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Water and Oxoanion Encapsulation Chemistry in a ^{1}H-Pirazole azacryptand

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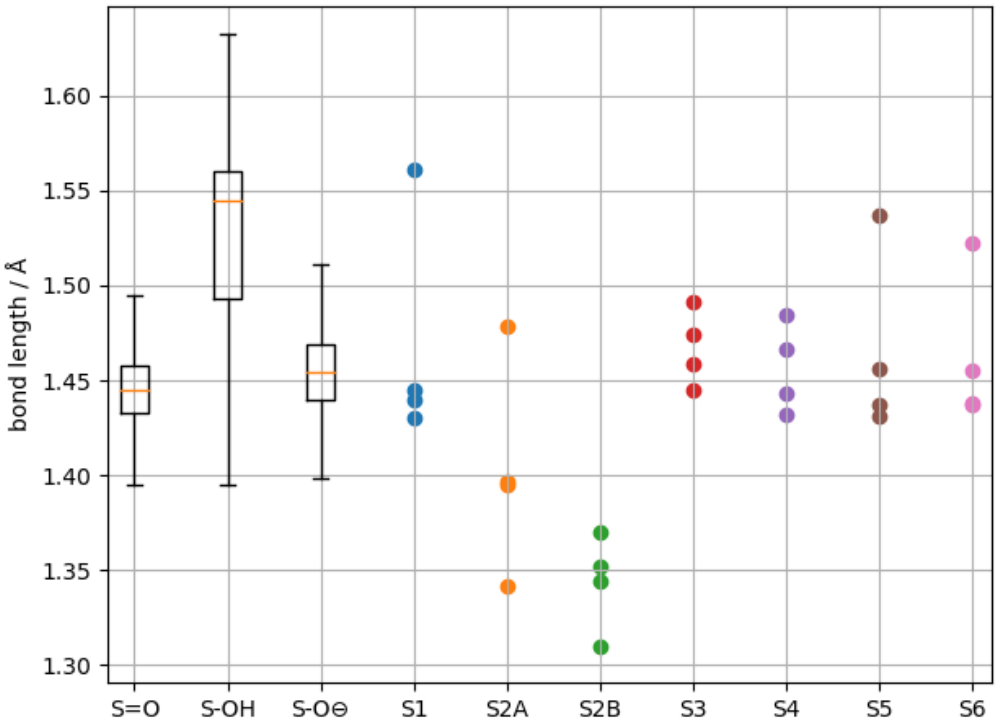

Figure S1: Sulfur-Oxygen bonding distances in structure **4** (dots). compared with analog bonds found in the Cambridge Structural Database (boxes plot)

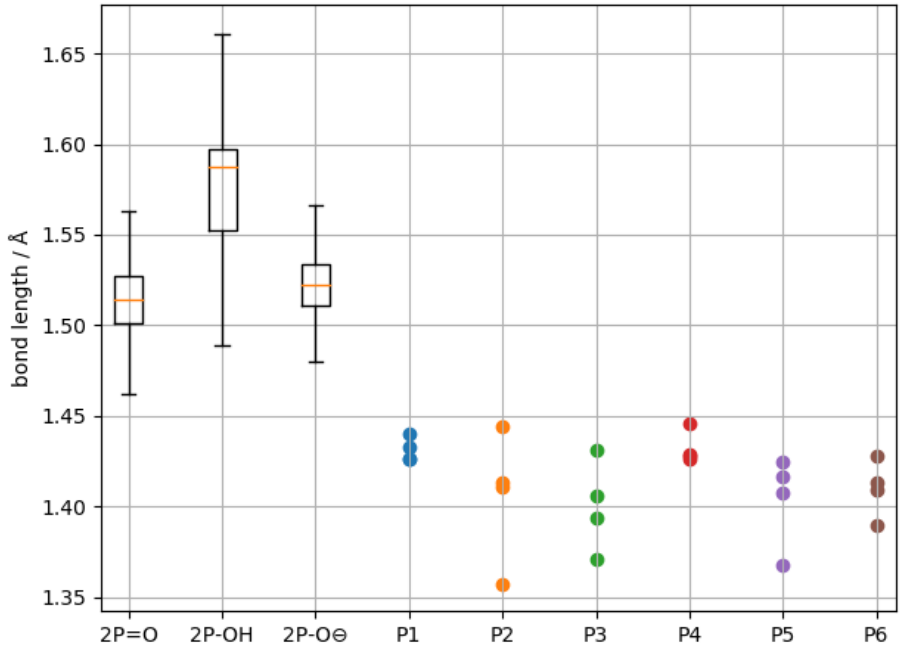

Figure S2: Phosphorous-Oxygen bonding distances in structure **5** (dots). compared with analog bonds found in the Cambridge Structural Database (boxes plot)

