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Syntheses, molecular structures and pH-dependent monomer-dimer equilibrium of Dawson α_2-mono-titanium(IV)-substituted polyoxomatalates†

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Contents:

Fig. S3 pH-Varied ^{31}P NMR of **MK-1** in water These spectra indicate that the species in solution are the mono-protonated dimer at pH 0.5, the dimer at pH 1.0 – 3.0, and the monomer at pH 6.0.

Table S1 Average bond distances (Å) and angles (o) [range] for the Dawson POM **1a** in **DK-1**

Table S2 Average bond distances (Å) and angles (o) [range] for the Dawson POM **1b** in **DH-1**

Table S3 Bond valence sum (BVS) calculations of W(1-17), Ti, P(1, 2) and O atoms for the Dawson POM **1a** in **DK-1**

Table S4 Bond valence sum (BVS) calculations of W(1-17), Ti, P(1, 2) and O atoms for the Dawson POM **1b** in **DH-1**

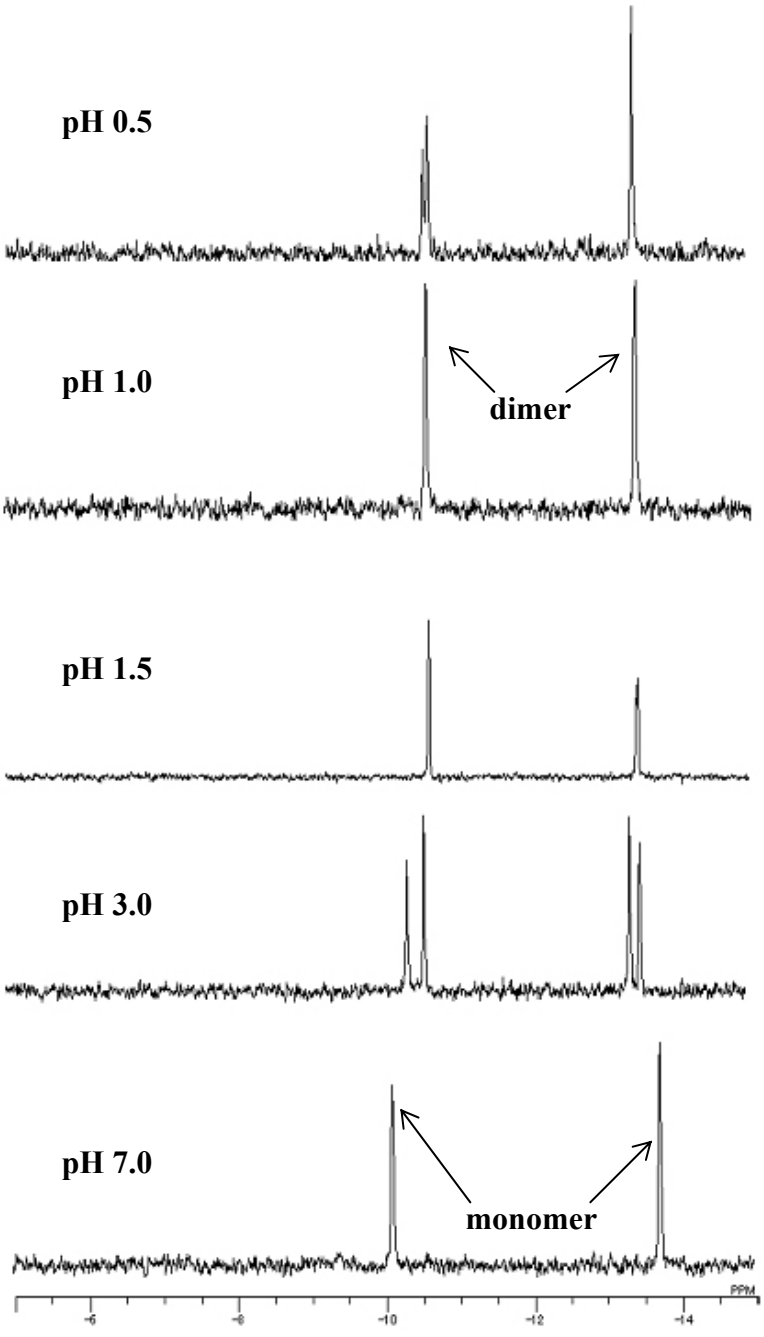

Fig. S1

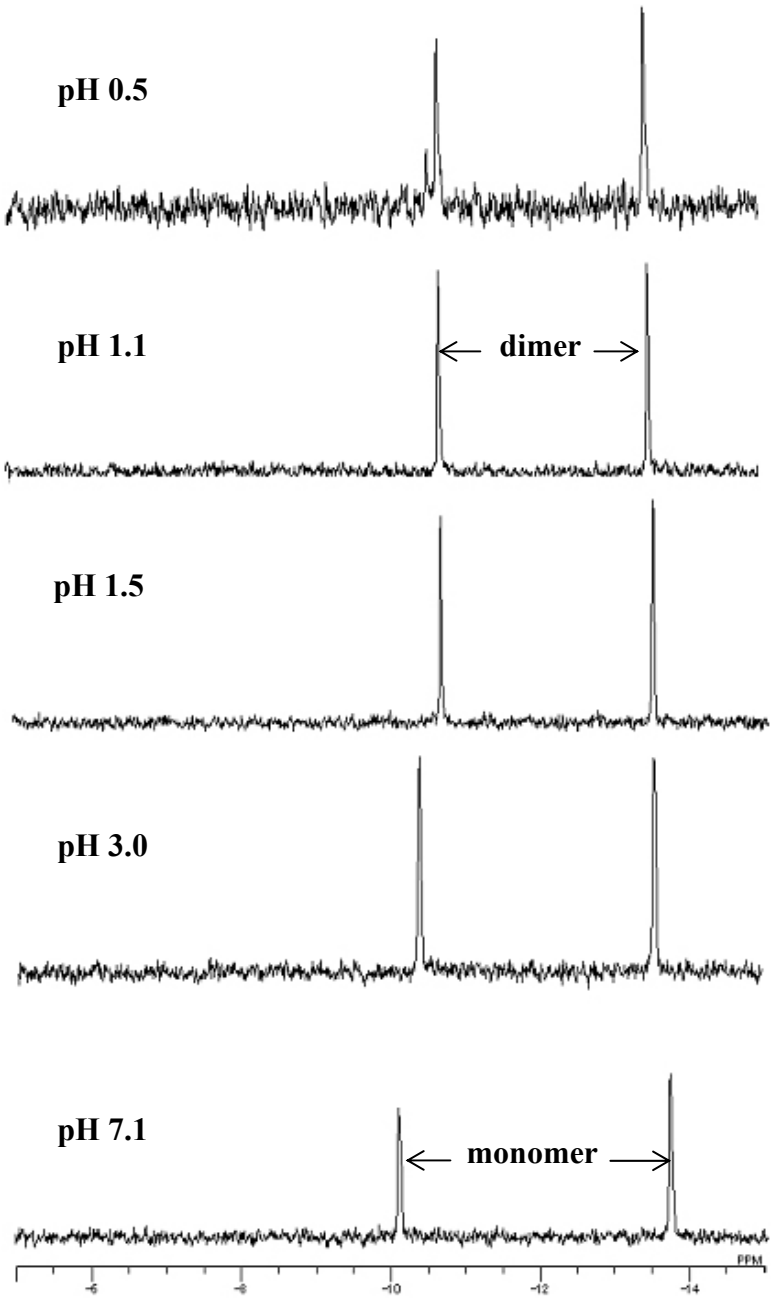

Fig. S2

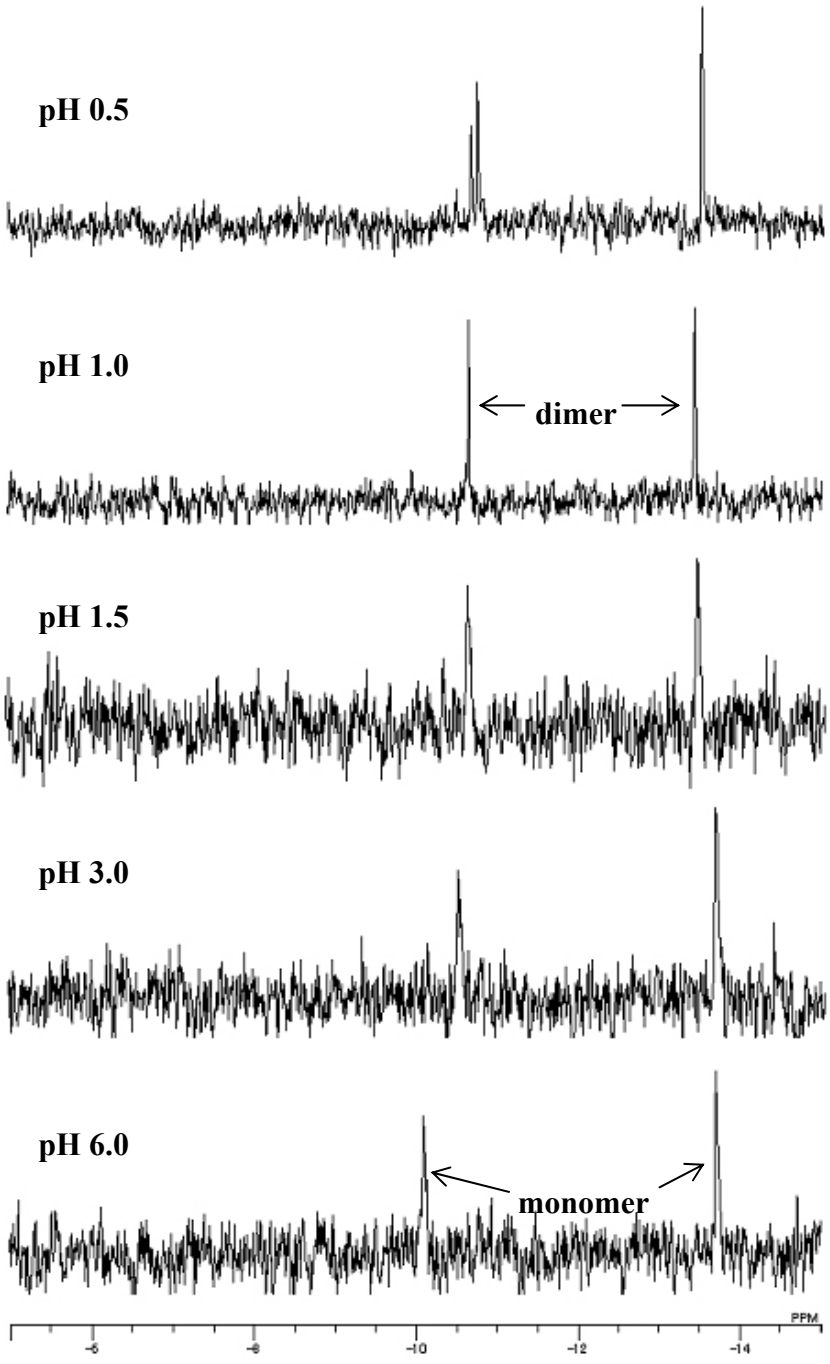

Fig. S3

Table S1 Average bond distances (Å) and angles (o) [range] for the Dawson POM **1a** in **DK-1**

