Support Information

Hydrates of Adenosine 3',5'-Cyclic Monophosphate Sodium and Their Transformation

Pengpeng Yang[a], Junyang Jin[a], Qingshi Wen[b], Chenguang Lin[a], JinQiu Fu[c], Wei Zhuang[a], Jinglan Wu[a], Dong Liu[a], Chenjie Zhu[a*], and Hanjie Ying[a]*

[a]*National Engineering Technique Research Center for Biotechnology, State Key Laboratory of Materials-Oriented Chemical Engineering, and College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 210009, China*

[b]*Industrial Biotechnology Institute of Jiangsu Industrial Technology Research Institute, Nanjing, China*

[c]*School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, China*

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The Crystallographic data of Form III and Form IV for the cAMPNa refers to our previous report[1].

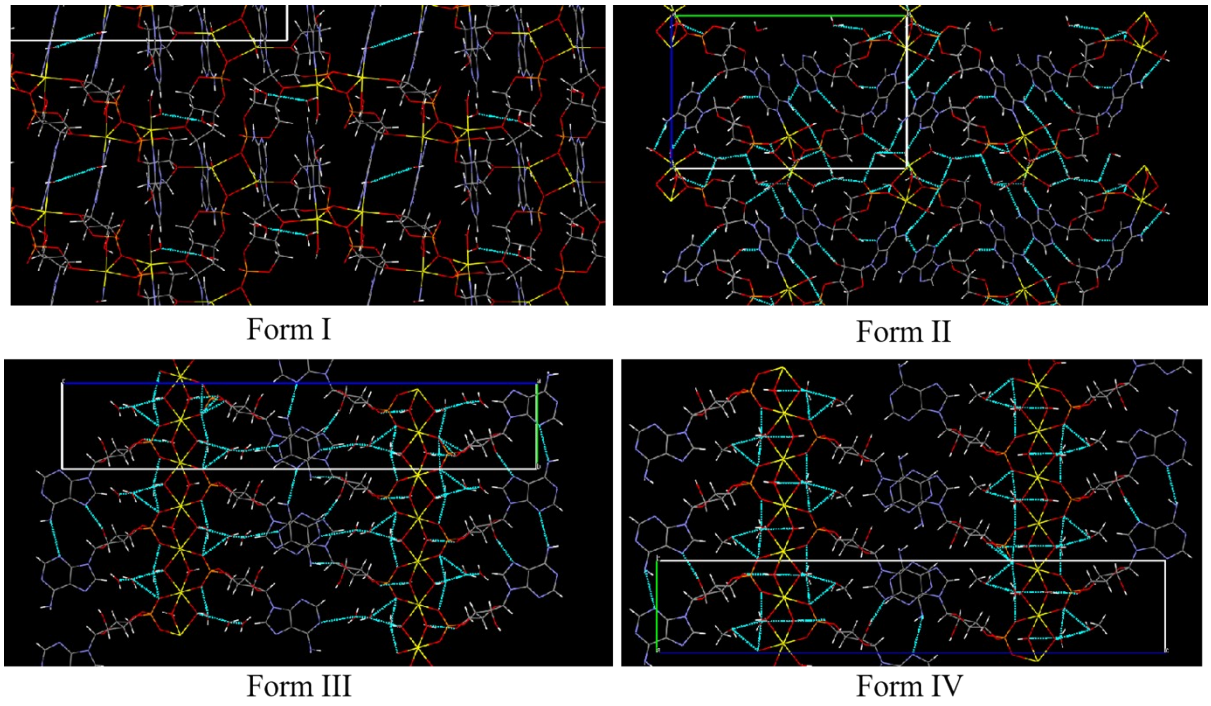

Figure S1. H-bond network pictures of water inclusion for the Forms I-IV. Cyan dash line denotes the hydrogen bond interaction. Yellow dots indicate the sodium ions.

