ELECTRONIC SUPPLEMENTARY INFORMATION FOR:

Gas sorption and luminescence properties of a Terbium(III)-phosphine oxide coordination material with two-dimensional pore topology

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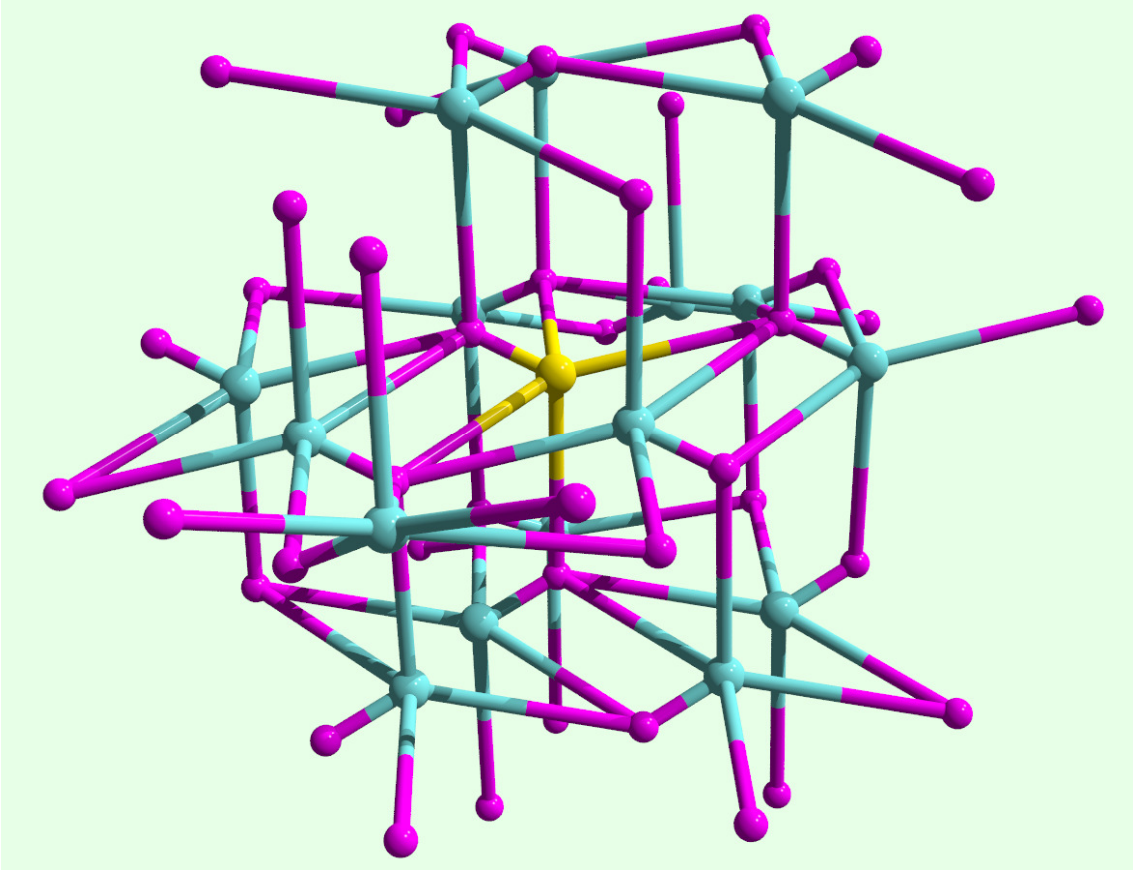

Figure S1. The 5,5-connected network topology representation of PCM-15: P = pink; Tb = turquoise; the central Tb atom is coloured yellow for clarity.