Table S1: Crystallographic data

structure	1	2	3	4
empirical formula	$C_{27}H_{50}N_{14}$, 2.65(H_2O), 2(ClO_4)	$C_{27}H_{56}N_{14}$, 6NO_3, 5H_2O	$C_{27}H_{58}N_{14}$, 11(H_2PO_4), 4(H_2O)	$C_{27}H_{54}N_{14}$, 6(H_2PO_4), 8(H_2O)
formula weight / g mol^{-1}	817.17	1036.98	1717.78	1300.88
temperature / K	293(2)	293(2)	288(2)	120(1)
crystal system	triclinic	monoclinic	monoclinic	orthorhombic
space group	P 1	$P2_1/c$	$P2_1/c$	Pbca
a / Å	10.5140(3)	19.1317(8)	14.8632(2)	50.9218(10)
b / Å	13.1320(5)	13.6910(6)	20.1186(2)	11.2705(4)
c / Å	15.7580(96)	19.6870(8)	24.7970(4)	18.5910(5)
α / º	94.242(2)	90	90	90.0
β / º	13.1320(2)	114.465(2)	112.3250(10)	90.0
γ / º	111.844(2)	90	90	90.0
V / Å^3	1928.43(12)	4693.7(3)	6859.17(17)	10669.6(5)
Z	2	4	4	8
ρ_{calc} g/cm^{-3}	1.406	1.467	1.663	1.620
μ /mm^{-1}	0.241	0.127	3.626	0.310
F(000)	867	2200	3588	5504
radiation	MoKα	MoKα	CuKα	MoKα

structure	1	2	3	4
2Θ range / °	1.996–52.746	1.996–50.056	5.984–150.966	5.82–58.224
index ranges	$-12 \le h \le 12$ $-15 \le k \le 15$ $-18 \le l \le 18$	$-22 \le h \le 22$ $-16 \le k \le 16$ $-23 \le l \le 23$	$-18 \le h \le 18$ $-25 \le k \le 24$ $-30 \le l \le 31$	$-69 \le h \le 39$ $-15 \le k \le 13$ $-25 \le l \le 24$
reflections collected	6772	28873	61232	40015
unique reflections	6772	8257	14093	12642
data	6772	8257	14093	12642
restraints	68	26	105	1
parameters	626	690	1076	748
goodness-of-fit on F^2	1.043	1.019	1.066	1.197
final *R* indices [I>2σ(I)]	*R*1=0.0560 *wR*2=0.1257	*R*1=0.0594 *wR*2=0.1472	*R*1=0.0741 *wR*2=0.2239	*R*1=0.1396 *wR*2=0.2466
final *R* indices [all data]	*R*1=0.0891 *wR*2=0.1416	*R*1=0.1368 *wR*2=0.1939	*R*1=0.0884 *wR*2=0.2432	*R*1=0.1644 *wR*2=0.2588
CCDC no.	1912378	1912379	1912380	1912381