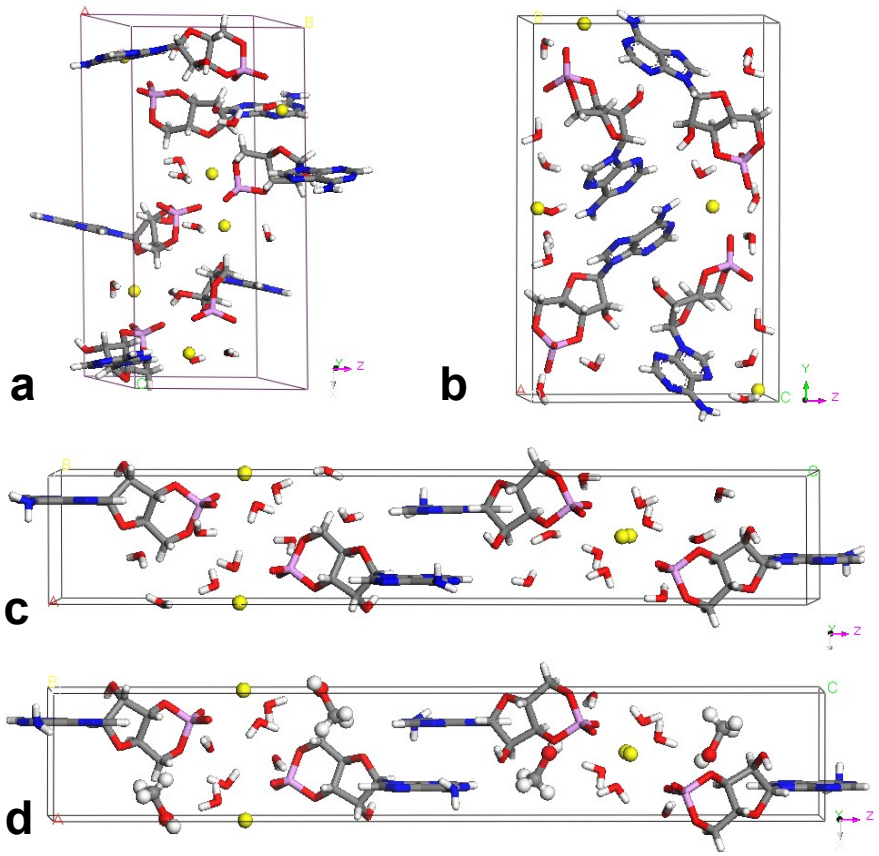

Figure S2. The crystal packing diagrams for the Forms I-IV.

(a) Form I, (b) Form II, (c) Form III, (d) Form IV

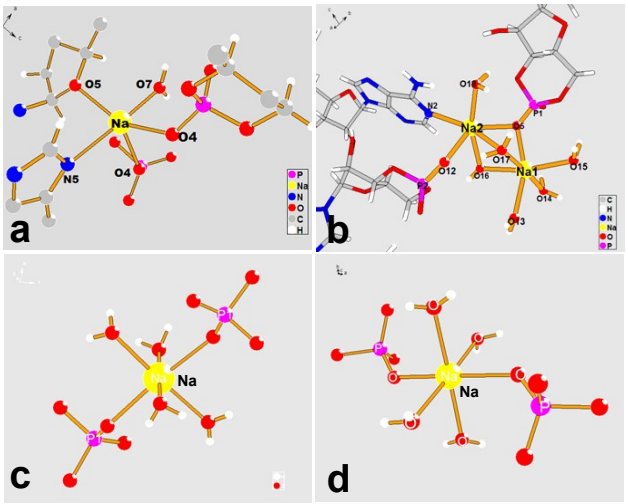

Figure S3. Sodium coordination spheres for the Forms I-IV.

