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Monoaminophosphorylated Pillar[5]arenes as Hosts for Alkaneamines

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Electronic Supplementary Information (98 pages)





Fig. S2. ¹H NMR spectrum of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-hydroxypillar[5]arene (2), CDCl₃, 298 K, 400 MHz.



Fig. S3. ¹H NMR spectrum of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-(3'-phthalimidepropoxy)-pillar[5]arene (3), CDCl₃, 298 K, 400 MHz.



Fig. S4. ¹H NMR spectrum of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-(3'-aminopropoxy)-pillar[5]arene (4), DMSO-d₆, 298K, 400 MHz.



Fig. S5. ¹H NMR spectrum of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-methylethyl]-(3'-aminopropoxy}-pillar[5]arene (5), CDCl₃, 298 K, 400 MHz.



Fig. S6. ¹H NMR spectrum of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-cyclopentyl]-(3'-aminopropoxy}-pillar[5]arene (6), CDCl₃, 298 K, 400 MHz.



Fig. S7. ¹H NMR spectrum 4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-cyclohexyl]-(3'-aminopropoxy}-pillar[5]arene (7), CDCl₃, 298 K, 400 MHz.



Fig. S8. ${}^{31}P{}^{1}H$ NMR spectrum of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-methylethyl]-(3'-aminopropoxy}-pillar[5]arene (5), CDCl₃, 298 K, 162 MHz.



Fig. S9. ${}^{31}P{}^{1}H$ NMR spectrum of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-cyclopentyl]-(3'-aminopropoxy}-pillar[5]arene (6), CDCl₃, 298 K, 162 MHz.



Fig. S10. ³¹P{¹H} NMR spectrum 4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-cyclohexyl]-(3'-aminopropoxy}-pillar[5]arene (7), CDCl₃, 298 K, 162 MHz.



62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 ppm

Fig. S11. ¹³C NMR spectrum of4,8,14,18,23,26,28,31,32-nonamethoxy-35-(3'-phthalimidepropoxy)-pillar[5]arene (3), CDCl₃, 298 K, 100 MHz.



Fig. S12. ¹³C NMR spectrum of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-(3'-aminopropoxy)-pillar[5]arene (4), DMSO-d₆, 298 K, 100 MHz.



Fig. S13. ¹³C NMR spectrum of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-methylethyl]-(3'-aminopropoxy}-pillar[5]arene (5), DMSO-d₆, 298 K, 100 MHz.



Fig. S14. ¹³C NMR spectrum of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-cyclopentyl]-(3'-aminopropoxy}-pillar[5]arene (6), CDCl₃, 298 K, 100 MHz.



Fig. S15. ¹³C NMR spectrum of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-cyclohexyl]-(3'-aminopropoxy}-pillar[5]arene (7), DMSO-d₆, 298 K, 100 MHz.





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m/z (Da)

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ես Միհան

ان بالأراسين

ببالاسل بتعديد

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Fig. S16. Mass spectrum (MALDI-TOF) of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-(3'-phthalimidepropoxy)-pillar[5]arene (3).

Fig. S17. Mass spectrum (MALDI-TOF) of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-(3'-aminopropoxy)-pillar[5]arene (4).



Fig. S18. Mass spectrum (ESI) of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-methylethyl]-(3'-aminopropoxy}-pillar[5]arene (5).





Fig. S19. Mass spectrum (ESI) of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-cyclopentyl]-(3'-aminopropoxy}-pillar[5]arene (6).



Fig. S20. Mass spectrum (ESI) of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-cyclohexyl]-(3'-aminopropoxy}-pillar[5]arene (7).



Fig. S21. IR spectrum of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-(3'-phthalimidepropoxy)-pillar[5]arene (3).



Fig. S22. IR spectrum of 4, 8, 14, 18, 23, 26, 28, 31, 32-nonamethoxy-35-(3'-aminopropoxy)-pillar [5] arene (4).

Fig. S23. IRspectrum4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-methylethyl]-(3'-aminopropoxy}-pillar[5]arene (5).







Fig. S25. IR spectrum of 4,8,14,18,23,26,28,31,32-nonamethoxy-35-{N-[1-(O,O-diethylphosphoryl)-1-cyclohexyl]-(3'-aminopropoxy}-pillar[5]arene (7).



Fig. S26. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) isopropylamine (G1) (0.01 M); b) isopropylamine (G1) (0.01 M) + 4 (0.01 M); c) 4 (0.01 M).



Fig. S27. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) benzylamine (G2) (0.01 M); b) benzylamine (G2) (0.01 M) + 4 (0.01 M); c) 4 (0.01 M).



7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 ppm



Fig. S28. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) octylamine (G3) (0.01 M); b) octylamine (G3) (0.01 M) + 4 (0.01 M); c) 4 (0.01 M).