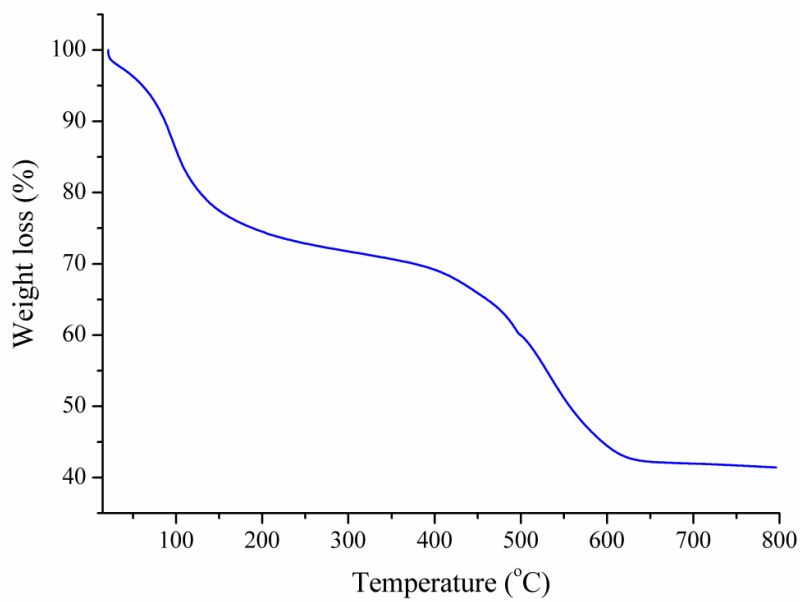

Figure S2. TGA plot for as-synthesized PCM-15 under He carrier gas.

Derivation of the Isosteric Heat of Adsorption

Volumetric CO_2 adsorption was measured from 0−1 bar at 278K and 298K for PCM-15. All the CO_2 sorption isotherms show good reversibility and absence of hysteresis. The isosteric heats of adsorption were determinated by fitting a virial-type equation to both 278 and 298 K adsorption isotherms. The $ln(n/p)$ values for a given amount adsorbed (n) were calculated from the linear regressions from the viral equation analysis using the following viral equation:[1,2]

$$ln(n/p) = A_0 + A_1 n + A_2 n^2 \ldots (1)$$

where p is pressure, n is amount adsorbed and A_0, A_1 etc. are viral coefficients. A_0 is related to adsorbate-adsorbent interactions, while A_1 describes adsorbate-adsorbate interactions.[2] Henry's Law constant (K_H) is equal to $exp(A_0)$, and at low surface coverage, A_2 and higher terms can be ignored. Then, a graph of $ln(n/p)$ versus n should give a straight line at low surface coverage.

The simulation data for CO_2 adsorption at 278 and 298 K for PCM-15 between 50 and 400 mbar using equation (1) are presented in Figures 2S and 3S. All the regression coefficients were larger than 0.998, corroborating that the model fits the data very well. The virial method based on equation (1) is preferred at low pressure because the linearity in the low pressure part of the isotherm provides direct confirmation of the accuracy of the interpolations. Also, the intercept of the graph gives A_0, where the Henry's Law constant $K_H = exp(A_0)$ and this is a measure of the CO_2 surface interaction. The isosteric enthalpy for CO_2 adsorption on PCM-15 was calculated as a function of surface coverage. The estimated error in the measured isosteric enthalpies is 0.1 kJ/mol.

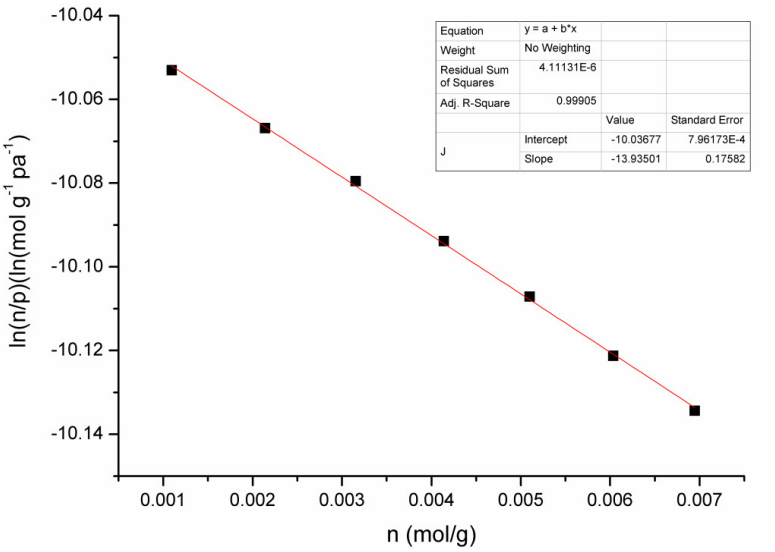

Figure S3A. Virial fitting plots for adsorption of CO_2 on PCM-15 at 278 K.