(a) Form I, (b) Form II, (c) Form III, (d) Form IV

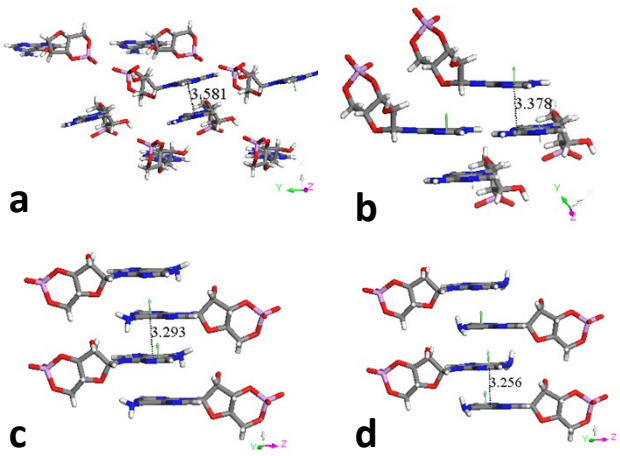

Figure S4. Arrangement profiles of the host molecule packing for four cAMPNa crystal forms. (a) Form I, (b) Form II, (c) Form III, (d) Form IV

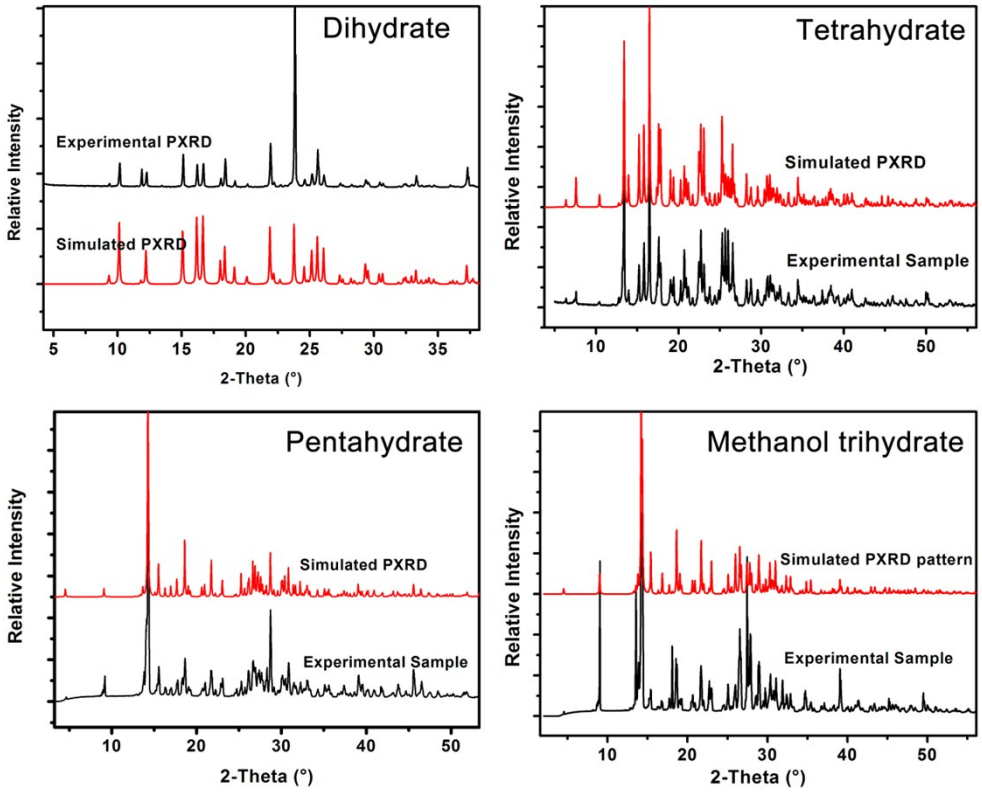

Figure S5. Comparison of the PXRD patterns of sample used in experiments and simulated lines from single-crystal structure.

Table S1. The sodium ions coordination for the Forms I-IV.

