Electronic Supplementary Information

Cyclen-based bismacrocycles for biological anion recognition. A potentiometric and NMR study of AMP, ADP and ATP nucleotide complexation.

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Figure 1: Species distribution diagrams for the ***BMC*** and ***BPyC*** ligands as a function of p[H] (H_2O ; I = 0.1 M (NaCl) ; T = 25.0±0.2°C ; $[L]_{tot} = 10^{-3}$ M)

Figure 2: Species distribution diagrams for substrates (*H_2O; I = 0.1 M (NaCl) ; T = 25.0±0.2°C ; $[Anion]_{tot} = 10^{-3}$ M*)

Table 1: Logarithm recognition constants, log K_{alh}, for the two bismacrocycles with AMP, ADP and ATP (*I* = 0.1 M (NaCl); T = 25°C).

Table 2: Logarithm recognition constants, log K_{alh}, for the two bismacrocycles with inorganic phosphates: orthophosphate, pyrophosphate, triphosphate (*I* = 0.1 M (NaCl); T = 25°C).

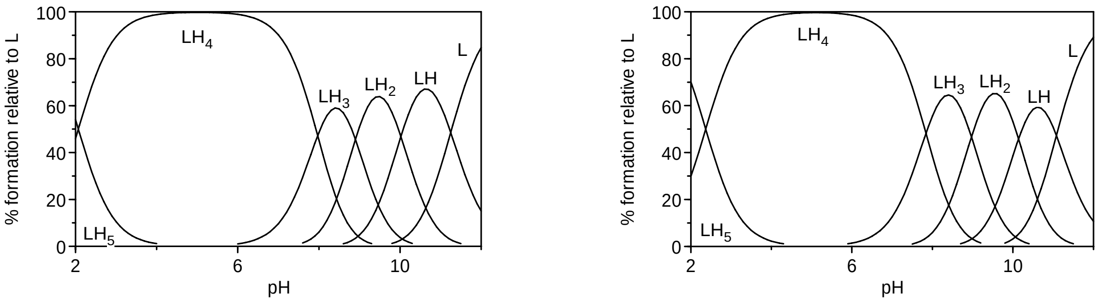
Figure 3: Species distribution diagrams for ***AMP*** with (a) ***BMC*** and (b) ***BPyC*** as a function of p[H]

Figure 4: Species distribution diagrams for ***ADP*** with (a) ***BMC*** and (b) ***BPyC*** as a function of p[H]

Figure 5: Species distribution diagrams for ***ATP*** with (a) ***BMC*** and (b) ***BPyC*** as a function of p[H]

Figure 6: Experimental ^{1}H chemical shifts for the proton of the ***BMC***: ligand free and in presence of triphosphate.

Figure 7: Experimental ^{1}H chemical shifts for the proton of the ***BPyC***: ligand free and in presence of triphosphate.



BMC ***BPyC***

Figure 1: Species distribution diagrams for the ***BMC*** and ***BPyC*** ligands as a function of p[H] (H_2O ; I = 0.1 M (NaCl) ; T = 25.0±0.2°C ; $[L]_{tot} = 10^{-3}$ M)