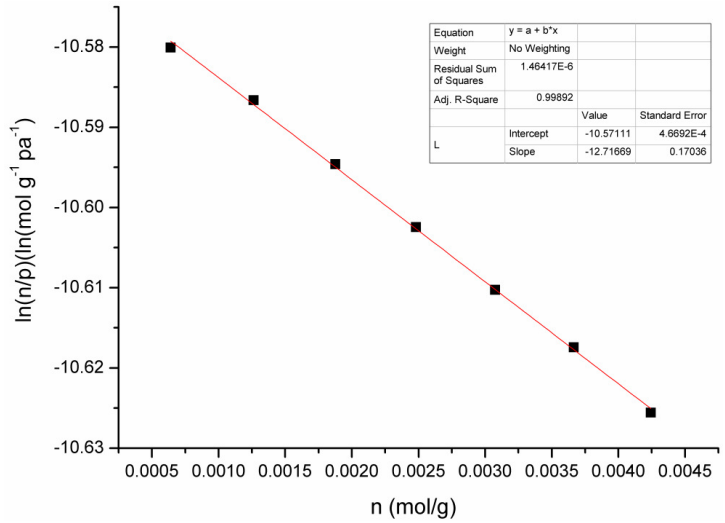

Figure S3B. Virial fitting plots for adsorption of CO_2 on PCM-15 at 298 K

References:

1. (a) X. B. Zhao, S. Villar-Rodil, A. J. Fletcher and K. M. Thomas, *J. Phys. Chem. B*, 2006, **110**, 9947; (b) X. B. Zhao, B. Xiao, A. J. Fletcher and K. M. Thomas, *J. Phys. Chem. B*, 2005, **109**, 8880; (c) I. P. Okoye, M. Benham and K. M. Thomas, *Langmuir*, 1997, **13**, 4054; (d) C. R. Reid, I. P. O'Koye and K. M. Thomas, *Langmuir*, 1998, **14**, 2415; (e) C. R. Reid and K. M. Thomas, *Langmuir*, 1999, **15**, 3206; (f) C. R. Reid and K. M. Thomas, *J. Phys. Chem. B*, 2001, **105**, 10619.
2. J. H. Cole, D. H. Everett, C. T. Marshall, A. R. Paniego, J. C. Powl and Rodrigue.F, *Journal of the Chemical Society-Faraday Transactions I*, 1974, **70**, 2154.

Table 1. Crystal data and structure refinement for sh11018.

Identification code	sh11018	
Empirical formula	C24 H19 N O10 P Tb	
Formula weight	671.29	
Temperature	120(2) K	
Wavelength	0.71075 Å	
Crystal system	Orthorhombic	
Space group	Pccn	
Unit cell dimensions	a = 27.185(5) Å	α= 90°.
	b = 12.100(2) Å	β= 90°.
	c = 20.605(4) Å	γ = 90°.
Volume	6778(2) $Å^3$	
Z	8	
Density (calculated)	1.316 Mg/m^3	
Absorption coefficient	2.177 mm^{-1}	
F(000)	2640	
Crystal size	0.10 x 0.02 x 0.02 mm^3	
Theta range for data collection	3.59 to 25.00°.	
Index ranges	-32<=h<=32, -14<=k<=14, -24<=l<=24	
Reflections collected	60180	
Independent reflections	5944 [R(int) = 0.1849]	
Completeness to theta = 25.00°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.334	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5944 / 10 / 305	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0795, wR2 = 0.1603	
R indices (all data)	R1 = 0.1513, wR2 = 0.1894	
Largest diff. peak and hole	1.310 and -0.826 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for sh11018. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	8921(1)	1218(2)	960(1)	29(1)
Tb(1)	5714(1)	1109(1)	223(1)	30(1)
O(1P)	9202(3)	2079(5)	592(4)	31(2)
O(1)	9176(3)	-4205(6)	360(4)	47(3)
O(2)	9904(3)	-3655(6)	24(4)	42(2)
O(3)	9348(3)	368(6)	4135(3)	42(2)
O(4)	9210(3)	2173(6)	4195(4)	36(2)
O(5)	6410(3)	982(6)	980(4)	36(2)
O(6)	6566(3)	1020(7)	-78(3)	37(2)
O(7)	5251(4)	754(7)	1191(4)	49(3)
C(1)	9085(4)	-156(9)	709(5)	27(3)
C(2)	8734(5)	-969(9)	657(7)	53(4)
C(3)	8877(5)	-2059(10)	519(8)	57(4)
C(4)	9350(4)	-2298(9)	408(5)	29(3)
C(5)	9708(5)	-1480(9)	442(6)	44(3)
C(6)	9565(5)	-426(9)	580(6)	38(3)
C(7)	9492(4)	-3471(9)	254(6)	32(3)
C(8)	9039(5)	1252(8)	1820(5)	32(3)
C(9)	9105(6)	262(11)	2156(6)	58(4)
C(10)	9173(6)	287(10)	2824(6)	51(4)
C(11)	9189(5)	1293(9)	3155(5)	36(3)
C(12)	9152(6)	2261(10)	2807(7)	60(5)
C(13)	9090(6)	2216(9)	2129(6)	48(4)
C(14)	9257(5)	1309(9)	3869(5)	33(3)
C(15)	8275(5)	1265(8)	856(5)	33(3)
C(16)	7930(5)	1179(10)	1374(6)	40(3)
C(17)	7430(5)	1106(11)	1265(6)	45(3)
C(18)	7264(4)	1082(9)	630(5)	33(3)
C(19)	7589(5)	1151(11)	114(6)	45(3)
C(20)	8094(4)	1259(9)	235(6)	37(3)
C(21)	6719(4)	1013(9)	508(6)	32(3)
O(100)	5536(8)	160(20)	2425(11)	210(9)
N(100)	5589(10)	-1030(20)	3345(13)	350(30)