Table S1 (continued): Crystallographic data

compound	5	6	7
empirical formula	$C_{27}H_{57}N_{14}$, $3SO_4$, $3HSO_4$, $6H_2O$	$C_{27}H_{55}N_{14}$, $7ClO_4$, $4H_2O$	$C_{27}H_{55}N_{14}$, $2H_2AsO_4$, H_3AsO_4, $4CF_3O_3S$, $3H_2O$
formula weight / g mol^{-1}	1265.34	1344.06	1649.99
temperature / K	293(2)	293(2)	120.0(1)
crystal system	monoclinic	orthorhombic	triclinic
space group	P 2_1/c	P $2_12_12_1$	P 1
a / Å	11.4324(2)	13.816(1)	12.6927(4)
b / Å	17.2812(3)	13.970(1)	15.1722(5)
c / Å	26.4489(4)	28.683(1)	17.0426(5)
α / °	90	90	96.081(3)
β / °	96.7130(10)	90	90.171(3)
γ / °	90	90	109.012(3)
V / Å^3	5189.57(15)	5536.1(6)	3083.06(18)
Z	4	4	2
ρ_{calc} g/cm^{-3}	1.620	1.413	1.777
μ /mm^{-1}	0.370	0.463	1.878
F(000)	2672	2792	1678
radiation	MoKα	MoKα	MoKα
2Θ range / °	3.896–54.906	2.840–54.906	6.696–55.870

compound	5	6	7
index ranges	$-14 \le h \le 14$ $-22 \le k \le 22$ $-34 \le l \le 34$	$-17 \le h \le 17$ $-18 \le k \le 18$ $-37 \le l \le 36$	$-15 \le h \le 16$ $-18 \le k \le 19$ $-21 \le l \le 20$
reflections collected	20583	43512	22380
unique reflections	11838	12640	15491
data restraints parameters	11838 53 756	12640 6 738	15491 104 1735
goodness-of-fit on F^2	1.026	1.041	1.024
final *R* indices [I>2σ(I)]	*R*1=0.0553 *wR*2=0.1309	*R*1=0.0923 *wR*2=0.2567	*R*1=0.0553 *wR*2=0.1351
final *R* indices [all data]	*R*1=0.1236 *wR*2=0.1604	*R*1=0.1542 *wR*2=0.2928	*R*1=0.0628 *wR*2=0.1420
CCDC no.	1912382	1912383	1912384

Table S2: Hydrogen bonds for structure **1**. Symmetry operations: (i) intramolecular bonds; (ii) 1+*x*, *y*, *z*; (iii) 1−*x*, 1−*y*, 1−*z* ; (iv) 1−*x*, 1−*y*, −*z*; (v) *x*, −1+*y*, *z*.

donor	hydrogen	acceptor	distance A...H	distance D-H	distance D-A	angle D-H..A
O1	H1C	N14	0.85	1.99	2.836(3)	173
O1	H1D	N7	0.85	2.02	2.866(4)	178
N2	H2	O24^{ii}	0.86(3)	2.47(4)	3.205(14)	145(3)
N2	H2	O4	0.86(3)	2.33(4)	3.109(12)	151(3)
O2	H2C	O1	0.85	2.06	2.867(3)	159
O2	H2D	N2	0.85	1.99	2.825(4)	167
N3	H3	O22^{ii}	0.86	1.99	2.842(8)	174
N3	H3	O26^{ii}	0.86	2.35	3.158(15)	157
N5	H5A	N5^{iii}	0.96(7)	1.81(7)	2.777(4)	176(12)
N5	H5B	O1	0.83(5)	2.39(4)	3.201(4)	168(3)
N5	H5B	N6^{i}	0.83(5)	2.57(4)	2.963(4)	110(3)
N7	H7	N4^{iii}	0.78(4)	2.52(3)	3.294(4)	168(4)
N9	H9	O17	0.93(5)	2.09(5)	2.903(10)	145(4)
N9	H9	O11	0.93(5)	1.93(5)	2.84(2)	163(4)
N10	H10A	N12^{iv}	0.85(3)	2.05(3)	2.895(4)	174(3)
N10	H10B	O2	0.94(4)	1.85(4)	2.791(4)	177(3)
N11	H11	N11^{iv}	0.98(8)	1.78(9)	2.752(3)	176(12)
N11	H11A	O2	0.89(3)	2.26(3)	3.119(3)	162(3)
N11	H11A	N1^{i}	0.89(3)	2.62(3)	2.991(3)	106.4(19)
N13	H13	O15^{v}	0.86	2.26	3.051(11)	152
N13	H13	O12^{v}	0.86	2.51	3.276(19)	148
N13	H13	O15^{iv}	0.86	2.41	3.025(13)	129
N13	H13	O12^{iv}	0.86	2.50	3.062(18)	124
N14	H14	O18^{v}	0.80(3)	2.46(4)	3.239(13)	162(3)
N14	H14	O14^{v}	0.80(3)	2.35(4)	3.131(14)	164(3)

