Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

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Crystallographic data of $Cs_2[W_6I_{14}]$

Table 1. Crystal data and structure refinement for $Cs_2W_6I_{14}$.

Empirical formula	$Cs_2\ I_{14}\ W_6$
ICSD No.	429577
Formula weight	3145.52
Temperature	293(2) K
Wavelength	71.073 pm
Crystal system	Trigonal
Space group	P $\bar{3}$1c (No. 163)
Unit cell dimensions	a = 1078.31(9) pm
	b = 1078.31(9) pm
	c = 1618.8(2) pm
Volume	1.6301(3) nm^3
Z	2
Density (calculated)	6.409 g/cm^3
Absorption coefficient	36.536 mm^{-1}
F(000)	2592
Crystal size	0.018 x 0.012 x 0.012 mm^3
Theta range for data collection	3.331 to 25.091°.
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-19 \le l \le 19$
Reflections collected	15572
Independent reflections	969 [R(int) = 0.0376]
Completeness to theta = 25.091°	99.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	969 / 0 / 35
Goodness-of-fit on F^2	1.206
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0401, wR_2 = 0.0705
R indices (all data)	R_1 = 0.0501, wR_2 = 0.0744
Largest diff. peak and hole	1.156 and -2.391 e.$Å^{-3}$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for $Cs_2W_6I_{14}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
W(1)	0.5242(1)	0.3342(1)	0.6831(1)	33(1)
I(1)	⅔	⅓	0.5400(1)	42(1)
I(2)	0.3650(1)	0.0356(1)	0.6777(1)	44(1)
I(3)	0.3110(1)	0.3429(2)	0.5852(1)	57(1)
Cs(1)	⅓	-⅓	¾	115(2)
Cs(2)	0	0	½	120(2)

Table 3. Bond lengths [pm] and angles [°] for $Cs_2W_6I_{14}$.

W(1)-W(1)#1	265.0(1)
W(1)-W(1)#2	266.7(1)
W(1)-W(1)#3	266.9(1)
W(1)-W(1)#4	266.9(1)
W(1)-I(1)	278.2(2)
W(1)-I(2)	279.2(1)
W(1)-I(2)#4	281.0(1)
W(1)-I(2)#2	281.7(1)
W(1)-I(3)	283.2(1)
I(1)-W(1)#4	278.2(2)
I(1)-W(1)#3	278.2(2)
I(2)-W(1)#3	281.0(1)
I(2)-W(1)#2	281.7(1)
I(2)-Cs(1)	399.4(1)
I(3)-Cs(2)	379.8(1)
I(3)-Cs(1)#5	430.4(1)
Cs(1)-I(2)#6	399.4(1)
Cs(1)-I(2)#7	399.4(1)
Cs(1)-I(2)#8	399.4(1)
Cs(1)-I(2)#9	399.4(1)
Cs(1)-I(2)#10	399.4(1)
Cs(1)-I(3)#2	430.4(1)
Cs(1)-I(3)#11	430.4(1)
Cs(1)-I(3)#12	430.4(1)
Cs(1)-I(3)#3	430.4(1)

Cs(1)-I(3)#13	430.4(1)
Cs(1)-I(3)#14	430.4(1)
Cs(2)-I(3)#15	379.8(1)
Cs(2)-I(3)#16	379.8(1)
Cs(2)-I(3)#17	379.8(1)
Cs(2)-I(3)#18	379.8(1)
Cs(2)-I(3)#11	379.8(1)