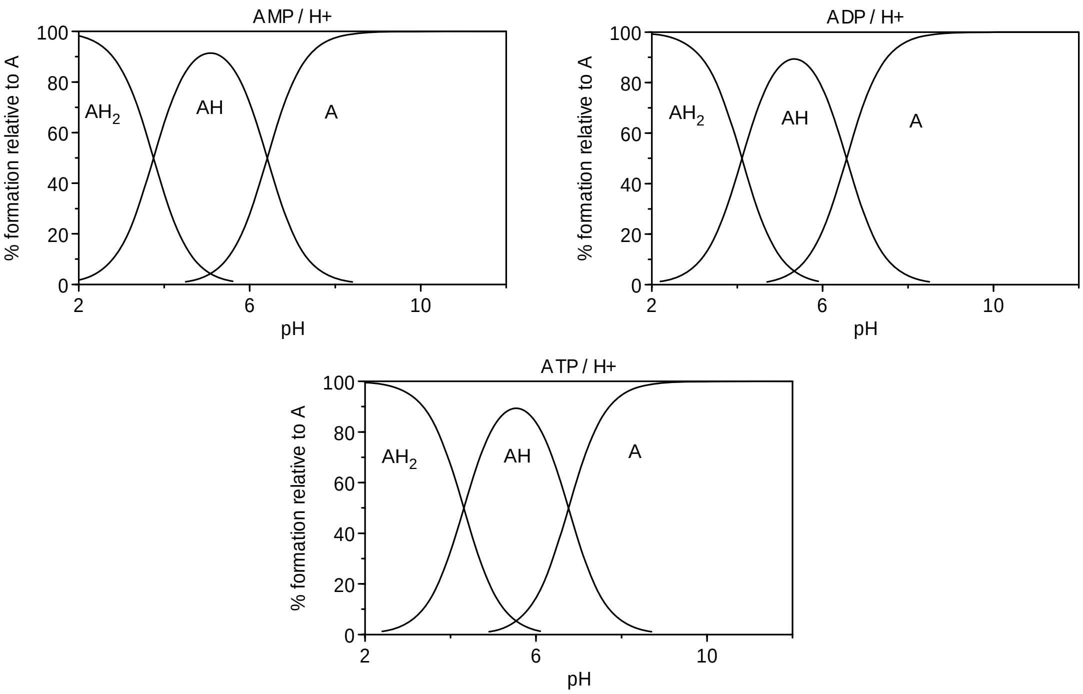


Figure 2: Species distribution diagrams for substrates
H_2O ; I = 0.1 M (NaCl) ; T = 25.0±0,2°C ; $[Anion]_{tot} = 10^{-3}$ M

Table 1: Logarithm recognition constants, log K_{alh}, for the two bismacrocycles with AMP, ADP and ATP (I = 0.1 M (NaCl); T = 25°C).

BMC	**AMP**	**ADP**	**ATP**
A+L =AL			
A+L+H = ALH A+LH = ALH			
A+L+2H=ALH_2 A+LH_2=ALH_2	24.45 3.18	23.71 2.44	
A+L+3H=ALH_3 A+LH_3=ALH_3	33.62(9.17) 3.45	32.76(9.05) 2.59	33.13 2.98
A+L+4H=ALH_4 A+LH_4=ALH_4	42.05(8.43) 3.91	41.44(8.68) 3.30	41.87(8.74) 3.73
A+L+5H=ALH_5 A+LH_5=ALH_5 AH+LH_4=ALH_5	48.20(6.15) 3.65	47.46(6.02) 2.91	47.83(5.96) 2.93
A+L+6H=ALH_6 AH+LH_5=ALH_6 AH_2+LH_4=ALH_6	52.41(4.21) 4.11	52.12(4.66) 3.31	52.47(4.64) 3.26
A+L+7H=ALH_7 AH_2+LH_5=ALH_7	55.51(3.10) 5.14	54.53(2.41) 3.65	55.38(2.91) 4.10
BPyC			
A+L =AL			
A+L+H = ALH A+LH = ALH		14.01 2.93	
A+L+2H=ALH_2 A+LH_2=ALH_2	24.65 3.43	24.63(10.62) 3.41	24.56 3.34
A+L+3H=ALH_3 A+LH_3=ALH_3	34.01(9.36) 3.82	34.25(9.62) 4.06	34.83(10.27) 4.64
A+L+4H=ALH_4 A+LH_4=ALH_4	42.20(8.19) 4.17	42.92(8.67) 4.89	43.67(8.84) 5.64
A+L+5H=ALH_5 A+LH_5=ALH_5 AH+LH_4=ALH_5	48.38(6.18) 3.94	49.60(6.68) 5.01	51.58(7.91) 6.79
A+L+6H=ALH_6 AH+LH_5=ALH_6 AH_2+LH_4=ALH_6	52.29(3.91) 4.10	54.02(4.42) 5.32	57.73(6.15) 8.63
A+L+7H=ALH_7 AH_2+LH_5=ALH_7	54.80(2.51) 4.31	56.76(2.74) 5.76	61.66(3.93) 10.26

Table 2: Logarithm recognition constants, log K_{alh}, for the two bismacrocycles with inorganic phosphates: orthophosphate, pyrophosphate, triphosphate (I = 0.1 M (NaCl); T = 25°C).

	Ref 11		
BMC	PO_4^{3-}	$P_2O_7^{4-}$	$P_3O_{10}^{5-}$
A+LH = ALH		2.88	4.87
A+LH_2=ALH_2		3.12	4.10
AH+LH=ALH_2	3.19		
A+LH_3=ALH_3		2.88	4.03
AH+LH_2=ALH_3	2.92		
A+LH_4=ALH_4			
AH+LH_3=ALH_4	2.89	3.52	4.19
A+LH_5=ALH_5			
AH+LH_4=ALH_5	2.90	3.23	1.90
AH+LH_5=ALH_6			
AH_2+LH_4=ALH_6		3.11	3.18
AH_2+LH_5=ALH_7		4.24	4.33
BPyC			
A+LH = ALH		4.65	
A+LH_2=ALH_2		4.52	3.71
AH+LH=ALH_2	4.02		
A+LH_3=ALH_3		4.47	4.22
AH+LH_2=ALH_3	3.83		
A+LH_4=ALH_4			
AH+LH_3=ALH_4	3.80	4.45	5.18
A+LH_5=ALH_5			
AH+LH_4=ALH_5	3.88	3.60	5.42
AH+LH_5=ALH_6			
AH_2+LH_4=ALH_6	3.56	3.49	6.69
AH_2+LH_5=ALH_7			10.10
AH_3+LH_5=ALH_8			10.71