Table S3: Relevant hydrogen bonds for structure **2** which are involved in embedding or groove binding to **L**. Distances in Å, angles in degrees. Symmetry operations: (i) x, $^3/_2-y$, $-^1/_2+z$; (ii) $-x$, $-^1/_2+y$, $^1/_2-z$; (iii) $-x$, $1-y$, $-z$; (iv) x, $-1+y$, z; (v) $1-x$, $^1/_2+y$, $1/2-z$; (vi) $1-x$, $1-y$, $1-z$; (vii) x, $1/2-y$, $1/2+z$; (viii) $1-x$, $-1/2+y$, $1/2-z$.

	donor	hydrogen	acceptor	distance A...H	distance D-H	distance D-A	angle D-H..A
disordered fragment A	N7	H7D	O12A	2.41	0.89	2.9691(1)	121
	O3	H3C	O12A	2.13	0.84	2.9425(1)	163
	N2	H2D	O13A	2.08	0.89	2.9613(1)	171
	N10	H10D	O13A	2.31	0.89	3.0067(1)	135
	C5	H5	O12A	2.438	0.93	3.2147(1)	142
disordered fragment B	C23	H23	O11B	2.51	0.93	3.2729(1)	140
	N11	H11A	O11B	2.48	0.89	3.0010(1)	118
	N7	H7D	O12B	2.07	0.89	2.8938(1)	153
	O3	H3C	O13B	2.08	0.84	2.6384(1)	124
groove I binders	N9	H9	O32^{i}	2.43	0.86	3.0540(1)	130
	N9	H9	O33^{i}	2.05	0.86	2.8870(1)	134
	N7	H7C	O33^{ii}	1.99	0.89	2.8482(1)	161
	N5	H5C	O31	1.93	0.84	2.7580(1)	173
	O3	H3D	N8^{iii}	2.10	0.84	2.8932(1)	157
	O4	H4B	O3	1.97	0.86	2.7200(1)	145
	O4	H4A	O33^{i}	2,34	0.85	3.0304(1)	145
	N10	N10C	O4	1,79	0.89	2.6663(1)	168
groove II binders	O1	H1C	O43^{iv}	2.06	0.85	2.9027(1)	169
	O1	H1D	O22	2.36	0.85	3.1167(1)	149
	N10	H10D	O53	2.51	0.89	3.0830(1)	123
	N11	H11D	O51	2.35	0.89	2.9708(1)	127
	N11	H11D	O53	2.06	0.89	2.9472(1)	175
groove III binders	N2	H2C	O63^{v}	2.10	0.89	2.9725(1)	165
	O2	H2E	N12^{vi}	2.24	0.83	3.0247(1)	158
	N5	H5A	O23^{vii}	2.08	0.89	2.8494(1)	145
	N11	H11C	O2	2.01	0.89	2.8155(1)	150
	N13	H13	O62^{vii}	2.51	0.86	3.3015(1)	153
	N13	H13	O63^{vii}	2.12	0.86	2.8370(1)	140
	N14	H14A	O61^{viii}	1.93	0.89	2.8193(1)	175

Table S4: Relevant hydrogen bonds for structure **3** which are involved in embedding or groove binding to **L**. Distances in Å, angles in degrees. Symmetry operations: (i) x, $^1/_2-y$, $^1/_2+z$; (ii) $1-x$, $^1/_2+y$, $^1/_2-z$; (iii) $1-x$, $1-y$, $1-z$; (iv) $1-x$, $-^1/_2+y$, $^1/_2-z$; (v) $1-x$, $-y$, $1-z$; (vi) $-1+x$, y, z; (vii) $1+x$, y, z.

	donor	hydrogen	acceptor	distance A...H	distance D-H	distance D-A	angle D-H..A
embedded $H_2PO_4^-$	N1	H1	O14	1.63	0.98	2.589(4)	166
	N5	H5B	O13	1.91	0.89	2.796(4)	174
	N6	H6	O13	2.58	0.98	3.338(5)	135
	N10	H10A	O14	1.82	0.89	2.685(4)	163
	O12	H12C	O54	1.93	0.82	2.696(5)	155