W(1)#1-W(1)-W(1)#2	60.25(3)
W(1)#1-W(1)-W(1)#3	90.18(2)
W(1)#2-W(1)-W(1)#3	59.56(3)
W(1)#1-W(1)-W(1)#4	60.19(3)
W(1)#2-W(1)-W(1)#4	89.82(2)
W(1)#3-W(1)-W(1)#4	60.0
W(1)#1-W(1)-I(1)	121.51(4)
W(1)#2-W(1)-I(1)	120.89(4)
W(1)#3-W(1)-I(1)	61.34(2)
W(1)#4-W(1)-I(1)	61.34(2)
W(1)#1-W(1)-I(2)	122.31(4)
W(1)#2-W(1)-I(2)	62.09(3)
W(1)#3-W(1)-I(2)	61.89(4)
W(1)#4-W(1)-I(2)	121.85(4)
I(1)-W(1)-I(2)	89.56(3)
W(1)#1-W(1)-I(2)#4	62.04(3)
W(1)#2-W(1)-I(2)#4	122.29(4)
W(1)#3-W(1)-I(2)#4	121.18(4)
W(1)#4-W(1)-I(2)#4	61.22(4)
I(1)-W(1)-I(2)#4	89.20(3)
I(2)-W(1)-I(2)#4	175.31(4)
W(1)#1-W(1)-I(2)#2	61.76(3)
W(1)#2-W(1)-I(2)#2	61.14(3)
W(1)#3-W(1)-I(2)#2	120.67(3)
W(1)#4-W(1)-I(2)#2	121.95(3)
I(1)-W(1)-I(2)#2	176.57(4)
I(2)-W(1)-I(2)#2	89.21(4)
I(2)#4-W(1)-I(2)#2	91.78(4)
W(1)#1-W(1)-I(3)	132.97(3)
W(1)#2-W(1)-I(3)	135.27(3)
W(1)#3-W(1)-I(3)	136.85(4)
W(1)#4-W(1)-I(3)	134.86(4)
I(1)-W(1)-I(3)	89.60(4)

I(2)-W(1)-I(3)	88.84(4)
I(2)#4-W(1)-I(3)	86.64(4)
I(2)#2-W(1)-I(3)	87.18(4)
W(1)#4-I(1)-W(1)#3	57.33(4)
W(1)#4-I(1)-W(1)	57.33(4)
W(1)#3-I(1)-W(1)	57.33(4)
W(1)-I(2)-W(1)#3	56.90(3)
W(1)-I(2)-W(1)#2	56.78(3)
W(1)#3-I(2)-W(1)#2	56.20(3)
W(1)-I(2)-Cs(1)	146.80(4)
W(1)#3-I(2)-Cs(1)	94.58(3)
W(1)#2-I(2)-Cs(1)	94.46(3)
W(1)-I(3)-Cs(2)	120.49(5)
W(1)-I(3)-Cs(1)#5	87.88(3)
Cs(2)-I(3)-Cs(1)#5	132.76(3)
I(2)#6-Cs(1)-I(2)#7	171.49(3)
I(2)#6-Cs(1)-I(2)#8	111.80(1)
I(2)#7-Cs(1)-I(2)#8	60.77(3)
I(2)#6-Cs(1)-I(2)#9	111.80(1)
I(2)#7-Cs(1)-I(2)#9	75.92(3)
I(2)#8-Cs(1)-I(2)#9	111.80(1)
I(2)#6-Cs(1)-I(2)#10	75.92(3)
I(2)#7-Cs(1)-I(2)#10	111.80(1)
I(2)#8-Cs(1)-I(2)#10	171.49(3)
I(2)#9-Cs(1)-I(2)#10	60.77(3)
I(2)#6-Cs(1)-I(2)	60.77(3)
I(2)#7-Cs(1)-I(2)	111.80(1)
I(2)#8-Cs(1)-I(2)	75.92(3)
I(2)#9-Cs(1)-I(2)	171.49(3)
I(2)#10-Cs(1)-I(2)	111.80(1)
I(2)#6-Cs(1)-I(3)#2	55.46(2)
I(2)#7-Cs(1)-I(3)#2	117.57(2)
I(2)#8-Cs(1)-I(3)#2	56.89(2)
I(2)#9-Cs(1)-I(3)#2	124.66(2)
I(2)#10-Cs(1)-I(3)#2	130.04(2)
I(2)-Cs(1)-I(3)#2	55.84(2)
I(2)#6-Cs(1)-I(3)#11	117.57(2)
I(2)#7-Cs(1)-I(3)#11	55.46(2)
I(2)#8-Cs(1)-I(3)#11	55.84(2)
I(2)#9-Cs(1)-I(3)#11	130.04(2)
I(2)#10-Cs(1)-I(3)#11	124.66(2)