Ref 11: S. Develay, R. Tripier, M. Le Baccon , V. Patinec, G. Serratrice, H. Handel, *J. Chem. Soc. Dalton Trans.* 2005, 3016.

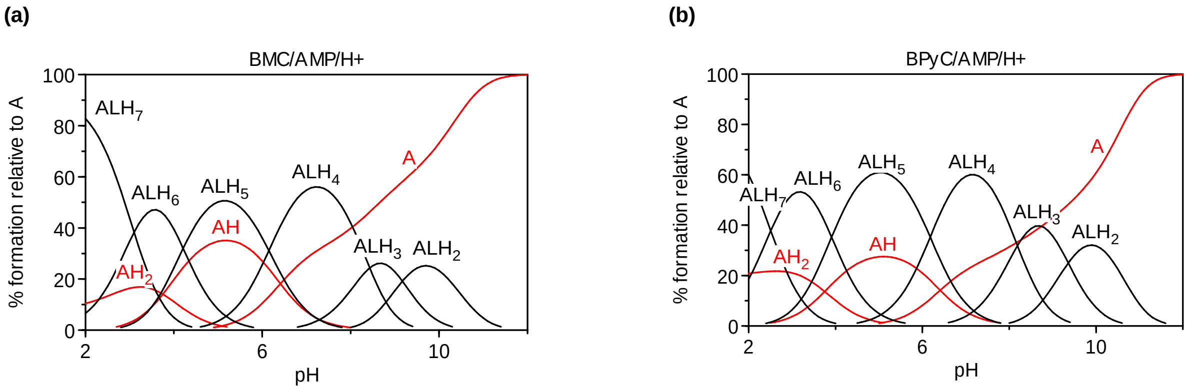


Figure 3 Species distribution diagrams for ***AMP*** with (a) ***BMC*** and (b) ***BPyC*** as a function of p[H]

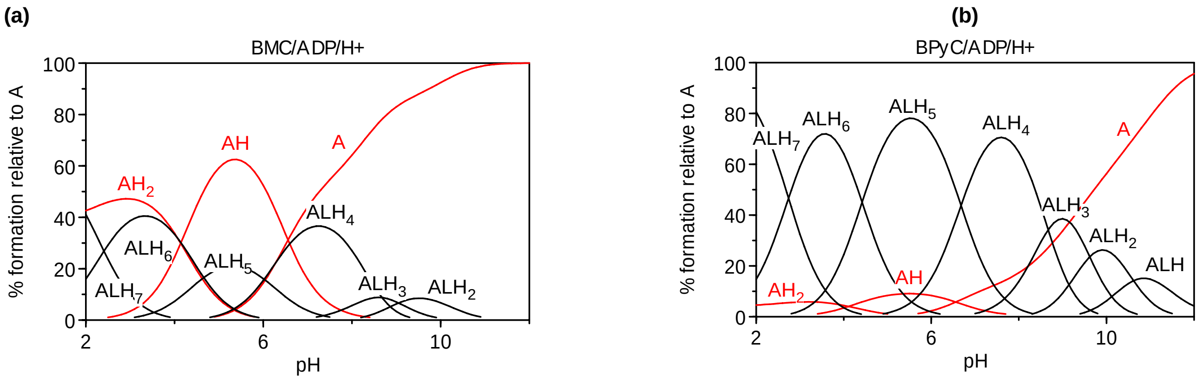


Figure 4 Species distribution diagrams for ***ADP*** with (a) ***BMC*** and (b) ***BPyC*** as a function of p[H]

