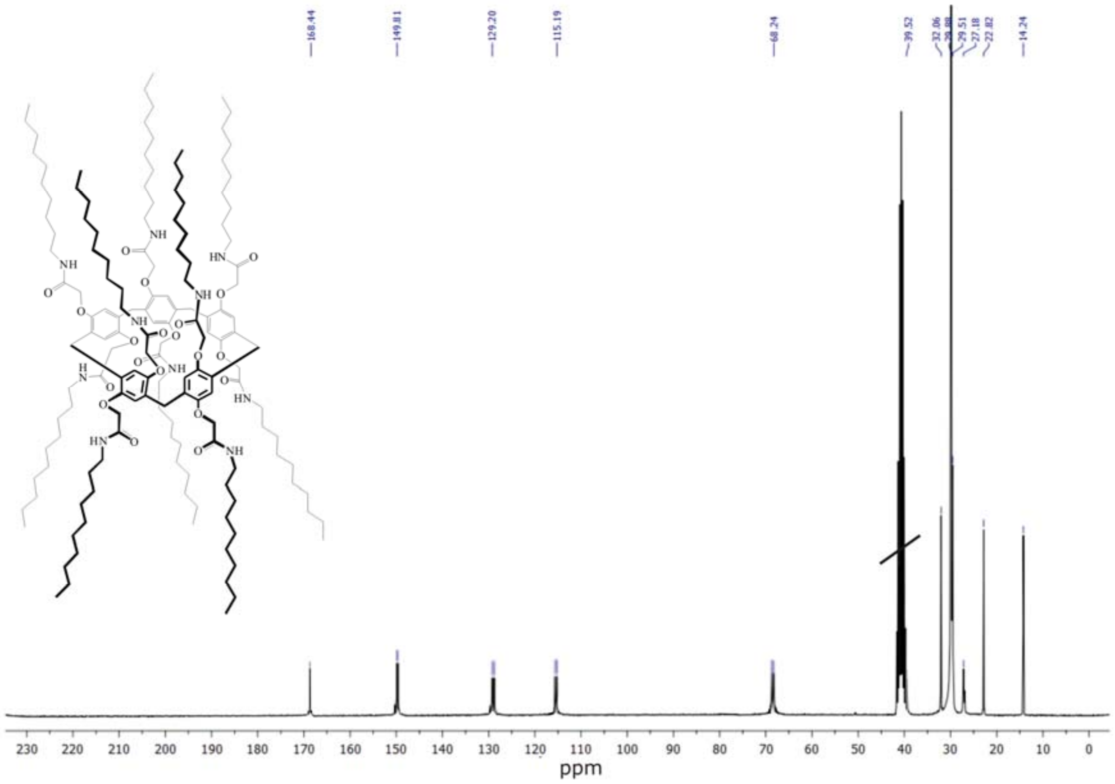

Fig. S10. ^{13}C NMR spectrum of 4,8,14,18,23,26,28,31,32,35-Deca-[(decylamidocarbonyl)methoxy]- pillar[5]arene (**3**), DMSO-d6, 298 K, 100 MHz

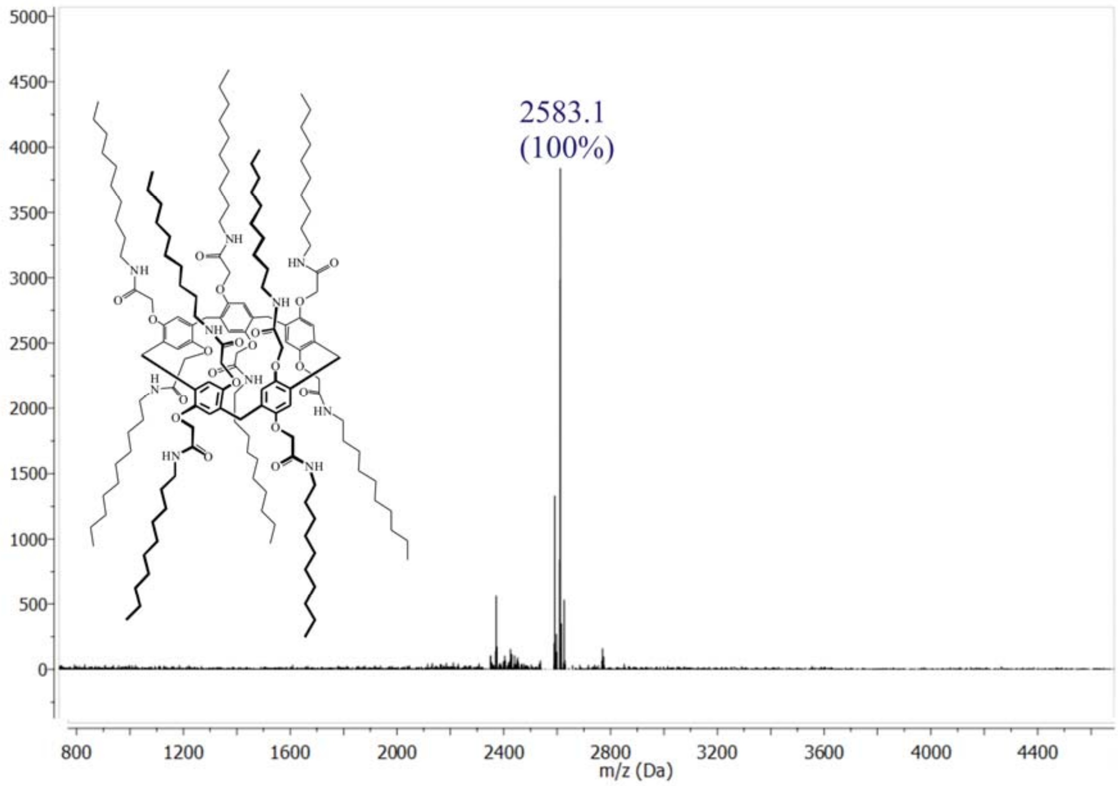

Fig. S11. Mass spectrum (MALDI-TOF, 4-nitroaniline matrix) of 4,8,14,18,23,26,28,31,32,35-Deca-[(decylamidocarbonyl)methoxy]- pillar[5]arene (**3**).