C(102)	5451(10)	-2040(20)	3593(11)	137(9)
C(101)	5850(15)	-270(30)	3719(18)	300(20)
C(100)	5448(11)	-810(30)	2720(13)	310(30)
O(50)	3307(14)	1190(30)	903(16)	148(12)
O(51)	6620(17)	8960(30)	1870(20)	193(17)

Table 3. Bond lengths [Å] and angles [°] for sh11018.

P(1)-O(1P)	1.497(8)
P(1)-C(15)	1.770(13)
P(1)-C(1)	1.797(11)
P(1)-C(8)	1.802(11)
Tb(1)-O(2)#1	2.278(9)
Tb(1)-O(1P)#2	2.333(7)
Tb(1)-O(1)#3	2.340(7)
Tb(1)-O(7)	2.398(8)
Tb(1)-O(6)	2.399(8)
Tb(1)-O(3)#4	2.420(7)
Tb(1)-O(5)	2.457(8)
Tb(1)-O(4)#4	2.486(7)
Tb(1)-C(21)	2.797(12)
Tb(1)-C(14)#4	2.800(11)
O(1P)-Tb(1)#2	2.333(7)
O(1)-C(7)	1.255(14)
O(1)-Tb(1)#3	2.340(7)
O(2)-C(7)	1.238(13)
O(2)-Tb(1)#5	2.278(9)
O(3)-C(14)	1.289(12)
O(3)-Tb(1)#6	2.420(7)
O(4)-C(14)	1.249(12)
O(4)-Tb(1)#6	2.486(7)
O(5)-C(21)	1.287(14)
O(6)-C(21)	1.277(13)
C(1)-C(6)	1.372(16)
C(1)-C(2)	1.375(15)
C(2)-C(3)	1.405(15)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.337(17)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.388(15)
C(4)-C(7)	1.504(15)
C(5)-C(6)	1.362(16)
C(5)-H(5A)	0.9500
C(6)-H(6A)	0.9500

C(8)-C(13)	1.336(15)
C(8)-C(9)	1.395(16)
C(9)-C(10)	1.388(17)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.397(16)
C(10)-H(10H)	0.9500
C(11)-C(12)	1.378(16)
C(11)-C(14)	1.482(15)
C(12)-C(13)	1.409(17)
C(12)-H(12A)	0.9500
C(13)-H(13A)	0.9500
C(14)-Tb(1)#6	2.800(11)
C(15)-C(20)	1.371(15)
C(15)-C(16)	1.425(17)
C(16)-C(17)	1.381(17)
C(16)-H(16A)	0.9500
C(17)-C(18)	1.385(16)
C(17)-H(17A)	0.9500
C(18)-C(19)	1.384(17)
C(18)-C(21)	1.504(16)
C(19)-C(20)	1.403(17)
C(19)-H(19A)	0.9500
C(20)-H(20A)	0.9500
O(100)-C(100)	1.34(2)
N(100)-C(100)	1.37(2)
N(100)-C(102)	1.378(19)
N(100)-C(101)	1.39(2)
C(102)-H(10A)	0.9800
C(102)-H(10B)	0.9800
C(102)-H(10C)	0.9800
C(101)-H(10D)	0.9800
C(101)-H(10E)	0.9800
C(101)-H(10F)	0.9800
C(100)-H(10G)	0.9500

