Supplementary Information

Encapsulation of the Vanadium Substituted Keggin Polyoxometalates [α-$PVW_{11}O_{40}]^{4-}$ and [α-$PV_2W_{10}O_{40}]^{5-}$ in HKUST-1

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Table of Contents

Structure of PV_2W_{10}@HKUST-1 (**2**)

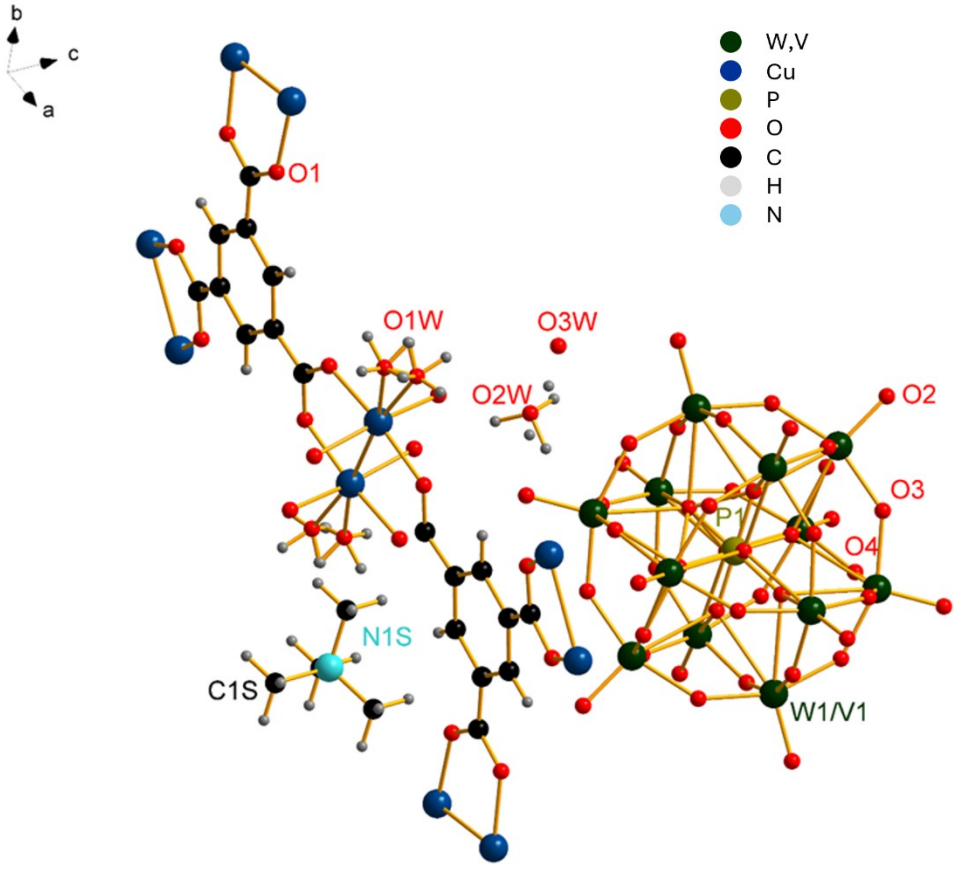

Fig. S1 Structural fragment of PV_2W_{10}@HKUST-1. The neighboring, corner sharing vanadium atoms appear randomly located in each $[PV_2W_{10}O_{40}]^{5-}$ anion and are not distinguished in the figure.