	Cap W(1, 2, 3)	Cap W (16,17)	Ti (1)
M-O(terminal)	1.707(16)[1.685(17)-1.728(16)]	1.718(16)[1.690(16)-1.746(16)]	1.803(7)
M-O(M cap)	1.927(17)[1.894(18)-1.959(17)]	1.895(16)[1.833(16)-1.975(16)]	1.941(18)[1.935(17)-1.947(18)]
M-O(W belt)	1.890(17)[1.820(17)-1.954(16)]	1.915(17)[1.859(17)-1.953(16)]	1.940(18)[1.923(17)-1.956(18)]
M-O(P)	2.376(16)[2.333(16)-2.407(16)]	2.365(17)[2.336(16)-2.394(17)]	2.315(16)
	Tetrahedral $P(1)O_4$	Tetrahedral $P(2)O_4$	
P-O	1.543(17)[1.518(17)-1.569(17)]	1.542(17)[1.531(17)-1.565(17)]	
O-P-O angles	109.4(9)[106.5(9)-112.1(10)]	109.4(9)[105.9(9)-115.2(10)]	
	Belt W(4 – 9)	Belt W(10 - 15)	
W-O(terminal)	1.716(17)[1.670(16)-1.775(19)]	1.716(17)[1.677(16)-1.747(16)]	
W-O(M cap)	1.939(16)[1.865(16)-2.007(16)]	1.900(16)[1.828(17)-1.989(16)]	
W-O(W belt)[a]	1.921(17)[1.901(16)-1.940(17)]	1.925(17)[1.905(17)-1.954(16)]	
W-O(W belt)[b]	1.900(16)[1.868(16)-1.923(16)]	1.905(16)[1.887(17)-1.938(17)]	
W-O(W belt)[c]	1.871(16)[1.820(16)-1.929(16)]	1.933(16)[1.855(16)-2.009(17)]	
W-O(P)	2.363(16)[2.302(16)-2.398(16)]	2.353(16)[2.294(17)-2.391(17)]	

[a] Edge sharing, between octahedra.
[b] Corner sharing, same belt.
[c] Corner sharing, between belts.

Table S2 Average bond distances (Å) and angles (o) [range] for the Dawson POM **1b** in **DH-1**

For Dawson unit A			
	Cap W(1, 2, 3)	Cap W (16,17)	Ti (1)
M-O(terminal)	1.694(9)[1.679(8)-1.707(9)]	1.699(8)[1.696(8)-1.701(8)]	1.803(8)
M-O(M cap)	1.927(9)[1.901(9)-1.959(8)]	1.946(8)[1.894(8)-2.003(8)]	2.001(9)[1.984(9)-2.018(8)]
M-O(W belt)	1.886(8)[1.857(9)-1.913(8)]	1.891(8)[1.853(8)-1.932(8)]	1.890(9)[1.885(8)-1.894(9)]
M-O(P)	2.378(8)[2.361(8)-2.392(8)]	2.383(8)[2.377(8)-2.389(8)]	2.304(8)
	Tetrahedral P(1A)O4	Tetrahedral P(2A)O4	
P-O	1.535(9)[1.514(9)-1.568(8)]	1.539(8)[1.526(8)-1.573(9)]	
O-P-O angles	109.4(5)[106.7(5)-112.0(5)]	109.5(5)[107.2(5)-111.7(5)]	
	Belt W(4 – 9)	Belt W(10 - 15)	
W-O(terminal)	1.711(9)[1.707(9)-1.717(9)]	1.711(9)[1.700(8)-1.724(9)]	
W-O(M cap)	1.938(8)[1.887(8)-1.980(8)]	1.900(8)[1.839(8)-1.970(8)]	
W-O(W belt)a	1.909(8)[1.890(8)-1.929(8)]	1.912(8)[1.890(8)-1.939(8)]	
W-O(W belt)b	1.896(8)[1.858(8)-1.921(8)]	1.893(8)[1.872(8)-1.909(8)]	
W-O(W belt)c	1.889(8)[1.824(8)-1.963(8)]	1.913(8)[1.840(8)-1.986(8)]	
W-O(P)	2.369(8)[2.352(8)-2.393(8)]	2.362(8)[2.350(8)-2.378(8)]	

[a] Edge sharing, between octahedra.
[b] Corner sharing, same belt.
[c] Corner sharing, between belts.