	O12	H12C	O56	1.71	0.82	2.412(14)	143
	N14	H14A	O12	2.42	0.89	3.007(5)	124
	O11	H11	O33	1.71	0.82	2.526(4)	172
	O42	H42	O13	1.69(6)	0.83(5)	2.519(4)	176(4)
groove I	N2	H2A	O3	1.8&	0.89	2.749(7)	169
binders	O3	H3C	O31	2.25	0.85	2.992(8)	146
	O3	H3D	O94	2.21	0.85	2.761(7)	122
	N5	H5A	O34	1.93	0.89	2.798(5)	164
	N14	H14A	O33	2.14	0.89	2.911(5)	144
	O11	H11	O33	1.71	0.82	2.526(4)	172
	O32	H32	O22	2.17	0.82	2.5250(1)	107
	O34	H34	O61	2.09	0.82	2.5733(1)	118
groove II	N3	H3	O21^{ii}	1.97	0.86	2.7356(1)	147
binders	N4	H4	O44	2.01	0.86	2.8647(1)	171
	N7	H7B	O41	1.91	0.89	2.7981(1)	180
	N8	H8	O41^{iii}	1.78	0.86	2.6289(1)	171
	N10	H10B	O24^{ii}	1.85	0.89	2.7120(1)	164
	O22	H22	O43^{iv}	1.84	0.82	2.6267(1)	161
	O23	H23A	O4	2.52	0.82	3.0197(1)	121
	O23	H23A	O113	2.02	0.82	2.8363(1)	171
	O32	H32	O22	2.17	0.82	2.5250(1)	107
	O42	H42	O13	1.75	0.80	2.5238(1)	162
	O44	H44	O92	2.03	0.82	2.6076(1)	127
	O52	H52	O24^{i}	1.80	0.84	2.5837(1)	154
groove III	O5	H5C	O64^{i}	2.24	0.85	2.9462(1)	140
binders	O5	H5D	O102^{i}	1.95	0.85	2.5783(1)	130
	O5	H5D	O105^{i}	2.45	0.85	2.9175(1)	116
	N11	H11A	O104^{i}	2.38	0.89	3.1122(1)	140
	N11	H11A	O106^{i}	1.68	0.89	2.5261(1)	157
	O12	H12C	O104^{i}	1.92	0.82	2.6919(1)	157
	O12	H12C	O105^{i}	1.64	0.82	2.4094(1)	155
	N13	H13	O5^{v}	2.17	0.86	2.8411(1)	134
	N14	H14	O5	2.10	0.89	2.9614(1)	163
	O84	H84	O106^{vi}	2.03	0.82	2.8334(1)	167
	O101	H101	O82^{vii}	1.74	0.82	2.4174(1)	138
	O103	H103	O73^{ii}	1.79	0.82	2.5967(1)	166
	O103	H103	O75^{ii}	1.85	0.82	2.3595(1)	119
	C14	H14	O102^{i}	2.51	0.93	3.3696(1)	153

Table S5: Relevant hydrogen bonds for structure **4** which are involved in embedding or groove binding to **L**. Distances in Å, angles in degrees. Symmetry operations: (i) x, $1+y$, z; (ii) x, $^3/_2-y$, $^1/_2+z$; (iii) $^1/_2-x$, $1-y$, $^1/_2+z$; (iv) x, $-1+y$, z.

	donor	hydrogen	acceptor	distance A...H	distance D-H	distance D-A	angle D-H..A
embedded	O12	H1C	O4^{i}	2.34	0.84	3.1120(1)	154
$H_2PO_4^-$	O1	H1F	O13	2.25	0.85	3.0562(1)	158
	N2	H2A	O11	2.59	0.91	3.0634(1)	113