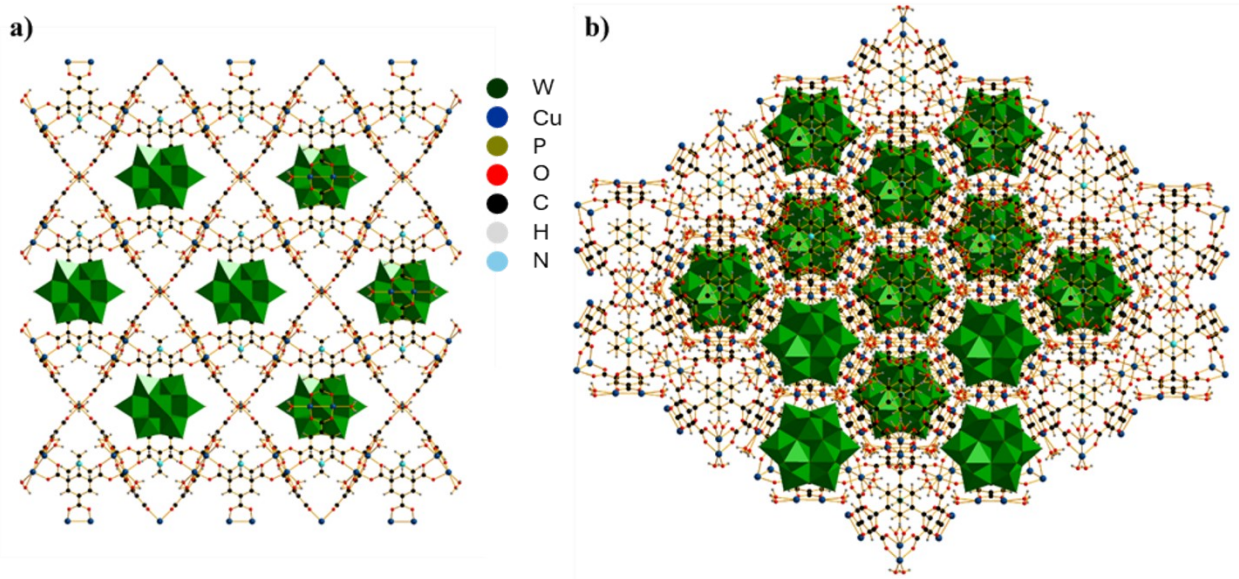

Fig. S2 PV_2W_{10}@HKUST-1 **2** viewed along a) the (101) and b) (111) planes; polyhedral representation of the $[PV_2W_{10}O_{40}]^{5-}$anions.

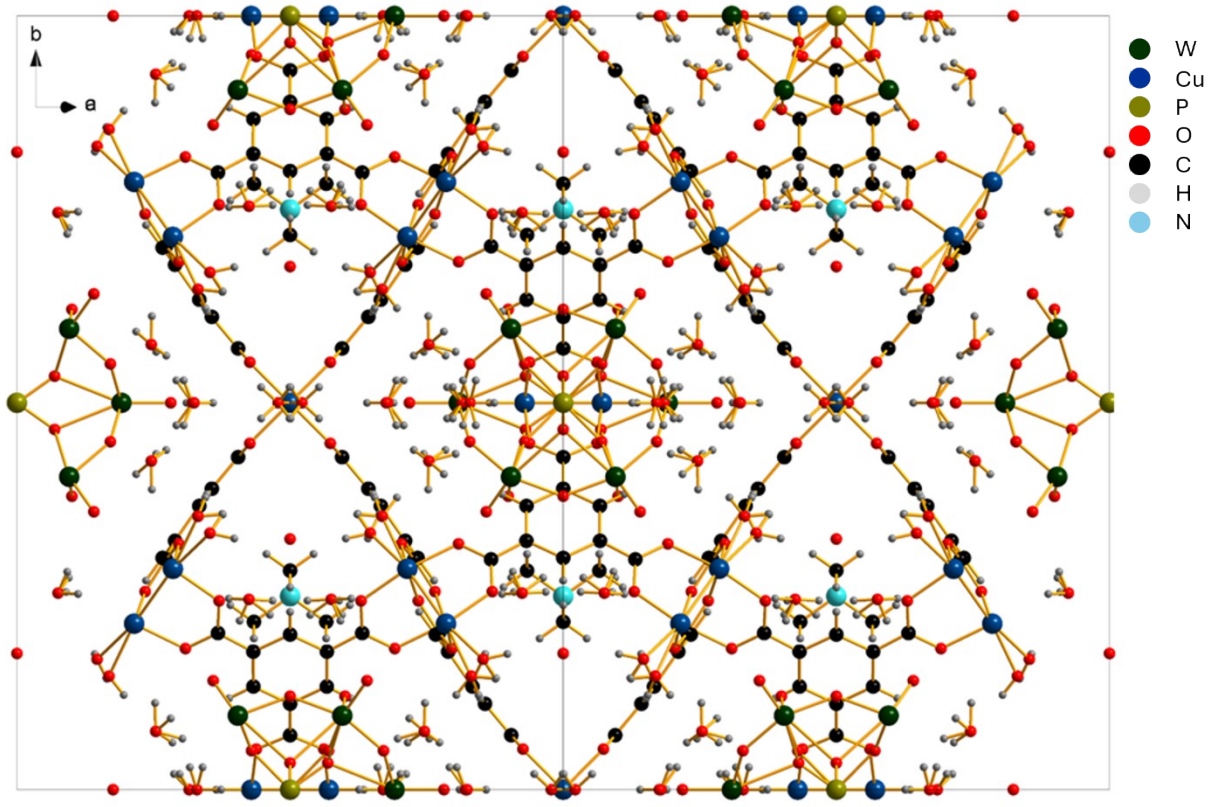

Fig. S3 Unit cell contents of PV_2W_{10}@HKUST-1 **2** viewed along (101) plane.