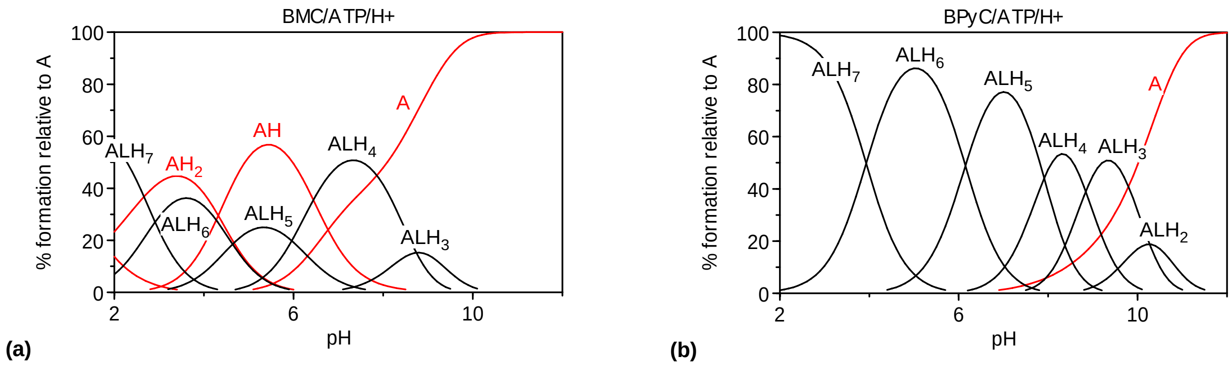


Figure 5 Species distribution diagrams for ***ATP*** with (a) ***BMC*** and (b) ***BPyC*** as a function of p[H]

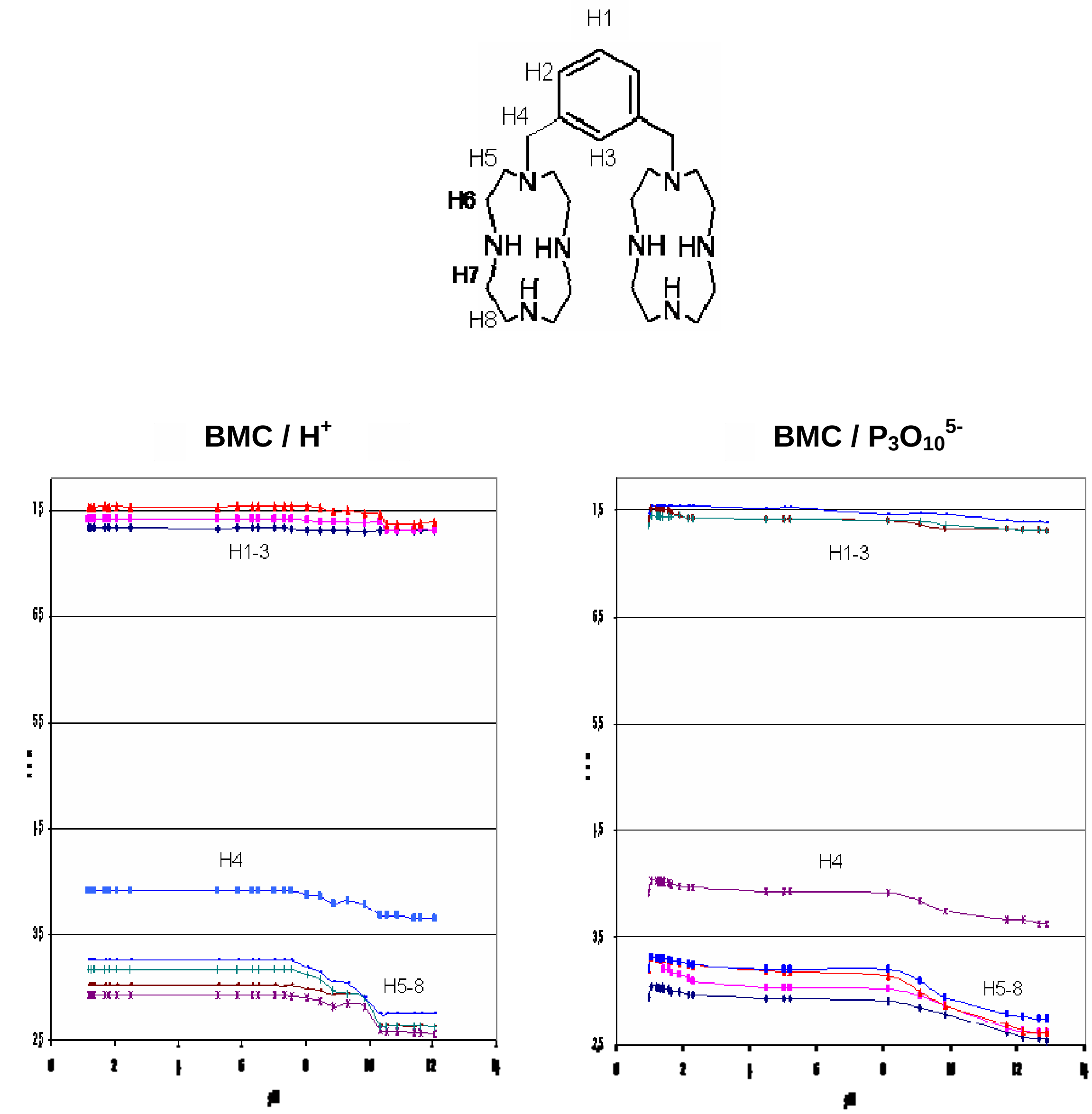


Figure 6: Experimental ^{1}H chemical shifts for the proton of the ***BMC***: ligand free and in presence of triphosphate.