O(1P)-P(1)-C(15)	115.0(5)
O(1P)-P(1)-C(1)	111.8(5)
C(15)-P(1)-C(1)	104.0(5)

O(1P)-P(1)-C(8)	113.0(5)
C(15)-P(1)-C(8)	107.2(6)
C(1)-P(1)-C(8)	105.0(5)
O(2)#1-Tb(1)-O(1P)#2	92.8(3)
O(2)#1-Tb(1)-O(1)#3	105.9(3)
O(1P)#2-Tb(1)-O(1)#3	150.9(3)
O(2)#1-Tb(1)-O(7)	72.6(3)
O(1P)#2-Tb(1)-O(7)	87.0(3)
O(1)#3-Tb(1)-O(7)	77.9(3)
O(2)#1-Tb(1)-O(6)	151.8(3)
O(1P)#2-Tb(1)-O(6)	91.8(3)
O(1)#3-Tb(1)-O(6)	82.2(3)
O(7)-Tb(1)-O(6)	135.5(3)
O(2)#1-Tb(1)-O(3)#4	76.8(3)
O(1P)#2-Tb(1)-O(3)#4	131.1(2)
O(1)#3-Tb(1)-O(3)#4	75.9(3)
O(7)-Tb(1)-O(3)#4	131.9(3)
O(6)-Tb(1)-O(3)#4	79.2(3)
O(2)#1-Tb(1)-O(5)	153.3(3)
O(1P)#2-Tb(1)-O(5)	77.1(3)
O(1)#3-Tb(1)-O(5)	76.3(3)
O(7)-Tb(1)-O(5)	82.2(3)
O(6)-Tb(1)-O(5)	54.4(2)
O(3)#4-Tb(1)-O(5)	128.3(3)
O(2)#1-Tb(1)-O(4)#4	80.0(3)
O(1P)#2-Tb(1)-O(4)#4	77.5(2)
O(1)#3-Tb(1)-O(4)#4	127.0(3)
O(7)-Tb(1)-O(4)#4	147.6(3)
O(6)-Tb(1)-O(4)#4	74.0(3)
O(3)#4-Tb(1)-O(4)#4	53.8(3)
O(5)-Tb(1)-O(4)#4	120.6(3)
O(2)#1-Tb(1)-C(21)	175.1(3)
O(1P)#2-Tb(1)-C(21)	82.8(3)
O(1)#3-Tb(1)-C(21)	79.0(3)
O(7)-Tb(1)-C(21)	109.3(3)
O(6)-Tb(1)-C(21)	27.1(3)
O(3)#4-Tb(1)-C(21)	104.4(3)
O(5)-Tb(1)-C(21)	27.4(3)