Crystallographic Data Tables for **1**

Table S1 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
W1	4042.7(2)	5000	4042.7(2)	76.1(4)
V1	4042.7(2)	5000	4042.7(2)	76.1(4)
Cu1	2144.8(5)	5000	2855.2(5)	73.1(6)
P1	5000	5000	5000	67(3)
O1	2561(2)	4475(2)	3173(2)	87.5(16)
O3	4499(3)	5501(3)	3800(4)	113(3)
O2	3590(3)	5000	3590(3)	107(4)
C1	2975(3)	4300(6)	2975(3)	84(3)
C2	3219(3)	3886(5)	3219(3)	86(3)
C3	3660(3)	3660(3)	3001(5)	85(3)
O4	4667(6)	5333(6)	4667(6)	79(7)
N1S	2500	2500	2500	190(30)
C1S	2169(2)	2169(2)	2169(2)	280(30)
O1W	1452(6)	5000	3317(7)	128(9)
O2W	2538(7)	5000	4266(8)	113(6)
O2U	2538(7)	5000	4266(8)	113(6)

Table S2 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	70.5(5)	87.5(6)	70.5(5)	0	-7.6(3)	0
V1	70.5(5)	87.5(6)	70.5(5)	0	-7.6(3)	0
Cu1	64.1(7)	91.0(14)	64.1(7)	0	6.8(8)	0
P1	67(3)	67(3)	67(3)	0	0	0
O1	84(4)	96(4)	83(4)	9(3)	-1(3)	-2(3)
O3	114(5)	114(5)	111(7)	-31(5)	31(5)	-25(6)
O2	94(6)	131(12)	94(6)	0	-20(7)	0
C1	74(5)	102(10)	74(5)	6(4)	-5(6)	6(4)
C2	81(5)	94(8)	81(5)	-10(5)	1(6)	-10(5)
C3	86(5)	86(5)	82(8)	1(4)	1(4)	-5(6)
O4	79(7)	79(7)	79(7)	13(7)	-13(7)	13(7)
N1S	90(30)	190(30)	190(30)	0	0	0
O1W	76(13)	210(20)	98(16)	0	37(13)	0
O2W	89(12)	159(19)	91(12)	0	10(11)	0
O2U	89(12)	159(19)	91(12)	0	10(11)	0

Table S3 Bond Lengths for **1**.

Atom	Atom	Length/ Å	Atom	Atom	Length/ Å
W1	O3	1.890(4)	P1	O4	1.52(3)
W1	O3[1]	1.891(4)	P1	O4[2]	1.52(3)
W1	O3[2]	1.891(4)	P1	O4[10]	1.52(3)
W1	O3[3]	1.891(4)	P1	O4[11]	1.52(3)
W1	O2	1.681(13)	P1	O4[12]	1.52(3)
W1	O4	2.478(14)	O1	C1	1.290(9)
W1	O4[2]	2.478(14)	C1	C2	1.415(18)
Cu1	Cu1[4]	2.639(4)	C2	C3	1.422(8)
Cu1	O1[5]	1.948(6)	C2	C3[13]	1.422(8)
Cu1	O1[6]	1.948(6)	O4	O4[7]	1.75(3)
Cu1	O1[2]	1.948(6)	O4	O4[2]	1.75(3)
Cu1	O1	1.948(6)	O4	O4[9]	1.75(3)
Cu1	O1W	2.187(15)	N1S	C1S[14]	1.506(10)
Cu1	O1W[6]	2.187(15)	N1S	C1S[15]	1.506(10)
P1	O4[7]	1.52(3)	N1S	C1S	1.506(10)
P1	O4[8]	1.52(3)	N1S	C1S[16]	1.506(10)
P1	O4[9]	1.52(3)	O1W	O1W[6]	0.86(4)

[1]+Z,1-X,1-Y; [2]+X,1-Y,+Z; [3]+Z,+X,1-Y; [4]1/2-X,1-Y,1/2-Z; [5]1/2-Z,1-Y,1/2-X; [6]1/2-Z,+Y,1/2-X; [7]+X,+Y,1-Z; [8]1-X,1-Y,+Z; [9]1-X,+Y,+Z; [10]1-X,1-Y,1-Z; [11]1-X,+Y,1-Z; [12]+X,1-Y,1-Z; [13]+Z,+X,+Y; [14]+X,1/2-Y,1/2-Z; [15]1/2-X,1/2-Y,+Z; [16]1/2-X,+Y,1/2-Z