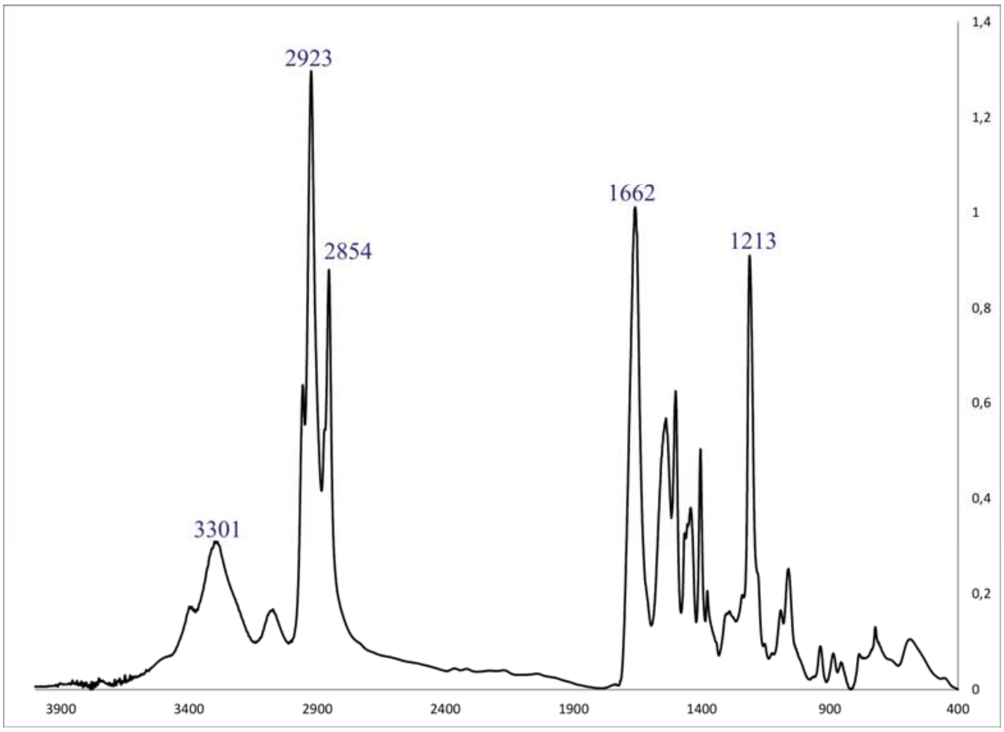

Fig. S12. IR spectrum of 4,8,14,18,23,26,28,31,32,35-Deca-[(decylamidocarbonyl)methoxy]- pillar[5]arene (**3**).