O(4)#4-Tb(1)-C(21)	96.9(3)
O(2)#1-Tb(1)-C(14)#4	78.1(3)
O(1P)#2-Tb(1)-C(14)#4	104.0(3)
O(1)#3-Tb(1)-C(14)#4	101.7(3)
O(7)-Tb(1)-C(14)#4	149.2(3)
O(6)-Tb(1)-C(14)#4	73.7(3)
O(3)#4-Tb(1)-C(14)#4	27.4(3)
O(5)-Tb(1)-C(14)#4	128.1(3)
O(4)#4-Tb(1)-C(14)#4	26.5(3)
C(21)-Tb(1)-C(14)#4	100.7(4)
P(1)-O(1P)-Tb(1)#2	150.3(5)
C(7)-O(1)-Tb(1)#3	126.1(8)
C(7)-O(2)-Tb(1)#5	169.7(8)
C(14)-O(3)-Tb(1)#6	93.0(7)
C(14)-O(4)-Tb(1)#6	90.9(6)
C(21)-O(5)-Tb(1)	91.2(7)
C(21)-O(6)-Tb(1)	94.1(7)
C(6)-C(1)-C(2)	118.3(11)
C(6)-C(1)-P(1)	120.9(8)
C(2)-C(1)-P(1)	120.8(9)
C(1)-C(2)-C(3)	119.7(12)
C(1)-C(2)-H(2A)	120.2
C(3)-C(2)-H(2A)	120.2
C(4)-C(3)-C(2)	120.3(12)
C(4)-C(3)-H(3A)	119.9
C(2)-C(3)-H(3A)	119.9
C(3)-C(4)-C(5)	120.7(11)
C(3)-C(4)-C(7)	119.0(10)
C(5)-C(4)-C(7)	120.3(11)
C(6)-C(5)-C(4)	118.6(12)
C(6)-C(5)-H(5A)	120.7
C(4)-C(5)-H(5A)	120.7
C(5)-C(6)-C(1)	122.3(11)
C(5)-C(6)-H(6A)	118.9
C(1)-C(6)-H(6A)	118.9
O(2)-C(7)-O(1)	123.9(10)
O(2)-C(7)-C(4)	118.9(10)
O(1)-C(7)-C(4)	117.2(10)

C(13)-C(8)-C(9)	120.0(11)
C(13)-C(8)-P(1)	120.5(8)
C(9)-C(8)-P(1)	119.5(8)
C(10)-C(9)-C(8)	119.4(11)
C(10)-C(9)-H(9A)	120.3
C(8)-C(9)-H(9A)	120.3
C(9)-C(10)-C(11)	120.5(11)
C(9)-C(10)-H(10H)	119.7
C(11)-C(10)-H(10H)	119.7
C(12)-C(11)-C(10)	119.0(11)
C(12)-C(11)-C(14)	120.9(10)
C(10)-C(11)-C(14)	120.1(10)
C(11)-C(12)-C(13)	119.5(11)
C(11)-C(12)-H(12A)	120.3
C(13)-C(12)-H(12A)	120.3
C(8)-C(13)-C(12)	121.3(11)
C(8)-C(13)-H(13A)	119.4
C(12)-C(13)-H(13A)	119.4
O(4)-C(14)-O(3)	122.1(10)
O(4)-C(14)-C(11)	122.2(9)
O(3)-C(14)-C(11)	115.7(10)
O(4)-C(14)-Tb(1)#6	62.6(6)
O(3)-C(14)-Tb(1)#6	59.6(5)
C(11)-C(14)-Tb(1)#6	172.1(9)
C(20)-C(15)-C(16)	117.7(12)
C(20)-C(15)-P(1)	117.9(10)
C(16)-C(15)-P(1)	124.0(9)
C(17)-C(16)-C(15)	122.0(12)
C(17)-C(16)-H(16A)	119.0
C(15)-C(16)-H(16A)	119.0
C(16)-C(17)-C(18)	118.4(12)
C(16)-C(17)-H(17A)	120.8
C(18)-C(17)-H(17A)	120.8
C(17)-C(18)-C(19)	121.2(12)
C(17)-C(18)-C(21)	118.6(11)
C(19)-C(18)-C(21)	120.2(11)
C(18)-C(19)-C(20)	119.6(11)
C(18)-C(19)-H(19A)	120.2

C(20)-C(19)-H(19A)	120.2
C(15)-C(20)-C(19)	121.1(12)
C(15)-C(20)-H(20A)	119.5
C(19)-C(20)-H(20A)	119.5
O(6)-C(21)-O(5)	120.1(11)
O(6)-C(21)-C(18)	118.6(11)
O(5)-C(21)-C(18)	121.3(11)
O(6)-C(21)-Tb(1)	58.8(6)
O(5)-C(21)-Tb(1)	61.4(6)
C(18)-C(21)-Tb(1)	173.9(8)
C(100)-N(100)-C(102)	116.4(17)
C(100)-N(100)-C(101)	122.4(17)
C(102)-N(100)-C(101)	121.1(17)
N(100)-C(102)-H(10A)	109.5
N(100)-C(102)-H(10B)	109.5
H(10A)-C(102)-H(10B)	109.5
N(100)-C(102)-H(10C)	109.5
H(10A)-C(102)-H(10C)	109.5
H(10B)-C(102)-H(10C)	109.5
N(100)-C(101)-H(10D)	109.5
N(100)-C(101)-H(10E)	109.5
H(10D)-C(101)-H(10E)	109.5
N(100)-C(101)-H(10F)	109.5
H(10D)-C(101)-H(10F)	109.5
H(10E)-C(101)-H(10F)	109.5
O(100)-C(100)-N(100)	123(2)
O(100)-C(100)-H(10G)	118.4
N(100)-C(100)-H(10G)	118.4