Coordination		Bond length(angstrom)	Acceptor
cAMPNa·2H_2O			
Na	-O4	2.311(5)	(P -O)
Na	-O7	2.375(7)	crystal water
Na	-N5_b	2.555(7)	base
Na	-O5_f	2.434(4)	ribose rings
Na	-O4_h	2.338(5)	(P -O)
cAMPNa·4H_2O			
Na1	-O5	2.375(2)	(P -O)
Na1	-O13	2.413(2)	crystal water
Na1	-O14	2.378(2)	crystal water
Na1	-O15	2.387(2)	crystal water
Na1	-O16	2.455(2)	crystal water
Na1	-O17	2.366(2)	crystal water
Na2	-O5	2.393(2)	(P -O)
Na2	-O12	2.664(2)	(P -O)
Na2	-O16	2.340(2)	crystal water
Na2	-O17	2.728(2)	crystal water
Na2	-O18	2.394(2)	crystal water
Na2	-N2_a	2.531(2)	base
cAMPNa·5H_2O			
Na1	-O9	2.461(5)	crystal water
Na1	-O10	2.368(4)	crystal water
Na1	-O5_a	2.372(4)	(P -O)
Na1	-O6	2.359(3)	(P -O)
Na1	-O9_a	2.483(5)	crystal water
Na1	-O10_a	2.413(4)	crystal water
cAMPNa· CH_3OH·3H_2O			
Na1	--O4	2.383(3)	(P -O)
Na1	--O8	2.370(3)	crystal water
Na1	--O11	2.483(4)	crystal water
Na1	--O8_a	2.408(3)	crystal water
Na1	--O3_b	2.430(3)	(P -O)
Na1	--O11_b	2.456(4)	crystal water

Table S2. The hydrogen bond information of the Forms I-IV.

D-H..A*	D(D-H) / Å	d(H..A) / Å	d(D..A)/ Å	<DHA>
cAMPNa·2H_2O				
OW -- HWB .. O2	0.8500	2.4200	3.061(10)	133.00
OW -- HWA .. N3	0.8500	2.5300	3.361(17)	166.00
N4 -- H4A .. O6	0.8600	2.4300	3.210(8)	150.00
N4 -- H4B .. O2	0.8600	2.5600	3.011(10)	114.00