4. UV spectra for the system host/guest

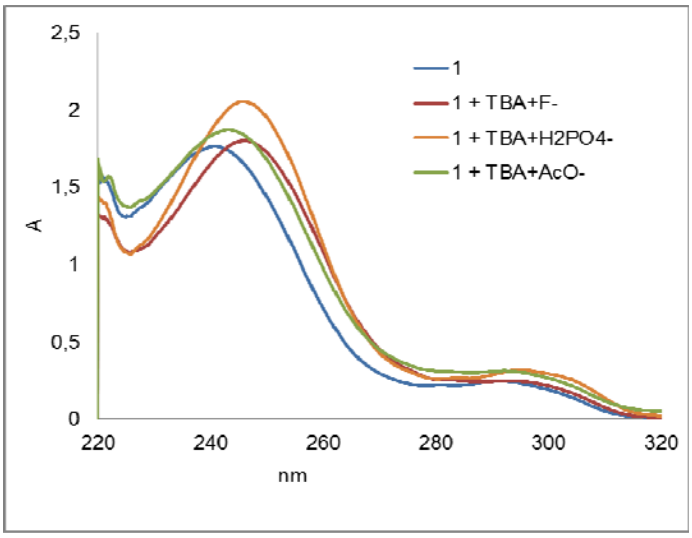

Fig. S13. UV spectra for the system host/guest

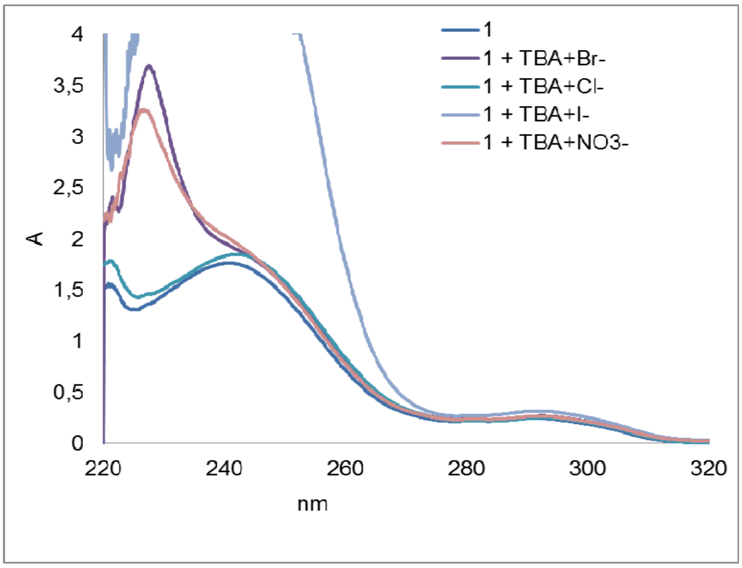

Fig. S14. UV spectra for the system host/guest

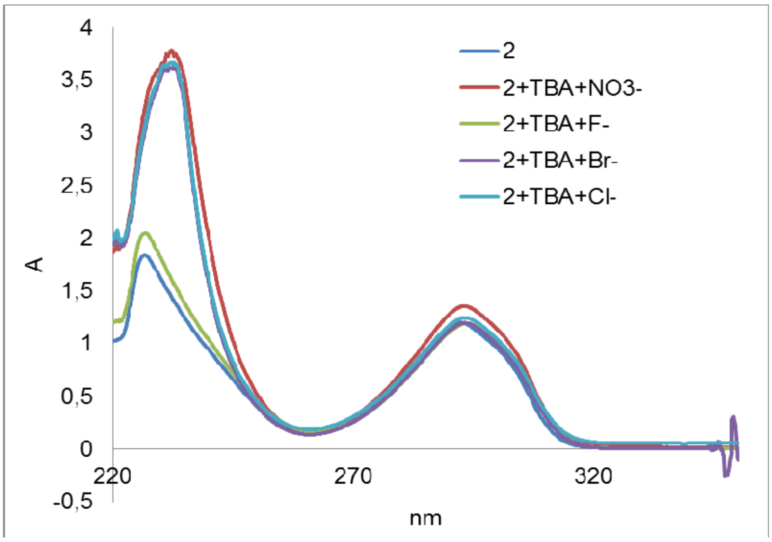

Fig. S15. UV spectra for the system host/guest

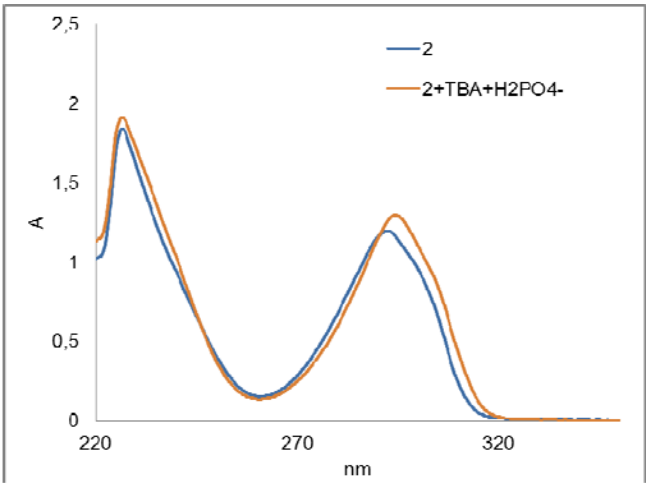

Fig. S16. UV spectra for the system host/guest

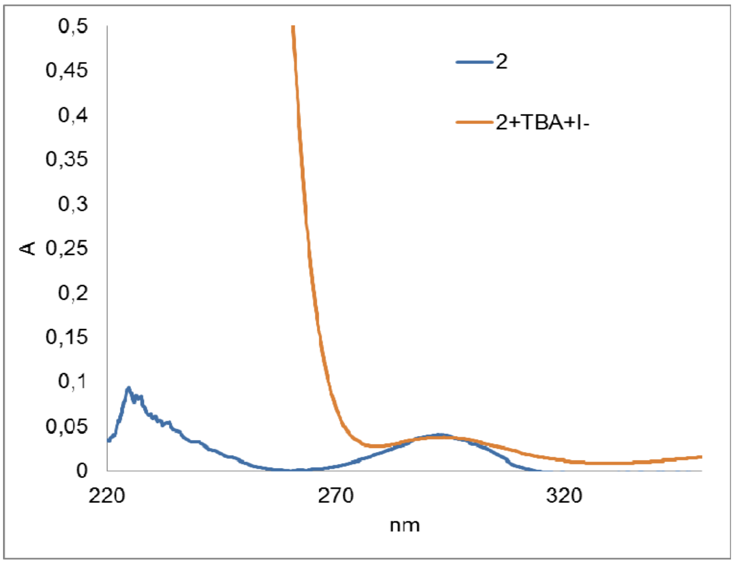

Fig. S17. UV spectra for the system host/guest

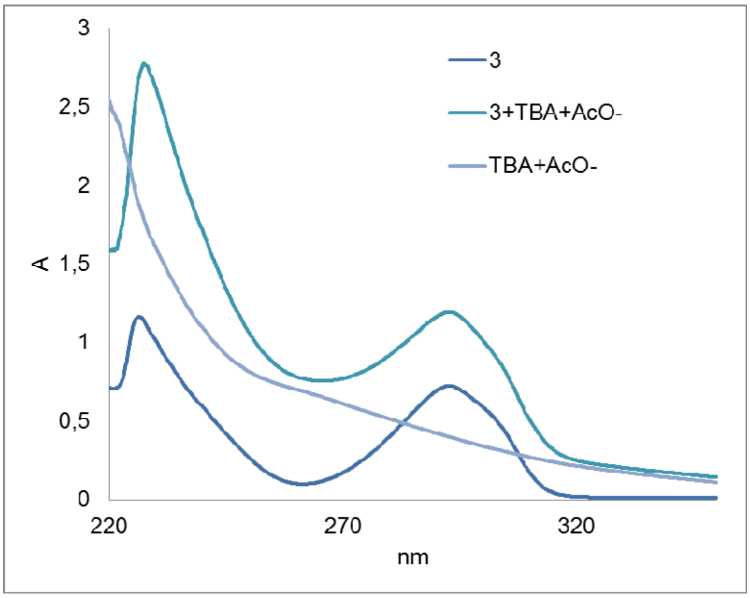

Fig. S18. UV spectra for the system host/guest

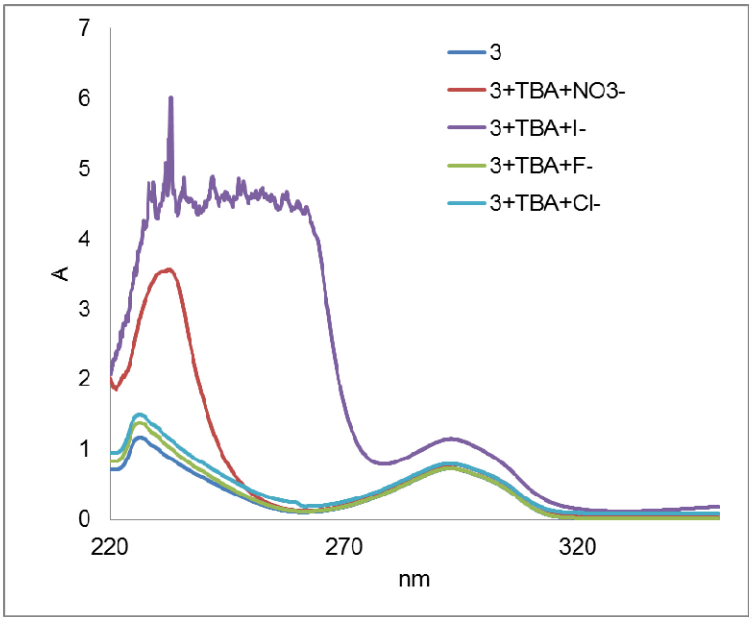

Fig. S19. UV spectra for the system host/guest

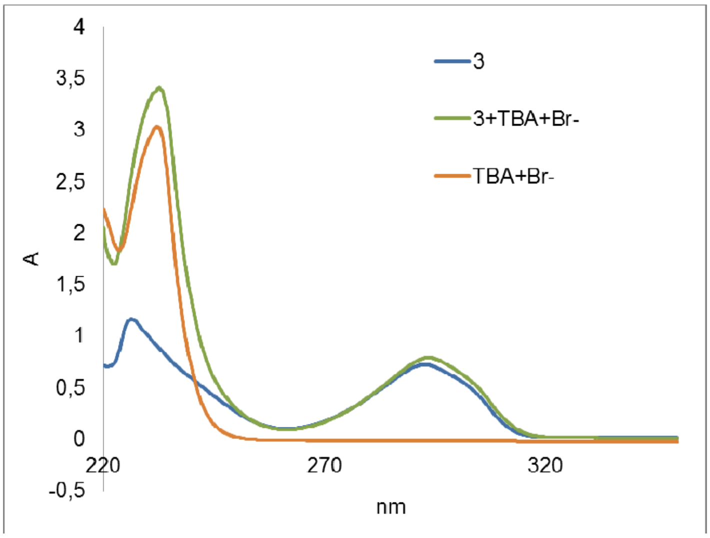

Fig. S20. UV spectra for the system host/guest