Fig. S29. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) dodecylamine (G4) (0.01 M); b) dodecylamine (G4) (0.01 M) + 4 (0.01 M); c) 4 (0.01 M).



7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 ppm

Fig. S30. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) octadecylamine (G5) (0.01 M); b) octadecylamine (G5) (0.01 M) + 4 (0.01 M); c) 4 (0.01 M).



Fig. S31. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) isopropylamine (G1) (0.01 M); b) isopropylamine (G1) (0.01 M) + 5 (0.01 M); c) 5 (0.01 M).



7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 ppm

Fig. S32. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) benzylamine (G2) (0.01 M); b) benzylamine (G2) (0.01 M) + 5 (0.01 M); c) 5 (0.01 M).



7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 ppm

Fig. S33. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) octylamine (G3) (0.01 M); b) octylamine (G3) (0.01 M) + 5 (0.01 M); c) 5 (0.01 M).



7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 ppm

Fig. S34. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) dodecylamine (G4) (0.01 M); b) dodecylamine (G4) (0.01 M) + 5 (0.01 M); c) 5 (0.01 M).



Fig. S35. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) octadecylamine (G5) (0.01 M); b) octadecylamine (G5) (0.01 M) + 5 (0.01 M); c) 5 (0.01 M).



7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 ppm
Fig. S36. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) isopropylamine (G1) (0.01 M); b) isopropylamine (G1) (0.01 M) + 6 (0.01 M); c) 6 (0.01 M).



Fig. S37. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) benzylamine (G2) (0.01 M); b) benzylamine (G2) (0.01 M) + 6 (0.01 M); c) 6 (0.01 M).



Fig. S38. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) octylamine (G3) (0.01 M); b) octylamine (G3) (0.01 M) + 6 (0.01 M); c) 6 (0.01 M).



Fig. S39. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) dodecylamine (G4) (0.01 M); b) dodecylamine (G4) (0.01 M) + 6 (0.01 M); c) 6 (0.01 M).



7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 ppm

Fig. S40. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) octadecylamine (G5) (0.01 M); b) octadecylamine (G5) (0.01 M) + 6 (0.01 M); c) 6 (0.01 M).



7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 ppm

Fig. S41. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) isopropylamine (G1) (0.01 M); b) isopropylamine (G1) (0.01 M) + 7 (0.01 M); c) 7 (0.01 M).



7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 ppm

Fig. S42. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) benzylamine (G2) (0.01 M); b) benzylamine (G2) (0.01 M) + 7 (0.01 M); c) 7 (0.01 M).



7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 ppm

Fig. S43. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) octylamine (G3) (0.01 M); b) octylamine (G3) (0.01 M) + 7 (0.01 M); c) 7 (0.01 M).



Fig. S44. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) dodecylamine (G4) (0.01 M); b) dodecylamine (G4) (0.01 M) + 7 (0.01 M); c) 7 (0.01 M).



7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 ppm

Fig. S45. ¹H NMR spectra (CDCl₃, 293 K, 400 MHz): a) octadecylamine (G5) (0.01 M); b) octadecylamine (G5) (0.01 M) + 7 (0.01 M); c) 7 (0.01 M).





Fig. S46. 2D NMR NOESY ¹H-¹H spectra for (4), CDCl₃, 293 K, 400 MHz.



Fig. S47. 2D NMR NOESY ¹H-¹H spectra for (5), CDCl₃, 293 K, 400 MHz.



Fig. S48. 2D NMR NOESY ¹H-¹H spectra for (6), CDCl₃, 293 K, 400 MHz.



Fig. S49. 2D NMR NOESY ¹H-¹H spectra for (7), CDCl₃, 293 K, 400 MHz.



Fig. S50. 2D NMR NOESY ¹H-¹H spectra for isopropylamine (G1) (0.01 M) + 5 (0.01 M), CDCl₃, 293 K, 400 MHz.



Fig. S51. 2D NMR NOESY ¹H-¹H spectra for benzylamine (G2) (0.01 M) + 5 (0.01 M), CDCl₃, 293 K, 400 MHz.



Fig. S52. 2D NMR NOESY ¹H-¹H spectra for octylamine (G3) (0.01 M) + 5 (0.01 M), CDCl₃, 293 K, 400 MHz.



Fig. S53. 2D NMR NOESY ¹H-¹H spectra for dodecylamine (G4) (0.01 M) + 5 (0.01 M), CDCl₃, 293 K, 400 MHz.









mdd









bpm





mdd



Fig. S59. 2D NMR NOESY ¹H-¹H spectra for octadecylamine (G5) (0.01 M) + 6 (0.01 M), CDCl₃, 293 K, 400 MHz.



Fig. S60. 2D NMR NOESY ¹H-¹H spectra for isopropylamine (G1) (0.01 M) + 7 (0.01 M), CDCl₃, 293 K, 400 MHz.