Table S4 Bond Angles for **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	W1	O3[1]	86.8(5)	O4[7]	P1	O4[12]	180.0(9)
O3[1]	W1	O3[2]	155.7(8)	O4	P1	O4[9]	70.529(4)
O3	W1	O3[2]	88.2(6)	O4	P1	O4[8]	109.471(8)
O3	W1	O3[3]	155.7(8)	O4[7]	P1	O4[10]	109.471(10)
O3[1]	W1	O3[3]	88.2(6)	O4[2]	P1	O4[9]	109.471(1)
O3[3]	W1	O3[2]	86.8(5)	O4[2]	P1	O4[8]	180.0(9)
O3[3]	W1	O4[2]	63.7(4)	O4[2]	P1	O4[12]	70.529(9)
O3	W1	O4[2]	92.8(5)	O4[9]	P1	O4[10]	109.471(2)
O3[3]	W1	O4	92.8(5)	O4[8]	P1	O4[7]	70.529(2)
O3[1]	W1	O4	63.7(4)	O4	P1	O4[12]	109.5
O3[1]	W1	O4[2]	92.8(5)	O4[11]	P1	O4[12]	109.471(2)
O3[2]	W1	O4	92.8(5)	O4[8]	P1	O4[12]	109.471(1)
O3	W1	O4	63.7(4)	O4[8]	P1	O4[11]	109.471(10)
O3[2]	W1	O4[2]	63.7(4)	O4[9]	P1	O4[12]	70.529(8)
O2	W1	O3	102.1(4)	O4[7]	P1	O4[11]	70.529(1)
O2	W1	O3[1]	102.1(4)	O4[10]	P1	O4[12]	70.529(7)
O2	W1	O3[2]	102.1(4)	C1	O1	Cu1	123.6(7)
O2	W1	O3[3]	102.1(4)	W1	O3	W1[13]	140.3(7)
O2	W1	O4	159.3(5)	O1	C1	O1[14]	123.5(12)
O2	W1	O4[2]	159.3(5)	O1[14]	C1	C2	118.2(6)
O4[2]	W1	O4	41.4(10)	O1	C1	C2	118.2(6)
O1[2]	Cu1	Cu1[4]	84.61(19)	C1	C2	C3	120.5(7)
O1	Cu1	Cu1[4]	84.61(19)	C1	C2	C3[15]	120.5(7)
O1[5]	Cu1	Cu1[4]	84.61(19)	C3	C2	C3[15]	
O1[6]	Cu1	Cu1[4]	84.61(19)	C2[16]	C3	C2	121.3(14)
O1[5]	Cu1	O1[6]	90.2(4)	W1	O4	W1[13]	91.7(7)
O1[2]	Cu1	O1	90.2(4)	W1	O4	W1[1]	91.7(7)
O1[5]	Cu1	O1	88.8(4)	W1[1]	O4	W1[13]	91.7(7)
O1[2]	Cu1	O1[6]	88.8(4)	P1	O4	W1[1]	124.0(5)
O1[5]	Cu1	O1[2]	169.2(4)	P1	O4	W1	124.0(5)
O1[6]	Cu1	O1	169.2(4)	P1	O4	W1[13]	
O1[5]	Cu1	O1W	87.4(4)	P1	O4	O4[7]	54.736(3)
O1[2]	Cu1	O1W	103.2(4)	P1	O4	O4[9]	54.736(3)

O1^{6}	Cu1	O1W	87.4(4)	P1	O4	O4^{2}	54.736(2)
O1	Cu1	O1W	103.2(4)	O4^{9}	O4	W1^{1}	69.3(5)
O1^{6}	Cu1	O1W^{5}	103.2(4)	O4^{7}	O4	W1^{13}	69.3(5)
O1^{2}	Cu1	O1W^{5}	87.4(4)	O4^{9}	O4	W1^{13}	131.41(16)
O1^{5}	Cu1	O1W^{5}	103.2(4)	O4^{2}	O4	W1^{13}	131.41(16)
O1	Cu1	O1W^{5}	87.4(4)	O4^{7}	O4	W1	131.41(16)
O1W^{5}	Cu1	Cu1^{4}	168.7(5)	O4^{9}	O4	W1	131.41(16)
O1W	Cu1	Cu1^{4}	168.7(5)	O4^{2}	O4	W1	69.3(5)
O1W^{5}	Cu1	O1W	22.6(10)	O4^{7}	O4	W1^{1}	131.41(16)
O4	P1	O4^{7}	70.529(3)	O4^{2}	O4	W1^{1}	131.41(17)
O4^{8}	P1	O4^{9}	70.529(2)	O4^{2}	O4	W1^{1}	131.41(17)
O4^{2}	P1	O4^{10}	109.471(1)	O47	O4	O4^{9}	90.001(3)
O4	P1	O4^{2}	70.529(8)	O4^{2}	O4	O4^{9}	90.001(2)
O4	P1	O4^{11}	109.471(2)	C1S^{17}	N1S	C1S^{18}	109.5