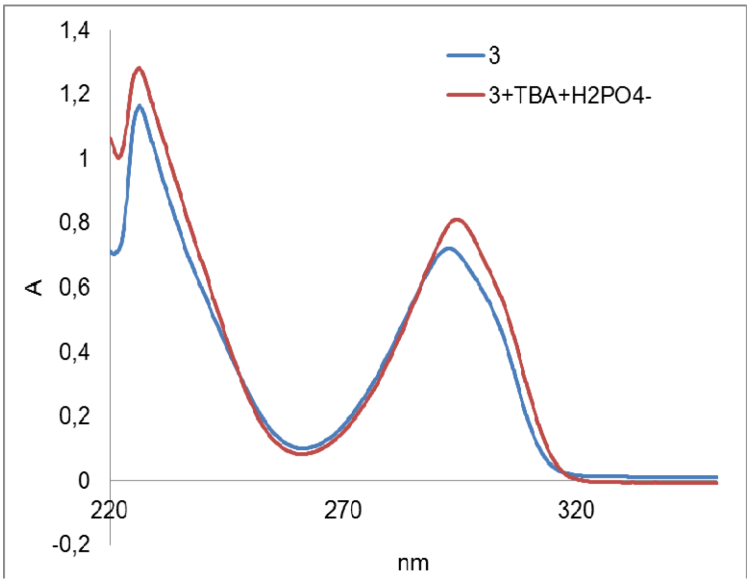

Fig. S21. UV spectra for the system host/guest

5. Determination of the stability constant and stoichiometry of the complex by the UV titration

The UV measurements were performed with “Shimadzu UV-3600” instrument. The $1 \cdot 10^{-3}$ M solution of the anion (100, 200, 300, 400, 500, 600, 70, 800, 900 and 1000 µl) in CH_2Cl_2 was added to 0.1 ml of the solution of host ($3 \cdot 10^{-4}$ M) in CH_2Cl_2 and diluted to final volume of 3 ml with water. The UV spectra of the solutions were then recorded. The stability constant and stoichiometry of complexes were calculated as described below. Three independent experiments were carried out for each series. Student’s *t*-test was applied in statistical data processing.