I(2)-Cs(1)-I(3)#11	56.89(2)
I(3)#2-Cs(1)-I(3)#11	90.74(3)
I(2)#6-Cs(1)-I(3)#12	124.66(2)
I(2)#7-Cs(1)-I(3)#12	55.84(2)
I(2)#8-Cs(1)-I(3)#12	55.46(2)
I(2)#9-Cs(1)-I(3)#12	56.89(2)
I(2)#10-Cs(1)-I(3)#12	117.57(2)
I(2)-Cs(1)-I(3)#12	130.04(2)
I(3)#2-Cs(1)-I(3)#12	85.63(2)
I(3)#11-Cs(1)-I(3)#12	98.29(3)
I(2)#6-Cs(1)-I(3)#3	55.84(2)
I(2)#7-Cs(1)-I(3)#3	124.66(2)
I(2)#8-Cs(1)-I(3)#3	130.04(2)
I(2)#9-Cs(1)-I(3)#3	117.57(2)
I(2)#10-Cs(1)-I(3)#3	56.89(2)
I(2)-Cs(1)-I(3)#3	55.46(2)
I(3)#2-Cs(1)-I(3)#3	98.29(3)
I(3)#11-Cs(1)-I(3)#3	85.63(2)
I(3)#12-Cs(1)-I(3)#3	174.45(3)
I(2)#6-Cs(1)-I(3)#13	56.89(2)
I(2)#7-Cs(1)-I(3)#13	130.04(2)
I(2)#8-Cs(1)-I(3)#13	124.66(2)
I(2)#9-Cs(1)-I(3)#13	55.46(2)
I(2)#10-Cs(1)-I(3)#13	55.84(2)
I(2)-Cs(1)-I(3)#13	117.57(2)
I(3)#2-Cs(1)-I(3)#13	85.63(2)
I(3)#11-Cs(1)-I(3)#13	174.45(3)
I(3)#12-Cs(1)-I(3)#13	85.63(2)
I(3)#3-Cs(1)-I(3)#13	90.74(4)
I(2)#6-Cs(1)-I(3)#14	130.04(2)
I(2)#7-Cs(1)-I(3)#14	56.89(2)
I(2)#8-Cs(1)-I(3)#14	117.57(2)
I(2)#9-Cs(1)-I(3)#14	55.84(2)
I(2)#10-Cs(1)-I(3)#14	55.46(2)
I(2)-Cs(1)-I(3)#14	124.66(2)
I(3)#2-Cs(1)-I(3)#14	174.45(3)
I(3)#11-Cs(1)-I(3)#14	85.63(2)
I(3)#12-Cs(1)-I(3)#14	90.74(4)
I(3)#3-Cs(1)-I(3)#14	85.63(2)
I(3)#13-Cs(1)-I(3)#14	98.29(3)
I(3)-Cs(2)-I(3)#15	180.0

I(3)-Cs(2)-I(3)#16	72.42(2)
I(3)#15-Cs(2)-I(3)#16	107.58(2)
I(3)-Cs(2)-I(3)#17	107.58(2)
I(3)#15-Cs(2)-I(3)#17	72.42(2)
I(3)#16-Cs(2)-I(3)#17	180.00(2)
I(3)-Cs(2)-I(3)#18	72.42(2)
I(3)#15-Cs(2)-I(3)#18	107.58(2)
I(3)#16-Cs(2)-I(3)#18	107.58(2)
I(3)#17-Cs(2)-I(3)#18	72.42(2)
I(3)-Cs(2)-I(3)#11	107.58(2)
I(3)#15-Cs(2)-I(3)#11	72.42(2)
I(3)#16-Cs(2)-I(3)#11	72.42(2)
I(3)#17-Cs(2)-I(3)#11	107.58(2)
I(3)#18-Cs(2)-I(3)#11	180.0

Symmetry transformations used to generate equivalent atoms:

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

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

#7 -y,x-y-1,z #8 -y,-x,-z+3/2 #9 x,x-y-1,-z+3/2

#10 -x+y+1,-x,z #11 -x+y,-x,z #12 -x+y,y-1,-z+3/2

#13 -y+1,-x,-z+3/2 #14 x,y-1,z #15 -x,-y,-z+1

#16 y,-x+y,-z+1 #17 -y,x-y,z #18 x-y,x,-z+1

Table 4. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$) for $Cs_2W_6I_{14}$. 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}
W(1)	31(1)	33(1)	37(1)	2(1)	-1(1)	17(1)
I(1)	45(1)	45(1)	36(1)	0	0	22(1)
I(2)	35(1)	37(1)	53(1)	-4(1)	-7(1)	12(1)
I(3)	49(1)	68(1)	62(1)	4(1)	-11(1)	34(1)
Cs(1)	74(2)	74(2)	198(5)	0	0	37(1)
Cs(2)	63(1)	63(1)	232(6)	0	0	32(1)