^{1}+Z,1-X,1-Y; ^{2}+X,1-Y,+Z; ^{3}+Z,+X,1-Y; ^{4}1/2-X,1-Y,1/2-Z; ^{5}1/2-Z,+Y,1/2-X; ^{6}1/2-Z,1-Y,1/2-X; ^{7}1-X,+Y,+Z; ^{8}1-X,+Y,1-Z; ^{9}+X,+Y,1-Z; ^{10}1-X,1-Y,1-Z; ^{11}1-X,1-Y,+Z;
^{12}+X,1-Y,1-Z; ^{13}+Y,1-Z,+X; ^{14}+Z,+Y,+X; ^{15}+Z,+X,+Y; ^{16}+Y,+Z,+X; ^{17}+X,1/2-Y,1/2-Z; ^{18}1/2-X,+Y,1/2-Z;

Table S5 Hydrogen Atom Coordinates (Å×10^{4}) and Isotropic Displacement Parameters (Å^{2}×10^{3}) for **1**.

Atom	***x***	***y***	***z***	**U(eq)**
H3	3805.36	3805.35	2703.97	102
H1SA	2384.37	1953.58	1953.58	415
H1SB	1953.58	1953.58	2384.37	415
H1SC	1953.58	2384.37	1953.58	415
H1WA	1425.99	4796.6	3574.3	153
H1WB	1210.39	5203.4	3248	153
H	2553.34	5289.7	4408.91	169
HA	2813.54	5000	4097.41	169
H2UA	2690(160)	5290(90)	4430(100)	169
H2UB	2700(200)	5000	3930(70)	169
H2UC	2690(160)	4710(90)	4430(100)	169

Crystallographic Data Tables for 2

Table S6 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
W1	4043.8(2)	5000	4043.8(2)	67.9(5)
V1	4043.8(2)	5000	4043.8(2)	67.9(5)
Cu1	2145.1(6)	5000	2854.9(6)	64.3(7)
P1	5000	5000	5000	56(3)
O1	2560(3)	4476(3)	3177(3)	78.5(18)
O3	4497(4)	5503(4)	3793(5)	107(4)
O2	3592(4)	5000	3592(4)	100(5)
C1	2976(4)	4297(6)	2976(4)	77(4)
C2	3216(4)	3890(5)	3216(4)	73(3)
C3	3667(4)	3667(4)	2995(6)	75(3)
O4	4655(7)	5345(7)	4655(7)	80(9)
N1S	2500	2500	2500	140(30)
C1S	2169(2)	2169(2)	2169(2)	250(40)
O1W	1467(11)	5000	3315(11)	130(16)
O2W	2541(10)	5000	4247(10)	125(9)
O2U	2541(10)	5000	4247(10)	125(9)
O3W	1760(20)	5000	5000	120(20)

Table S7 Anisotropic Displacement Parameters (Å2×10^3) for **2**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
W1	62.1(6)	79.4(7)	62.1(6)	0	-8.2(4)	0
V1	62.1(6)	79.4(7)	62.1(6)	0	-8.2(4)	0
Cu1	59.6(9)	73.8(14)	59.6(9)	0	6.3(9)	0
P1	56(3)	56(3)	56(3)	0	0	0
O1	74(4)	85(4)	76(4)	9(4)	3(3)	6(3)
O3	109(6)	109(6)	103(9)	-33(6)	33(6)	-31(8)
O2	81(6)	139(15)	81(6)	0	-20(8)	0
C1	70(5)	92(11)	70(5)	6(5)	-5(7)	6(5)
C2	73(5)	74(8)	73(5)	-5(5)	0(6)	-5(5)
C3	74(5)	74(5)	77(8)	4(5)	4(5)	-4(7)
O4	80(9)	80(9)	80(9)	14(9)	-14(9)	14(9)
N1S	140(30)	140(30)	140(30)	0	0	0
C1S	250(40)	250(40)	250(40)	60(40)	60(40)	60(40)
O1W	90(20)	180(20)	120(30)	0	50(20)	0
O2W	91(17)	190(30)	95(17)	0	12(14)	0
O2U	91(17)	190(30)	95(17)	0	12(14)	0
O3W	40(30)	160(30)	160(30)	0	0	0