The system equilibrium is described by Eq. (1), where H, G, G_nH denote the macrocycles **1**-**3**, guests **anions**, complex with guests, n – number of the guest with one macrocycle.

$nG + H \Leftrightarrow G_nH$ (1)

The association constant, K_{ass}, is defined by Eq. (2).

$K_{ass} = [G_nH] / [G]^n [H]$ (2)

To determine the stoichiometry coefficient n of the complexes forming in the water Eq. (2) was converted into Eq. (3).

$\lg K_{ass} = \lg [G_nH] - n \lg [G] - \lg [H]$ (3)

The solution absorbance A, is a sum of those related to complex, host and guest (A_{GnH}, A_H and A_G, respectevly) is equal to:

$A = A_{GnH} + A_H + A_G$ (4)

Assuming that the Beer-lambert law is obeyed for all the components considered Eq. 5, the absorbance A is expressed as:

$A_i = c_i \varepsilon_i l$ (5)

where c_i is a molar concentration of i-species, ε_i is the molar absorptivity, and l is the cell thickness. For complexation between the host and guest the absorbance mesurement is commonly conducted at the wavelength of absorbance maximum in the charge-transfer region where A_G=0. This gives Eq. 6.

$A = A_{GnH} + A_H$ (6)

Concentration of the complex $[G_nH]$ in the system is calculated according to equations (5) and (6).

The plot of $\lg [G_nH] - \lg [H]$ versus $\lg [G]$ (Fig. S15) presents a straight line, slope of which equals to n. Assotiation constants K_{ass} are calculated using the intercept values (b).

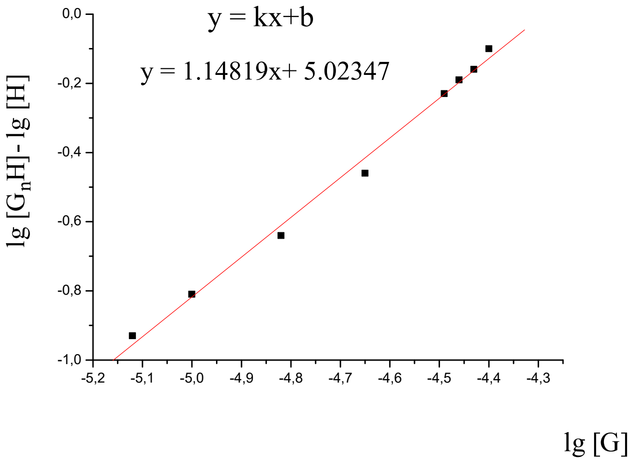

Fig. S22. Plot of lg [G_nH]- lg [H] versus lg [G] host/guest system.

$$b = \lg K_{ass} \qquad (7)$$

6. The Job's plot for the determination of the stoichiometry

Job Plots

Series of the solutions of pillar[5]arene derivatives **1-3** and anions were prepared in water. The volume of the host and guest solutions varied from 0.6:2.4 to 2.4:0.6, respectively, with the total concentration of the host (H) and guest (G) being constant and equal to $1\cdot10^{-5}$ M. The solutions were used without further stirring. The absorbance A_i of the complexation systems was measured at the maximum absorbance wavelength for the complex. The absorbance values were used to plot a diagram from which maximum the structures of the complexes were deduced. Three independent experiments were carried out for each system.

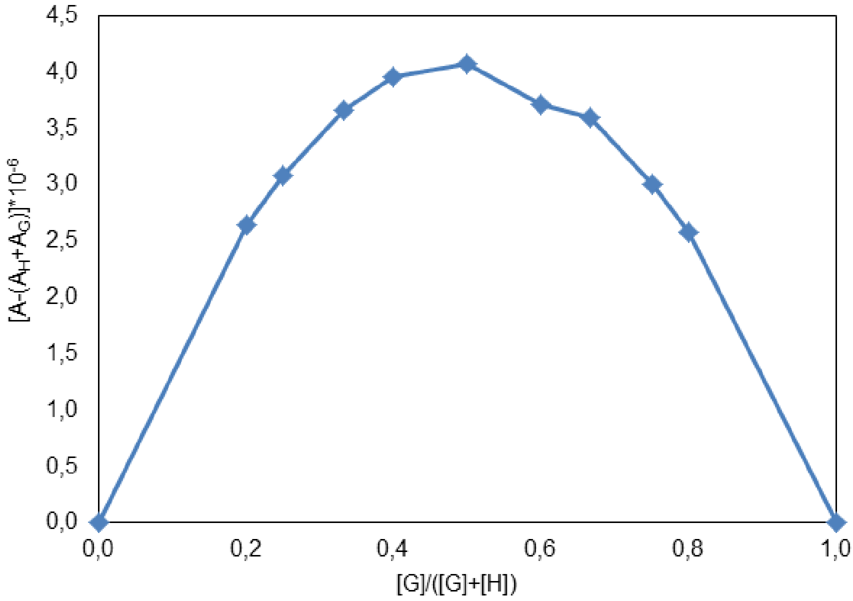

Fig. S23. The Job' s plot for the determination of the stoichiometry in the complex of the systems pillar[5]arene **1** and TBA^+F^- in CH_2Cl_2