Crystallographic data of $(TBA)_2[W_6I_{14}]$

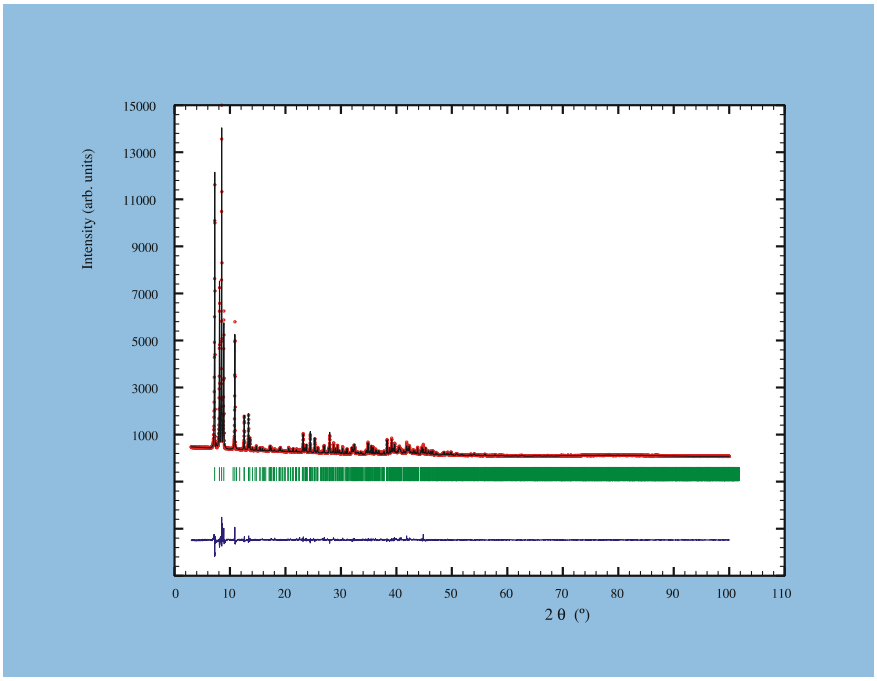

Figure 1: Powder XRD refinement pattern of $(NC_{16}H_{36})_2W_6I_{14}$ (*P* 2_1/n) (red) with the corresponding theoretical peaks (black), the Bragg positions (green) and the difference curve (blue) after Rietveld refinement.

Table 5. Crystal data and structure refinement for $(NC_{16}H_{36})_2W_6I_{14}$.

Empirical formula	$(NC_{16}H_{36})_2W_6I_{14}$
CCDC No.	1063061
Formula weight	3122.23 g/mol
Temperature	298(2) K
Wavelength	1.54060 Å
Crystal system	Monoclinic
Space group	*P* 2_1/n (No. 14)
Unit cell dimensions	a = 11.5768(2) Å
	b = 11.4916(3) Å
	c = 24.5672(5) Å
	β = 96.776(2)°
Volume	3245.5(1) $Å^3$
Z	2
μ (CuKa)	70.649 mm^{-1}
Density (calculated)	3.44 gcm^{-3}
Theta range for data collection	1.5 to 50 °
Total number of reflections	3475
Refined parameters	105
Number of restraints (only for TBA)	53
Refined structure parameters	92
R_p, R_{wp}	4.7759, 6.3352
R_{Bragg}	6.187
χ^2	1.0404