N4 -- H4B .. O4	0.8600	2.2200	3.066(10)	167.00
O6 -- H6A .. O3	0.8200	1.7900	2.602(8)	172.00
O7 -- H7B .. N2	0.8500	2.4100	2.948(9)	122.00
O7 -- H7C .. O6	0.8500	2.5600	3.394(7)	168.00
O7 -- H7C .. O3	0.8500	2.5600	2.929(7)	107.00
C5 -- H5B .. O1	0.9800	2.5200	3.359(8)	144.00
C10 -- H10A .. OW	0.9300	2.5400	3.411(18)	157.00
cAMPNa·4H_2O				
N1 -- H1A .. O18	0.8600	2.1100	2.927(3)	159.00
N1 -- H1B .. N7	0.8600	2.1100	2.929(3)	158.00
O1 -- H1C .. N8	0.8200	1.8900	2.700(3)	171.00
N6 -- H6A .. N5	0.8600	2.3100	3.171(3)	177.00
N6 -- H6B .. O13	0.8600	2.2000	3.024(3)	161.00
O7 -- H7A .. N3	0.8200	2.0700	2.874(3)	167.00
O13 -- H13A .. O2	0.8300	2.2200	2.944(2)	146.00
O13 -- H13B .. O19	0.8100	2.3600	3.153(3)	165.00
O14 -- H14A .. O17	0.9500	1.8400	2.768(3)	166.00
O14 -- H14B .. N10	0.9000	1.9500	2.827(3)	165.00
O15 -- H15A .. O3	0.9600	2.3400	3.132(3)	140.00
O15 -- H15B .. O20	0.8300	2.0300	2.847(4)	168.00
O16 -- H16A .. O12	0.9000	2.0000	2.884(3)	166.00
O16 -- H16B .. O9	0.8000	2.2000	2.906(2)	149.00
O17 -- H17B .. O4	0.8600	2.0500	2.886(3)	164.00
O18 -- H18A .. O1	0.9000	2.2500	3.046(2)	148.00
O18 -- H18A .. O6	0.9000	2.3200	3.035(2)	136.00
O18 -- H18B .. O4	0.8900	1.9200	2.772(2)	161.00
O19 -- H19A .. O14	1.0300	1.7800	2.785(3)	165.00
O19 -- H19C .. O11	0.8700	1.9500	2.815(3)	171.00
O20 -- H20C .. O11	0.9700	1.8400	2.799(3)	170.00
O20 -- H20D .. O4	0.9300	1.9700	2.895(3)	173.00
C1 -- H1 .. O10	0.9300	2.4900	3.258(3)	140.00
C5 -- H5 .. O19	0.9300	2.4800	3.367(3)	160.00
C14 -- H14 .. O15	0.9300	2.5700	3.466(3)	163.00
cAMPNa·5H_2O				
N1 -- H1A .. O1	0.8900	2.2200	3.070(4)	159.00
O2 -- H2A .. N5	0.8200	2.1100	2.928(4)	173.00
O7 -- H7A .. O8	0.8500	2.2100	2.757(6)	122.00
O7 -- H7B .. O3	0.8600	2.3300	3.087(5)	146.00
O7 -- H7B .. O6	0.8600	2.4200	3.014(4)	127.00
O8 -- H8A .. O7	0.8500	2.4100	2.757(6)	105.00
O8 -- H8B .. N2	0.8400	2.3400	3.025(5)	139.00
O9 -- H9A .. O4	0.8500	2.2200	3.012(4)	155.00
O10 -- H10C .. O11	0.7000	2.1300	2.831(5)	174.00
O10 -- H10D .. O7	0.7600	2.1200	2.865(5)	169.00
O11 -- H11A .. O6	1.0100	1.8000	2.795(5)	166.00
O11 -- H11B .. O9	0.8200	2.6000	3.298(6)	144.00
C2 -- H2 .. O2	0.9300	2.5600	3.293(5)	136.00
C4 -- H4 .. O7	0.9300	2.4200	3.239(5)	147.00
C6 -- H6 .. N3	0.9800	2.5800	3.015(4)	107.00

C8	-- H8 .. O7	0.9800	2.5800	3.378(5)	139.00
C10	-- H10B .. O2	0.9700	2.5400	3.431(5)	152.00
cAMPNa· $CH_3OH·3H_2O$					
O1	-- H1 .. N5	0.8200	2.0800	2.891(4)	168.00
N1	-- H1B .. N3	0.8900	2.5700	3.088(4)	118.00
O7	-- H7A .. O4	0.9200	1.8000	2.691(5)	164.00
O7	-- H7B .. O3	0.8700	1.9800	2.782(5)	153.00
O8	-- H8A .. O7	0.8000	1.9500	2.730(4)	163.00
O8	-- H8B .. O9	0.8800	2.0400	2.884(5)	161.00
O9	-- H9A .. O3	0.8200	2.1700	2.921(5)	152.00
O9	-- H9A .. O6	0.8200	2.5500	3.254(5)	145.00
O11	-- H11D .. O5	0.8800	2.1600	2.991(4)	158.00
O11	-- H11E .. O7	0.8300	2.1300	2.850(5)	146.00
C2	-- H2 .. O1	0.9300	2.5500	3.297(5)	138.00
C6	-- H6 .. N3	0.9800	2.5800	3.007(4)	106.00
C8	-- H8 .. O9	0.9800	2.5400	3.323(5)	137.00

Note：*D=Donor, A=Acceptor; Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > more than 110 deg.

Reference

(1) Yang, P.; Lin, C.; Zhuang, W.; Wen, Q.; Zou, F.; Zhou, J.; Wu, J.; Ying, H., Insight into a direct solid-solid transformation: a potential approach for the removal of residual solvents. *CrystEngComm* **2016,** 18, (10), 1699-1704.