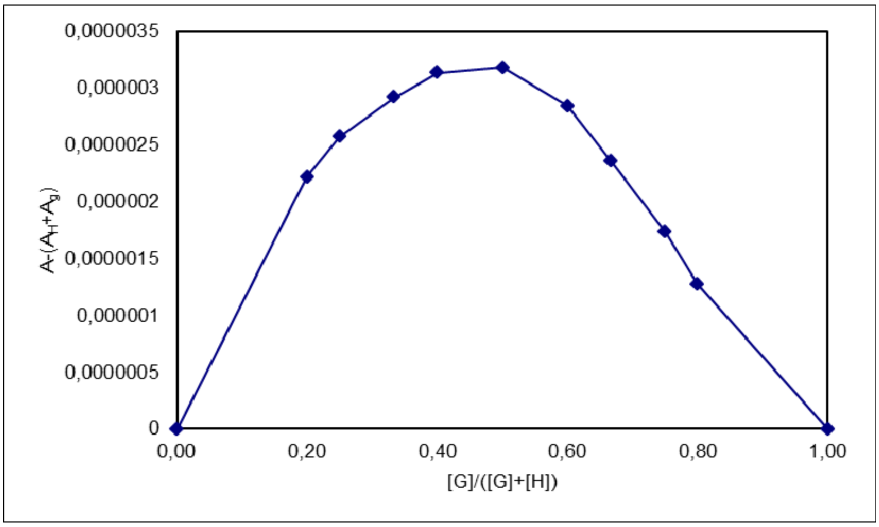

Fig. S24. The Job' s plot for the determination of the stoichiometry in the complex of the systems pillar[5]arene **1** and TBA^+AcO^- in CH_2Cl_2

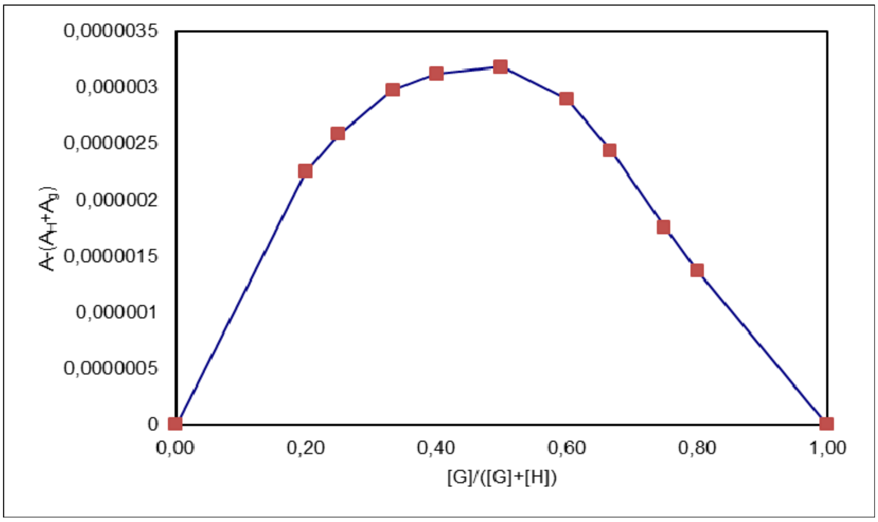

Fig. S25. The Job’s plot for the determination of the stoichiometry in the complex of the systems pillar[5]arene **1** and TBA$^+$H$_2$PO$_4^-$ in CH$_2$Cl$_2$

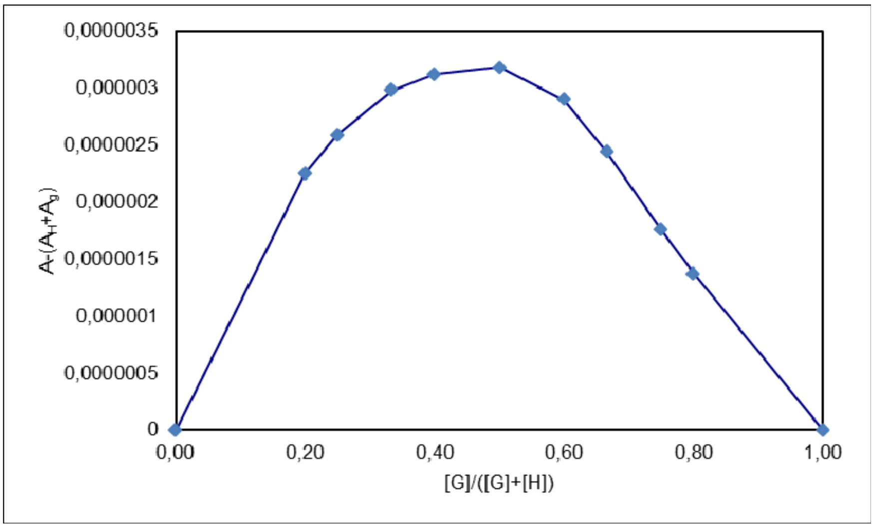

Fig. S26. The Job’s plot for the determination of the stoichiometry in the complex of the systems pillar[5]arene **2** and TBA$^+$H$_2$PO$_4^-$ in CH$_2$Cl$_2$