Table S8 Bond Lengths for **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	$O3^{1}$	1.896(5)	P1	O4	1.57(3)
W1	O3	1.896(5)	P1	$O4^{10}$	1.57(3)
W1	$O3^{2}$	1.896(5)	P1	$O4^{3}$	1.57(3)
W1	$O3^{3}$	1.896(5)	P1	$O4^{11}$	1.57(3)
W1	O2	1.679(14)	P1	$O4^{12}$	1.57(3)
W1	O4	2.445(17)	O1	C1	1.301(10)
W1	$O4^{3}$	2.445(17)	C1	C2	1.39(2)
Cu1	$Cu1^{4}$	2.637(4)	C2	C3	1.443(9)
Cu1	$O1^{5}$	1.950(7)	C2	$C3^{13}$	1.443(9)
Cu1	O1	1.950(7)	O4	$O4^{7}$	1.81(4)
Cu1	$O1^{3}$	1.950(7)	O4	$O4^{3}$	1.81(4)
Cu1	$O1^{6}$	1.950(7)	O4	$O4^{9}$	1.81(4)
Cu1	$O1W^{5}$	2.15(2)	N1S	C1S	1.505(10)
Cu1	O1W	2.15(2)	N1S	$C1S^{14}$	1.505(10)
P1	$O4^{7}$	1.57(3)	N1S	$C1S^{15}$	1.505(10)
P1	$O4^{8}$	1.57(3)	N1S	$C1S^{16}$	1.505(10)
P1	$O4^{9}$	1.57(3)	O1W	$O1W^{5}$	0.81(7)

Table S9 Bond Angles for **2.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3[1]	W1	O3[2]	157.0 (9)	O4[7]	P1	O4[12]	109.471 (4)
O3[2]	W1	O3	88.2 (7)	O4[12]	P1	O4[8]	180.0 (11)
O3[1]	W1	O3	87.2 (7)	O4[9]	P1	O4[7]	70.529 (2)
O3[1]	W1	O3	88.2 (7)	O4[2]	P1	O4[10]	109.471(1)
O3[2]	W1	O3[3]	87.2(7)	O4	P1	O4[12]	70.529 (5)
O3[3]	W1	O3	157.0 (9)	O4[7]	P1	O4[10]	109.471(11)
O3	W1	O4	63.7(5)	O4[2]	P1	O4[12]	109.471(1)
O3[1]	W1	O4	63.7(5)	O4	P1	O4[11]	109.471(1)
O3	W1	O4[2]	94.2(6)	O4[9]	P1	O4[12]	70.529(2)
O3[2]	W1	O4	63.7(5)	O4[9]	P1	O4[11]	109.471 (1)
O3[2]	W1	O4	94.2(6)	O4[7]	P1	O4[12]	109.471 (6)
O3[3]	W1	O4[2]	63.7(5)	O4[12]	P1	O4[11]	70.529 (10)
O3[1]	W1	O4[2]	94.2(6)	O4	P1	O4[8]	109.471 (3)
O3[3]	W1	O4	94.2(6)	O4[10]	P1	O4[11]	70.529(8)
O2	W1	O3[1]	101.5(4)	O4[2]	P1	O4[8]	70.529(1)
O2	W1	O3	101.5(4)	O4[12]	P1	O4[10]	109.471 (2)
O2	W1	O3[3]	101.5(4)	C1	O1	Cu1	123.3(7)
O2	W1	O3[2]	101.5(4)	W1[13]	O3	W1	139.0 (8)
O2	W1	O4	158.3(6)	O1[14]	C1	O1	123.4(13)
O2	W1	O4[2]	158.3(6)	O1	C1	C2	118.3(6)
O4[2]	W1	O4	43.5(12)	O1[14]	C1	C2	118.3(6)
O1	Cu1	Cu1[4]	84.9(2)	C1	C2	C3	120.0(8)
O1[2]	Cu1	Cu1[4]	84.9(2)	C1	C2	C3[15]	120.0(8)
O1[5]	Cu1	Cu1[4]	84.9(2)	C3	C2	C3[15]	119.9(15)
O1[6]	Cu1	Cu1[4]	84.9(2)	C2	C3	C2[16]	120.1(15)
O1	Cu1	O1[6]	89.2(4)	W1[13]	O4	W1	93.2(9)
O1[2]	Cu1	O1[6]	169.8(4)	W1[13]	O4	W1[1]	93.2(9)
O1	Cu1	O1[5]	169.8(4)	W1[1]	O4	W1	93.2(9)
O1[6]	Cu1	O1[5]	89.9(4)	P1	O4	W1[1]	123.0(6)
O1	Cu1	O1[2]	89.9(4)	P1	O4	W1[13]	123.0(6)
O1[2]	Cu1	O1[5]	89.2(4)	P1	O4	W1	123.0(6)
O1	Cu1	O1W[6]	87.4(7)	P1	O4	O4[7]	54.738(3)
O1[2]	Cu1	O1W	102.7(7)	P1	O4	O4[12]	54.738(4)

O1[5]	Cu1	O1W	87.4(7)	P1	O4	O4[2]	54.738(3)
O1[2]	Cu1	O1W[6]	87.4(7)	O4[12]	O4	W1[1]	68.3(6)
O1[6]	Cu1	O1W	87.4(7)	O4[7]	O4	W1[13]	68.3(6)
O1[6]	Cu1	O1W[6]	102.7(7)	O4[2]	O4	W1	68.3(6)
O1	Cu1	O1W	102.7(7)	O4[7]	O4	W1	131.1(2)