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,y+1/2,-z #2 -x+3/2,-y+1/2,z #3 -x+3/2,-y-1/2,z

#4 -x+3/2,y,z-1/2 #5 x+1/2,y-1/2,-z #6 -x+3/2,y,z+1/2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sh11018. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	33(2)	18(1)	35(2)	-3(1)	-5(1)	3(1)
Tb(1)	32(1)	20(1)	37(1)	3(1)	0(1)	-2(1)
O(1P)	29(5)	18(4)	45(4)	0(3)	-3(4)	0(3)
O(1)	65(7)	16(4)	61(6)	-7(4)	19(5)	-14(4)
O(2)	34(5)	24(4)	67(5)	-21(4)	4(4)	0(4)
O(3)	62(7)	33(5)	31(4)	7(4)	-5(4)	6(5)
O(4)	35(6)	24(4)	50(5)	1(4)	6(4)	5(4)
O(5)	38(5)	31(5)	40(5)	-1(4)	0(4)	-2(4)
O(6)	43(5)	48(5)	21(4)	-1(4)	-5(4)	13(4)
O(7)	60(7)	52(6)	35(5)	-3(4)	13(4)	-8(5)
C(1)	14(6)	21(6)	44(7)	-3(5)	-15(5)	-1(5)
C(2)	34(8)	15(6)	111(11)	-24(7)	18(8)	-3(6)
C(3)	24(8)	23(7)	125(13)	-14(7)	15(8)	-1(6)
C(5)	36(8)	20(6)	76(9)	-11(6)	13(7)	-12(6)
C(6)	37(9)	20(6)	57(8)	0(6)	-9(7)	-7(6)
C(7)	26(7)	30(6)	39(7)	-15(6)	13(6)	6(5)
C(8)	51(8)	11(5)	36(6)	-2(5)	-7(6)	7(5)
C(9)	93(13)	36(8)	46(8)	-16(6)	-19(8)	1(8)
C(10)	81(13)	28(7)	44(8)	14(6)	-1(7)	11(7)
C(11)	47(9)	32(7)	30(6)	7(5)	-14(6)	16(6)
C(12)	92(14)	19(7)	69(10)	-3(6)	-7(9)	-11(7)
C(13)	91(12)	21(6)	32(7)	12(5)	-16(7)	-7(7)
C(14)	28(7)	35(7)	36(6)	11(5)	-8(6)	24(6)
C(15)	43(8)	16(6)	41(7)	-5(5)	-9(6)	-5(5)
C(16)	41(8)	35(7)	43(7)	-3(6)	-2(6)	6(7)
C(17)	44(9)	47(8)	43(8)	-3(7)	1(6)	7(7)
C(18)	32(7)	30(6)	37(7)	-6(6)	3(6)	-3(6)
C(19)	45(9)	53(8)	37(7)	-17(7)	-13(6)	18(7)
C(20)	35(7)	39(7)	35(6)	3(6)	1(6)	12(6)
C(21)	29(7)	22(6)	46(7)	9(6)	-2(6)	3(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for sh11018.

	x	y	z	U(eq)
H(2A)	8396	-795	714	64
H(3A)	8638	-2630	505	69
H(5A)	10044	-1651	371	53
H(6A)	9807	141	586	45
H(9A)	9103	-423	1930	70
H(10H)	9210	-386	3057	62
H(12A)	9168	2954	3023	72
H(13A)	9084	2883	1886	58
H(16A)	8048	1171	1808	48
H(17A)	7205	1073	1618	53
H(19A)	7470	1125	-319	54
H(20A)	8315	1329	-120	44
H(10A)	5255	-2439	3269	205
H(10B)	5253	-1928	3986	205
H(10C)	5745	-2470	3700	205
H(10D)	5917	390	3461	453
H(10E)	6161	-606	3858	453
H(10F)	5655	-72	4101	453
H(10G)	5280	-1368	2485	374

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