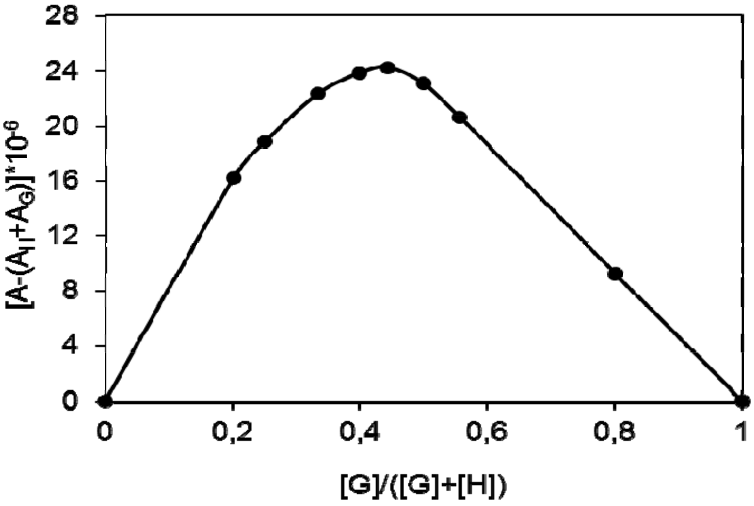

Fig. S27. The Job’s plot for the determination of the stoichiometry in the complex of the systems pillar[5]arene **3** and TBA$^+$H$_2$PO$_4^-$ in CH$_2$Cl$_2$

7. ^{1}H NMR spectra for host–guest complexes in solution

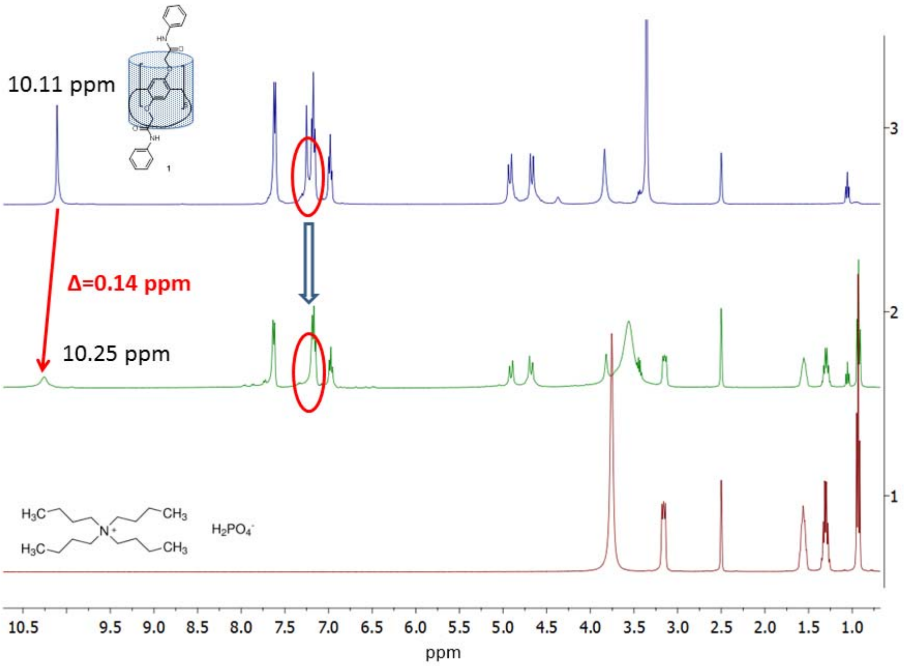

Fig. S28. ^{1}H NMR spectra of initial pillar[5]arene **1** and host/guest system for **1** and $TBA^+H_2PO_4^-$ (1:1) (DMSO-d_6, 25 °C, 400 *MHz*).

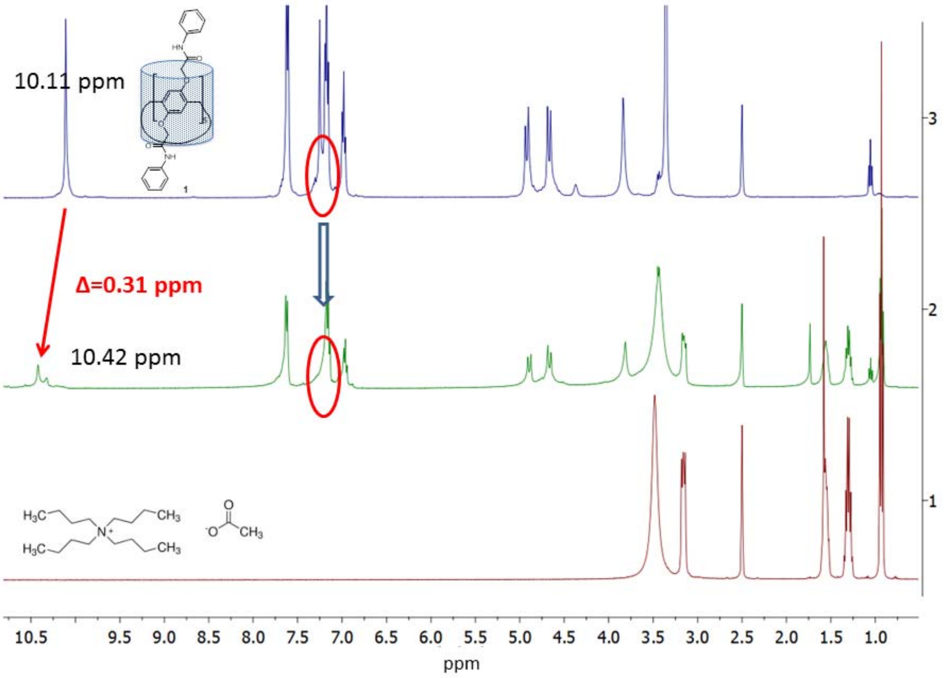

Fig. S29. ^{1}H NMR spectra of initial pillar[5]arene **1** and host/guest system for **1** and TBA^+AcO^- (1:1) (DMSO-d_6, 25 °C, 400 *MHz*).