Fig. S61. 2D NMR NOESY ¹H-¹H spectra for benzylamine (G2) (0.01 M) + 7 (0.01 M), CDCl₃, 293 K, 400 MHz.



Fig. S62. 2D NMR NOESY ¹H-¹H spectra for octylamine (G3) (0.01 M) + 7 (0.01 M), CDCl₃, 293 K, 400 MHz.





mdd



Fig. S64. 2D NMR NOESY ¹H-¹H spectra for octadecylamine (G5) (0.01 M) + 7 (0.01 M), CDCl₃, 293 K, 400 MHz.



Fig. S65. Size distribution of self-assembles of macrocycle 4 in chloroform (3·10⁻⁴M).

Fig. S66. UV spectra of mixtures of the macrocycle 5 with the aliphatic amines, taken in molar ratio 1:30 and spectra of individual components in the concentration studied.





Fig. S67. UV spectra of mixtures of the macrocycle 5 with the benzylamine, taken in molar ratio 1:30 and spectra of individual components in the concentration studied.

Fig. S68. UV spectra of mixtures of the macrocycle 6 with the aliphatic amines, taken in molar ratio 1:30 and spectra of individual components in the concentration studied.



Fig. S69. UV spectra of mixtures of the macrocycle 6 with the benzylamine, taken in molar ratio 1:30 and spectra of individual components in the concentration studied.



Fig. S70. UV spectra of mixtures of the macrocycle 7 with the aliphatic amines, taken in molar ratio 1:30 and spectra of individual components in the concentration studied.



Fig. S71. UV spectra of mixtures of the macrocycle 7 with the benzylamine, taken in molar ratio 1:30 and spectra of individual components in the concentration studied.


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

 $1 \cdot 10^{-3}$ M solution of amines G1, G3-G5 (120, 150, 200, 250, 300, 350, 400, 450, 500, and 550 µL) in CHCl₃ was added to 0.1 ml of the solution of receptors 5-7 ($3 \cdot 10^{-4}$ M) in CHCl₃ and diluted to final volume of 3 mL with CHCl₃. The UV spectra of the solutions were recorded. 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 5-7, guests G1, G3-G5, complex with guests, respectively, n – number of the guest is bound 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).

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

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

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

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

 $A_i = c_i \varepsilon_i l \qquad (5)$

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. Association constants K_{ass} are calculated using the intercept values (b).

Fig. S72. Plot of lg [GnH]- lg [H] versus lg [G] host/guest system.



 $b = \lg K_a \qquad (7)$













Fig. S76. The spectrophotometric titration of the system pillar[5]arene 5 and guest G3 in CHCl₃.



Fig. S77. The spectrophotometric titration of the system pillar[5]arene 6 and guest G3 in CHCl₃.



Fig. S78. The spectrophotometric titration of the system pillar[5]arene 7 and guest G3 in CHCl₃.



Fig. S79. The spectrophotometric titration of the system pillar[5]arene 5 and guest G4 in CHCl₃.



Fig. S80. The spectrophotometric titration of the system pillar[5]arene 6 and guest G4 in CHCl₃.



Fig. S81. The spectrophotometric titration of the system pillar[5]arene 7 and guest G4 in CHCl₃.



Fig. S82. The spectrophotometric titration of the system pillar[5]arene 5 and guest G5 in CHCl₃.













Fig. S85. The Job's plot for the determination of the stoichiometry in the complex of the system pillar[5] arene 5 and G1 in CHCl₃.



Fig. S86. The Job's plot for the determination of the stoichiometry in the complex of the system pillar[5] arene 5 and G3 in CHCl3.

Fig. S87. The Job's plot for the determination of the stoichiometry in the complex of the system pillar[5]arene 5 and G4 in CHCl₃.





Fig. S88. The Job's plot for the determination of the stoichiometry in the complex of the system pillar[5] arene 5 and G5 in CHCl₃.



Fig. S89. The Job's plot for the determination of the stoichiometry in the complex of the system pillar[5] arene 6 and G1 in CHCl₃.

Fig. S90. The Job's plot for the determination of the stoichiometry in the complex of the system pillar[5]arene 6 and G3 in CHCl₃.









Fig. S92. The Job's plot for the determination of the stoichiometry in the complex of the system pillar[5] arene 6 and G5 in CHCl₃.



Fig. S93. The Job's plot for the determination of the stoichiometry in the complex of the system pillar[5] arene 7 and G1 in CHCl₃.



Fig. S94. The Job's plot for the determination of the stoichiometry in the complex of the system pillar[5] arene 7 and G3 in CHCl₃.



Fig. S95. The Job's plot for the determination of the stoichiometry in the complex of the system pillar[5] arene 7 and G4 in CHCl₃.



Fig. S96. The Job's plot for the determination of the stoichiometry in the complex of the system pillar[5]arene 7 and G5 in CHCl₃.