	N2	H2A	O14	2.27	0.91	3.1104(1)	154
	O3	H3F	O14	2.58	0.85	2.8764(1)	102
	N5	H5A	O12	2.56	0.91	3.1253(1)	121
	N10	H10B	O11	2.11	0.91	3.0052(1)	167
	N10	H10B	O13	2.57	0.91	3.1055(1)	118
	N11	H11B	O13	2.37	0.91	3.2558(1)	164
groove I binders	O1	H1E	O6	2.20	0.85	2.9063(1)	140
	O1	H1F	O13	2.25	0.85	3.0562(1)	158
	O1	H1F	O23	2.59	0.85	3.1292(1)	122
	O2	H2G	O22^{ii}	2.10	0.85	2.9100(1)	158
	O2	H2G	O23^{ii}	2.59	0.85	3.0289(1)	113
	O2	H2H	O23^{ii}	2.50	0.88	3.0289(1)	119
	O3	H3F	O22^{ii}	2.09	0.85	2.9097(1)	161
	O44	H4B	O1	2.56	0.84	3.0947(1)	123
	N7	H7B	O1	2.01	0.91	2.9170(1)	172
	N10	H10A	O24	1.88	0.91	2.7657(1)	163
	N14	H14B	O1	2.06	0.91	2.9337(1)	160
groove II binders	O2	H2G	O22^{ii}	2.10	0.85	2.9100(1)	158
	O2	H2G	O23^{ii}	2.59	0.85	3.0289(1)	113
	O2	H2H	O6^{ii}	2.01	0.88	2.8093(1)	150
	O2	H2H	O23^{ii}	2.50	0.88	3.0289(1)	119
	O3	H3E	O8^{iii}	1.91	0.85	2.7292(1)	162
	O3	H3F	O14	2.58	0.85	2.8764(1)	102
	O3	H3F	O22^{ii}	2.09	0.85	2.9097(1)	161
	N5	H5B	O2	1.87	0.91	2.7585(1)	166
	N11	H11A	O3	1.88	0.91	2.7916(1)	177
	N14	H14A	O2	2.04	0.91	2.8740(1)	153
groove III binders	O12	H1C	O4^{i}	2.34	0.84	3.1120(1)	154
	N2	H2B	O2^{i}	1.98	0.91	2.8857(1)	173
	N3	H3	O5^{i}	2.18	0.88	2.9073(1)	140
	O4	H4C	O42	2.37	0.85	2.9893(1)	130
	O4	H4C	O62	2.45	0.85	3.0411(1)	127
	O4	H4D	N4^{iv}	2.28	0.85	3.0421(1)	149
	N5	H5A	O4^{i}	2.06	0.91	2.8772(1)	149
	O5	H5E	O7	2.03	0.85	2.8053(1)	151
	O5	H5F	O33	2.02	0.85	2.8456(1)	165
	N7	H7A	O4^{i}	1.93	0.91	2.8210(1)	164

Table S6: Relevant hydrogen bonds for structure **5** which are involved in embedding or groove binding to **L**. Distances in Å, angles in degrees. Symmetry operations: (i) x, ½ − y, − ½ + z; (ii) 1 − x, ½ + y, ½ − z; (iii) −x, ½+y, ½−z.

	donor	hydrogen	acceptor	distance A...H	distance D-H	distance D-A	angle D-H..A
embedded HSO_4^-	O1	H1D	O14	2.07	0.84	2.795(4)	144
	N2	H2B	O11	2.13	0.89	2.779(4)	129
	N5	H5A	O12	2.43	0.89	3.067(3)	129
	N7	H7A	O12	2.32	0.89	2.963(3)	129
	N10	H10B	O11	2.11	0.89	2.934(3)	153
	N11	H11B	O13	2.50	0.89	3.020(4)	118
	O13	H13A	O53	1.81	0.82	2.621(4)	169