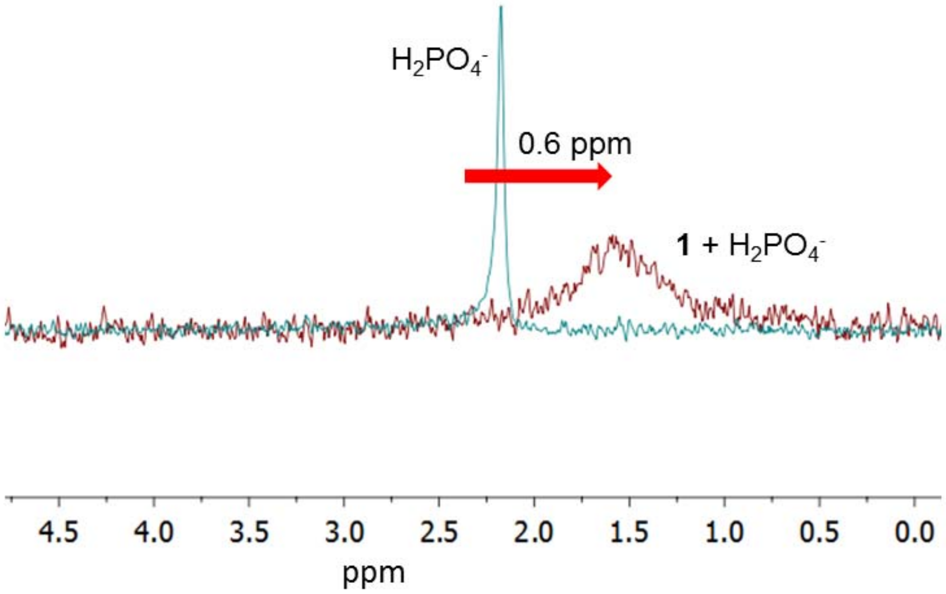

Fig. 30 ^{31}H NMR spectrum of initial pillar[5]arene **1** and host/guest system for **1** and TBA$^+$H$_2$PO$_4^-$ (1:1) (DMSO-d_6, 25 °C, 162 *MHz*).

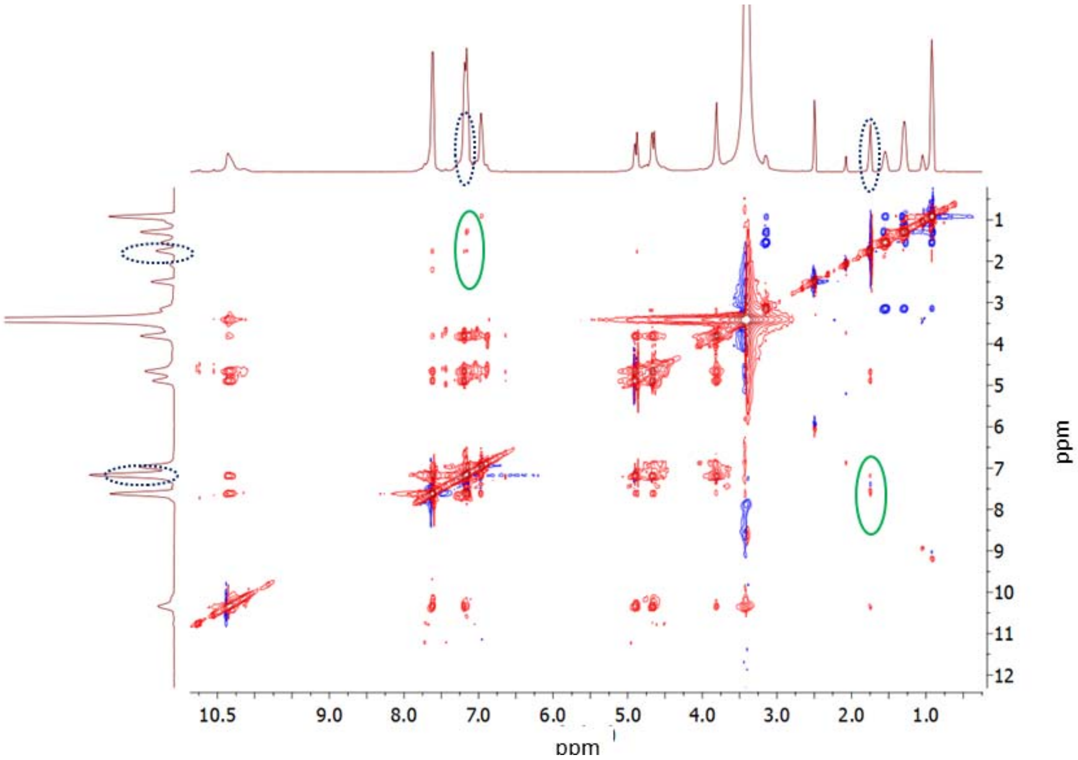

Fig. S31. 2D NOESY (500 MHz) analysis of **1** with TBA$^+$AcO$^-$ in DMSO-d_6. The concentrations of the host and the guest are 0.0112 M

9. References

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