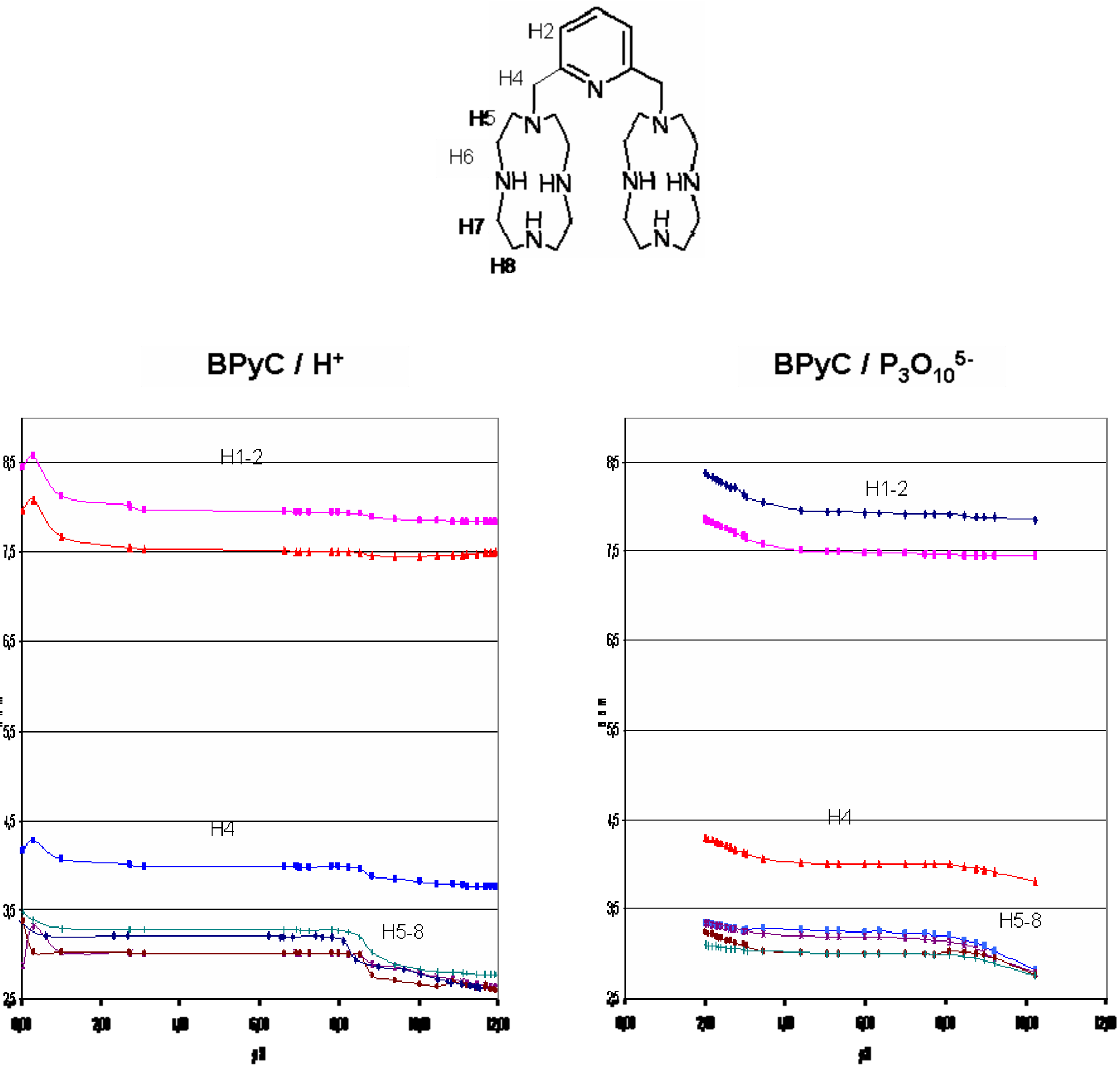


Figure 7: Experimental ^{1}H chemical shifts for the proton of the ***BPyC***: ligand free and in presence of triphosphate.