[1]+Z,1-X,1-Y; [2]+X,1-Y,+Z; [3]+Z,+X,1-Y; [4]1/2-X,1-Y,1/2-Z; [5]1/2-Z,1-Y,1/2-X; [6]1/2-Z,+Y,1/2-X; [7]1-X,+Y,+Z; [8]1-X,1-Y,+Z; [9]1-X,+Y,1-Z; [10]1-X,1-Y,1-Z; [11]+X,1-Y,1-Z;[12]+X,+Y,1-Z; [13]+Y,1-Z,+X; [14]+Z,+Y,+X; [15]+Z,+X,+Y; [16]+Y,+Z,+X

Table S10 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å2×10^3) for **2**.

Atom	***x***	***y***	***z***	**U(eq)**
H3	3817.99	3818.01	2702.65	90
H1SA	2384.58	1953.79	1953.79	380
H1SB	1953.79	1953.79	2384.58	380
H1SC	1953.79	2384.58	1953.79	380
H1WA	1442.34	4797.3	3566.34	156
H1WB	1224.64	5202.7	3246.64	156
H	2556.08	5289.7	4390.03	187
HA	2815.98	5000	4078.53	187
H2UA	2740(140)	5290(90)	4340(100)	187
H2UB	2530(180)	5000	3880(20)	187
H2UC	2740(140)	4710(90)	4340(100)	187

Crystal Structure of 1 and 2: Hydronium Ion Positions

The possible sites of hydronium (H_3O^+) were O1w, O2w, and O3W. The position of O1w (at the open Cu sites) was less likely because the presence of the Keggin species can weaken the coordination between Cu^{2+} and BTC ligands, thus making copper more positive to repel H_3O^+. The O2w sites were closer to negatively charged POMs than the O3w sites were, as indicated H_3O^+ may prefer the O2w sites to the O3w sites. Therefore, two and three H_3O^+ counterions were assigned on the O2w sites of **1** and **2**, respectively, to achieve charge balance.

To resolve the high residue on the O2w sites, reasonable solvent amount in the pores of POM@HKUST-1 should be considered. The TGA data revealed that approximately 10 wt% of solvent (most likely H_2O) was present in the structure. Besides the O1w site for coordinated H_2O (12 H_2O per POM@HKUST-1), the O2w sites were assigned to be H_3O^+ and H_2O for reaching

10% solvent amount. The ratio between H_3O^+ / H_2O on the O2w sites were 3/ 9 in the W10 structure (**1**) and 2/10 in the W11 structure (**2**). Regarding those disorders shown in the structures, the coordinated H_2O (O1w) at the open Cu sites was split into two disorder parts for elimination of an alert B in CIF check (low main mol Ueq as compared to neighbor of Cu). Coordinated water molecules bound to copper sites account for approximately 3% of the structure.

Infrared Spectroscopy

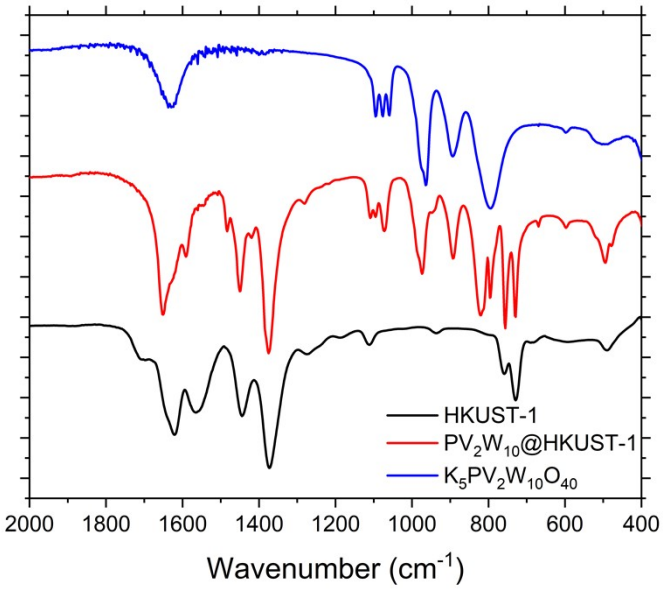

Fig. S4 FTIR spectra of **2** and its constituents HKUST-1 and the divanadium substituted Keggin POM $K_5[\alpha\text{-}PV_2W_{10}O_{40}]$. Prominent bands in the FTIR spectrum of **2**: 1651 (s), 1591 (m), 1483 (m), 1450 (s), 1419 (m, sh), 1375 (s), 1280 (w), 1109 (w), 1095 (w), 1072 (w), 974 (m), 949 (w, sh), 893 (m), 820 (s), 796 (s), 756 (s), 729 (s), 669 (w), 598 (w), 494 (m), 478 (w, sh).