For Dawson unit B			
	Cap W(1, 2, 3)	Cap W (16,17)	Ti (1)
M-O(terminal)	1.715(8)[1.712(8)-1.717(8)]	1.720(9)[1.712(8)-1.727(9)]	1.791(9)
M-O(M cap)	1.942(8)[1.889(8)-1.998(8)]	1.906(9)[1.846(8)-1.951(9)]	1.962(9)[1.955(9)-1.969(8)]
M-O(W belt)	1.943(8)[1.834(8)-1.916(8)]	1.908(8)[1.873(9)-1.944(8)]	1.906(9)[1.889(8)-1.923(9)]
M-O(P)	2.381(8)[2.374(8)-2.385(8)]	2.372(8)[2.362(8)-2.381(8)]	2.263(8)
	Tetrahedral $P(1B)O_4$	Tetrahedral $P(2B)O_4$	
P-O	1.542(9)[1.522(9)-1.571(9)]	1.541(9)[1.513(8)-1.591(9)]	
O-P-O angles	109.4(5)[106.2(5)-112.4(5)]	109.5(5)[107.0(5)-111.9(5)]	
	Belt W(4 – 9)	Belt W(10 - 15)	
W-O(terminal)	1.705(9)[1.693(9)-1.714(8)]	1.713(9)[1.704(8)-1.726(9)]	
W-O(M cap)	1.943(8)[1.895(8)-1.994(8)]	1.896(8)[1.845(8)-1.947(9)]	
W-O(W belt)[a]	1.912(8)[1.890(8)-1.945(8)]	1.919(8)[1.901(8)-1.949(8)]	
W-O(W belt)[b]	1.897(8)[1.865(8)-1.916(8)]	1.896(8)[1.882(8)-1.909(8)]	
W-O(W belt)[c]	1.873(8)[1.832(8)-1.913(8)]	1.931(8)[1.872(8)-1.989(9)]	
W-O(P)	2.358(8)[2.319(8)-2.377(8)]	2.369(8)[2.348(8)-2.403(8)]	

[a] Edge sharing, between octahedra.
[b] Corner sharing, same belt.
[c] Corner sharing, between belts.

Table S3 Bond valence sum (BVS) calculations of W(1-17), Ti, P(1, 2) and O atoms for the Dawson POM **1a** in **DK-1**

O(1)	1.667	O(29)	2.150	O(57)	1.588	W(1)	5.899
O(2)	1.872	O(30)	2.080	O(58)	1.847	W(2)	6.369
O(3)	1.759	O(31)	2.137	O(59)	1.935	W(3)	6.250
O(4)	1.957	O(32)	2.078	O(60)	1.955	W(4)	6.209
O(5)	1.922	O(33)	2.094	O(61)	1.828	W(5)	5.994
O(6)	1.969	O(34)	2.097	O(1X)	2.063	W(6)	5.930
O(7)	2.026	O(35)	1.778			W(7)	6.214
O(8)	2.084	O(36)	1.703			W(8)	6.323
O(9)	1.943	O(37)	1.644			W(9)	6.290
O(10)	2.039	O(38)	1.583			W(10)	6.150
O(11)	2.046	O(39)	1.726			W(11)	5.973
O(12)	2.056	O(40)	1.913			W(12)	6.006
O(13)	2.011	O(41)	2.000			W(13)	5.955
O(14)	1.949	O(42)	2.029			W(14)	6.004
O(15)	1.468	O(43)	1.938			W(15)	6.346
O(16)	1.472	O(44)	2.117			W(16)	6.175
O(17)	1.923	O(45)	1.938			W(17)	6.195
O(18)	1.807	O(46)	2.055				
O(19)	1.774	O(47)	1.872			P(1)	4.889
O(20)	1.998	O(48)	1.874			P(2)	4.903
O(21)	2.109	O(49)	1.864				
O(22)	1.929	O(50)	1.993			Ti(1)	4.145
O(23)	2.126	O(51)	1.955				
O(24)	2.012	O(52)	1.892				
O(25)	2.058	O(53)	2.006				
O(26)	1.819	O(54)	2.018				
O(27)	1.844	O(55)	1.960				
O(28)	1.893	O(56)	2.007				

Table S4 Bond valence sum (BVS) calculations of W(1-17), Ti, P(1, 2) and O atoms for the Dawson POM **1b** in **DH-1**