groove I binders	O1	H1C	O41	2.57	0.84	3.172(4)	130
	O1	H1C	O44	2.15	0.84	2.965(4)	163
	O1	H1D	O14	2.07	0.84	2.795(4)	144
	O2	H2E	O43	2.06	0.84	2.855(5)	157
	O4	H4B	O31	2.21	0.84	2.975(7)	153
	O4	H4B	O32	2.42	0.84	3.135(6)	144
	O5	H5C	O44^{i}	1.96	0.85	2.798(5)	165
	N7	H7B	O1	1.80	0.89	2.691(4)	174
	N10	H10A	O34	1.97	0.89	2.779(4)	151
	N11	H11A	O31	2.25	0.89	2.924(3)	122
	N12	H12	O33	1.81	0.86	2.629(3)	158
	N13	H13	O41	1.88	0.86	2.704(3)	161
	O63	H63	O43	1.71	0.82	2.508(4)	165
groove II binders	N2	H2A	O42^{ii}	2.03	0.89	2.893(4)	162
	N3	H3	O1^{ii}	2.42	0.86	3.064(5)	132
	N4	H4	O33^{ii}	2.44	0.86	3.130(4)	137
	N4	H4	O34^{ii}	2.09	0.86	2.852(4)	148
	N5	H5B	O32^{ii}	2.02	0.89	2.882(3)	162
	N5	H5B	O34^{ii}	2.51	0.89	3.114(3)	126
	N7	H7A	O32^{ii}	2.35	0.89	2.953(4)	125
	N8	H8	O32^{ii}	2.54	0.86	3.195(3)	134
	N8	H8	O33^{ii}	1.87	0.86	2.687(4)	158
	N9	H9	O41^{ii}	1.89	0.86	2.696(4)	155
	N9	H9	O42^{ii}	2.50	0.86	3.201(4)	140
groove III binders	N2	H2B	O62^{iii}	2.42	0.89	3.043(3)	127
	O3	H3D	O51	2.30	0.86	3.067(9)	149
	N5	H5A	O53^{iii}	2.24	0.89	2.926(3)	134
	O6	H6A	O64^{ii}	1.95	0.89	2.834(4)	176
	N11	H11B	O62^{iii}	2.01	0.89	2.858(4)	159
	O13	H13A	O53^{iii}	1.81	0.82	2.621(4)	169
	N14	H14B	O52^{iii}	1.89	0.89	2.775(4)	174
	O54	H54	O61	1.78	0.82	2.583(4)	164
	O63	H63	O43	1.71	0.82	2.508(4)	165

Table S7: Relevant hydrogen bonds for structure **6** which are involved in embedding or groove binding to **L**. Distances in Å, angles in degrees. Symmetry operations: (i) ½+*x*, ½ −*y*, 1−*z*; (ii) ½+*x*, $^{3}/_{2}$−*y*, 1−*z*; (iii) $^{3}/_{2}$−*x*, 1−*y*, −½+*z*; (iv) ½−*x*, 1−*y*, ½+*z*; (v) 1+*x*, *y*, *z*.

	donor	hydrogen	acceptor	distance A...H	distance D-H	distance D-A	angle D-H..A
embedded ClO_4^-	O2	H2E	O14	2.27	0.85	2.901(12)	131
	N5	H5A	O14	2.57	0.89	3.049(11)	115
	N5	H5B	O12	2.16	0.89	2.997(11)	157
	N11	H11B	O13	2.35	0.89	3.053(11)	136
	N14	H14A	O12	2.47	0.89	3.055(11)	124
	N14	H14B	O11	2.32	0.89	3.117(12)	149
groove I binders	N10	H10B	O1	2.13	0.89	3.000(14)	167
	N11	H11A	O1	2.04	0.89	2.889(12)	160

	O1	H1C	O24^{i}	2.49	0.85	3.023(14)	122
	O1	H1D	O71	2.31	0.85	3.011(18)	140
	N7	O23	O23^{i}	2.06	0.89	2.903(13)	158
	N9	H9	O21	2.48	0.86	3.142(15)	134
	N9	H9	O22	2.51	0.86	3.210(14)	139
	N14	H14B	O22	2.33	0.89	2.898(12)	122
groove II	N2	H2A	O2	2.08	0.89	2.957(12)	169
binders	O2	H2E	O14	2.27	0.85	2.901(12)	131
	O2	H2E	O32^{ii}	2.36	0.85	2.99(2)	131
	O2	H2F	O62	2.06	0.85	2.87(2)	159
	N5	H5A	O33^{ii}	2.05	0.89	2.806(15)	141
	N10	H10A	O2	2.02	0.89	2.898(13)	167
groove III	N2	H2A	O52iii	2.06	0.89	2.941(12)	168
binders	O3	H3D	O43iv	2.34(11)	0.87(10)	3.09(3)	144(16)
	N11	H11B	O52iii	2.18	0.89	2.950(12)	145
	N14	H14A	O41v	2.34	0.89	3.06(2)	137
	C23	H23	O41v	2.57	0.93	3.219(17)	127