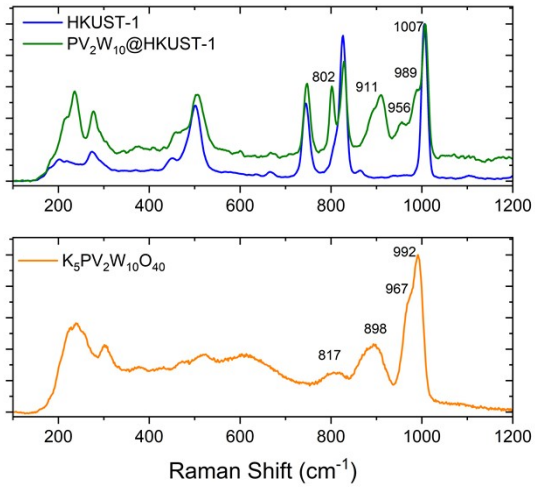

Fig. S5 Raman spectra of **2** and its constituents HKUST-1 and the di-vanadium substituted Keggin POM $K_5[\alpha\text{-}PV_2W_{10}O_{40}]$ in the 100 – 1200 cm^{-1} range.

Thermogravimetric Analysis

The TGA profiles of **1** and **2** (Figure S5) each show two marked weight loss regions below 400 °C. The first step is associated with water loss terminating below ca. 150 °C and the second corresponds to MOF decomposition initiating at ca. 250°C. HKUST-1 has a reported thermal stability of ca. 240 °C.[1] The water content of **1** (14%) and **2** (11%) determined by TGA is consistent with total water (coordinated and non-coordinated) content observed from single crystal structure analysis.

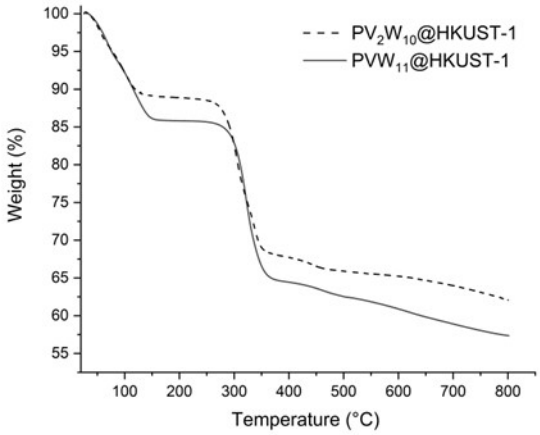

Fig. S6 TGA trace of PVW_{11}@HKUST-1 and PV_2W_{10}@HKUST-1 in the 25-800 °C range (Ar at 50 ml/min).

BET Surface Area Analysis

Figure S7 shows the nitrogen adsorption/desorption isotherms of HKUST-1, PV_2W_{10}@HKUST-1, and PVW_{11}@HKUST-1. The isotherms indicate that the encapsulation of POMs in HKUST-1 results in a decreased surface area (Table S11).

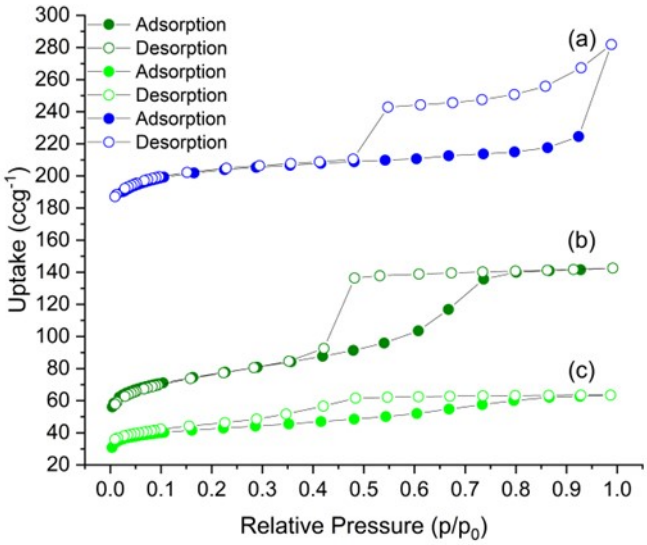

Fig. S7 Nitrogen adsorption/desorption isotherms of HKUST-1 (a), PV_2W_{10}@HKUST-1 (b), and PVW_{11}@HKUST-1 (c). BET surface area: 674 m^2/g (HKUST-1); 261 m^2/g (**2**); 145 m^2/g (**1**).

Table S11. BET surface areas

	BET surface area (m^2/g)
HKUST-1	674
PV_2W_{10}@HKUST-1	261
PVW_{11}@HKUST-1	145

References

1. S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148-1150.