(O1A)	1.903	(O32A)	2.14	(O1B)	1.717	(O32B)	2.147
(O2A)	1.764	(O33A)	2.114	(O2B)	1.74	(O33B)	2.087
(O3A)	1.822	(O34A)	2.086	(O3B)	1.726	(O34B)	2.057
(O4A)	2.014	(O35A)	1.736	(O4B)	2.029	(O35B)	1.774
(O5A)	1.937	(O36A)	1.764	(O5B)	1.859	(O36B)	1.778
(O6A)	1.909	(O37A)	1.685	(O6B)	1.761	(O37B)	1.676
(O7A)	1.988	(O38A)	1.798	(O7B)	2.13	(O38B)	1.769
(O8A)	2.019	(O39A)	1.698	(O8B)	2.063	(O39B)	1.722
(O9A)	1.996	(O40A)	1.798	(O9B)	1.986	(O40B)	1.703
(O10A)	2.045	(O41A)	1.989	(O10B)	2.045	(O41B)	1.933
(O11A)	2.095	(O42A)	2.129	(O11B)	2.064	(O42B)	2.121
(O12A)	2.071	(O43A)	2.023	(O12B)	2.052	(O43B)	2.004
(O13A)	2.006	(O44A)	2.134	(O13B)	1.989	(O44B)	2.069
(O14A)	1.74	(O45A)	2.079	(O14B)	1.832	(O45B)	2.03
(O15A)	1.717	(O46A)	2.151	(O15B)	1.731	(O46B)	2.172
(O16A)	1.764	(O47A)	1.856	(O16B)	1.788	(O47B)	1.879
(O17A)	1.731	(O48A)	1.873	(O17B)	1.793	(O48B)	1.863
(O18A)	1.754	(O49A)	1.889	(O18B)	1.731	(O49B)	1.89
(O19A)	1.759	(O50A)	2.059	(O19B)	1.769	(O50B)	2.048
(O20A)	2.009	(O51A)	2.01	(O20B)	2.081	(O51B)	1.962
(O21A)	2.135	(O52A)	2.043	(O21B)	2.096	(O52B)	1.998
(O22A)	2.026	(O53A)	2.035	(O22B)	1.957	(O53B)	1.997
(O23A)	2.058	(O54A)	2.056	(O23B)	2.077	(O54B)	2.057
(O24A)	2.098	(O55A)	2.062	(O24B)	2.052	(O55B)	1.994
(O25A)	2.162	(O56A)	1.96	(O25B)	2.173	(O56B)	1.956
(O26A)	1.896	(O57A)	1.793	(O26B)	1.873	(O57B)	1.74
(O27A)	1.868	(O58A)	1.817	(O27B)	1.881	(O58B)	1.671
(O28A)	1.868	(O59A)	1.55	(O28B)	1.84	(O59B)	1.872
(O29A)	2.097	(O60A)	1.371	(O29B)	2.14	(O60B)	1.65
(O30A)	2.116	(O61A)	2.009	(O30B)	2.081	(O61B)	1.968
(O31A)	2.084			(O31B)	2.082	(O1X)	2.1

W(1A)	6.326	W(12A)	6.17	W(6B)	6.145	W(17B)	6.032
W(2A)	6.173	W(13A)	6.278	W(7B)	6.26		
W(3A)	6.243	W(14A)	6.225	W(8B)	6.195	Ti(1A)	4.147
W(4A)	6.22	W(15A)	6.287	W(9B)	6.344	Ti(1B)	4.276
W(5A)	6.15	W(16A)	6.08	W(10B)	6.223		
W(6A)	6.187	W(17A)	6.122	W(11B)	6.133	P(1A)	5.004
W(7A)	6.143	W(1B)	6.219	W(12B)	6.093	P(2A)	4.942
W(8A)	6.077	W(2B)	6.112	W(13B)	6.117	P(1B)	4.902
W(9A)	6.153	W(3B)	6.082	W(14B)	6.052	P(2B)	4.932
W(10A)	6.179	W(4B)	6.183	W(15B)	6.1		
W(11A)	6.085	W(5B)	6.172	W(16B)	6.22		