Table S8: Relevant hydrogen bonds for structure **7** which are involved in embedding or groove binding to **L**. Distances in Å, angles in degrees. Symmetry operations: (i) *x*, *y*, 1+*z*; (ii) *x*, *y*, −1+*z*; (iii) 1+*x*, *y*, *z*.

	donor	hydrogen	acceptor	distance A...H	distance D-H	distance D-A	angle D-H..A
embedded	N1	H1	O13	2.45	0.98	3.393(11)	162
$H_2AsO_4^-$ (A)	N2	H2B	O13	1.91	0.89	2.752(12)	158
	N5	H5A	O14	1.92	0.89	2.794(12)	167
	N7	H7A	O14	1.97	0.89	2.831(12)	162
	N10	H10A	O13	2.43	0.89	2.783(12)	104
	N10	H10B	O13	2.32	0.89	2.783(12)	112
groove IA	N9	H9	O53^{i}	1.86	0.86	2.703(12)	166
binders	N10	H10A	O54^{i}	2.21	0.89	3.055(13)	160
	N11	H11A	O54^{i}	1.86	0.89	2.742(12)	169
	N14	H14B	O43^{i}	1.86	0.89	2.738(12)	170
	O41	H41A	N14^{ii}	2.57	0.82	3.243(12)	141
	C23	H23	O51^{i}	2.37	0.93	3.234(14)	154
groove IIA	N10	H10B	O65A	2.11	0.89	2.851(17)	140
binders	N10	H10B	O67B	1.99	0.89	2.86(3)	165
groove IIIA	N2	H2A	O64	1.94	0.89	2.776(12)	157
binders	N4	H4	O27	1.94	0.86	2.793(14)	174
	N5	H5B	O26	2.08	0.89	2.869(13)	147
	N11	H11B	O64	1.99	0.89	2.790(11)	148
	N13	H13	O1^{i}	1.95	0.86	2.785(15)	162
	O61	H61	N3	1.89	0.82	2.652(13)	154
	O63	H63	N12	1.89	0.82	2.689(14)	164
embedded	N16	H16C	O23	1.94	0.89	2.740(13)	149
$H_2AsO_4^-$ (B)	N19	H19D	O24	1.99	0.89	2.716(12)	138

	N20	H20	O24	2.44	0.98	3.397(11)	166
	N21	H21C	O24	1.96	0.89	2.803(12)	157
	N24	H24A	O23	1.86	0.89	2.729(12)	166
groove IB binders	N16	H16D	O66A[iii]	2.03	0.89	2.90(2)	165
	N16	H16D	O66B[iii]	2.07	0.89	2.80(3)	139
	N18	H18	O35[iii]	2.11	0.86	2.928(13)	158
	N19	H19C	O37[iii]	1.92	0.89	2.798(12)	167
groove IIB binders	N19	H19D	O44[iii]	2.54	0.89	3.164(11)	128
	N25	H25D	O53[iii]	1.79	0.89	2.648(11)	161
	N28	H28B	O44[iii]	1.81	0.89	2.697(12)	175
	O41	H41A	N14[ii]	2.57	0.82	3.243(12)	141
	O51	H51	O43	1.76	0.82	2.579(10)	173
	C32	H32	O51[iii]	2.57	0.93	3.493(15)	175
groove IIIB binders	N21	H21D	O34	2.06	0.89	2.887(11)	153
	N23	H23A	O17	1.97	0.86	2.822(13)	172
	N24	H24B	O16	2.16	0.89	2.938(12)	146
	N27	H27	O33	1.75	0.86	2.595(12)	166
	N28	H28A	O34	1.97	0.89	2.791(11)	152

Table S9: Protonation constants of arsenate determined by potentiometric titration. Conditions: 298K, $NaClO_4$ 0.15M. Numbers in parenthesis respresent standard deviation in the last significant figure.

Equilibria	**$\log_{10}$ K**
$AsO_4^{3-} + H^+ \rightleftharpoons HAsO_4^{2-}$	11.19(1)
$HAsO_4^{2-} + H^+ \rightleftharpoons H_2AsO_4^-$	6.62(1)
$H_2AsO_4^- + H^+ \rightleftharpoons H_3AsO_4$	2.16(2)