Table 6. Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for $(NC_{16}H_{36})_2W_6I_{14}$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
W1	0.4440(4)	0.0664(4)	0.5645(2)	0.0558(4)
W2	0.6496(4)	0.0665(4)	0.5169(2)	0.0529(4)
W3	0.4448(4)	0.1243(3)	0.4603(2)	0.0545(4)
I1	0.6480(5)	0.0036(6)	0.6280(2)	0.0946(6)
I2	0.5414(6)	0.2727(4)	0.5442(3)	0.0763(6)
I3	0.2407(6)	0.1358(7)	0.5057(3)	0.0827(6)
I4	0.3463(5)	0.8459(6)	0.5906(2)	0.0575(5)
I5	0.3565(5)	0.1574(6)	0.6614(2)	0.0939(6)
I6	0.8723(6)	0.1529(6)	0.5461(2)	0.1085(6)
I7	0.3772(6)	0.3259(6)	0.3930(3)	0.1359(7)
N1	0.49052(8)	0.97433(8)	0.82997(3)	0.073(1)
C1	0.42405(7)	0.91814(8)	0.78936(3)	0.073(1)
C2	0.44472(8)	0.79247(7)	0.79575(4)	0.073(1)
C3	0.39323(8)	0.72942(8)	0.74553(3)	0.073(1)
C4	0.40370(8)	0.59936(7)	0.74116(4)	0.073(1)
C5	0.60509(7)	0.94961(8)	0.83697(4)	0.073(1)
C6	0.66466(8)	0.96549(8)	0.78852(4)	0.073(1)
C7	0.78198(7)	0.91687(8)	0.78768(4)	0.073(1)
C8	0.79759(8)	0.80274(7)	0.78174(4)	0.073(1)
C9	0.46647(8)	0.94486(8)	0.88080(3)	0.073(1)
C10	0.34333(7)	0.98464(8)	0.87947(3)	0.073(1)
C11	0.3232(1)	0.96165(9)	0.93849(3)	0.073(1)
C12	0.25196(8)	0.98757(8)	0.96765(3)	0.073(1)
C13	0.45686(8)	0.08037(7)	0.81064(4)	0.073(1)
C14	0.50521(8)	0.16872(8)	0.85083(4)	0.073(1)
C15	0.45641(8)	0.28635(7)	0.83457(4)	0.073(1)
C16	0.48221(8)	0.39744(7)	0.86660(4)	0.073(1)

Table 7. Selected Bond lengths [Å] for $(NC_{16}H_{36})_2W_6I_{14}$.

W1	W2	2.773(7)
W1	W2	2.645(6)
W1	W3	2.647(7)
W1	W3	2.649(6)
W1	I1	2.768(7)
W1	I2	2.697(7)
W1	I3	2.732(8)
W1	I4	2.878(8)
W1	I5	2.890(7)
W2	W3	2.687(6)
W2	W3	2.542(6)
W2	I1	2.826(7)
W2	I2	2.799(7)
W2	I3	2.737(9)
W2	I4	2.832(7)
W2	I6	2.777(8)
W3	I1	2.733(7)
W3	I2	2.804(7)
W3	I3	2.732(9)
W3	I4	2.871(8)
W3	I7	2.900(8)

Table 8. Hydrogen coordinates and isotropic displacement parameters (pm2x 10 -1) for $(NC_{16}H_{36})_2W_6I_{14}$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
H1	0.44400	0.92786	0.75164	0.073(1)
H2	0.33904	0.91568	0.78582	0.073(1)
H3	0.40898	0.74111	0.82231	0.073(1)
H4	0.52512	0.75591	0.79593	0.073(1)
H5	0.30422	0.72572	0.73468	0.073(1)
H6	0.41906	0.74333	0.70779	0.073(1)
H7	0.37087	0.54723	0.70736	0.073(1)
H8	0.37406	0.54864	0.77127	0.073(1)
H9	0.48910	0.56624	0.74448	0.073(1)
H10	0.65124	0.00302	0.86400	0.073(1)
H11	0.62510	0.87111	0.85021	0.073(1)
H12	0.67678	0.04548	0.77665	0.073(1)
H13	0.62290	0.92595	0.75525	0.073(1)
H14	0.83154	0.94607	0.75858	0.073(1)
H15	0.83623	0.93108	0.82208	0.073(1)
H16	0.87484	0.76285	0.78257	0.073(1)
H17	0.75391	0.76677	0.74655	0.073(1)
H18	0.76010	0.75178	0.81015	0.073(1)
H19	0.45029	0.86588	0.89343	0.073(1)
H20	0.49499	0.98913	0.91483	0.073(1)
H21	0.26810	0.94003	0.86676	0.073(1)
H22	0.31150	0.06852	0.88146	0.073(1)
H23	0.30701	0.88107	0.95684	0.073(1)
H24	0.37286	0.99638	0.97316	0.073(1)
H25	0.24755	0.96609	0.00893	0.073(1)
H26	0.16503	0.96086	0.95356	0.073(1)
H27	0.23248	0.07687	0.97087	0.073(1)
H28	0.49389	0.11651	0.78073	0.073(1)
H29	0.37795	0.11289	0.80722	0.073(1)
H30	0.59008	0.19821	0.85588	0.073(1)
H31	0.48561	0.17588	0.89006	0.073(1)
H32	0.47444	0.32811	0.79839	0.073(1)
H33	0.36887	0.30436	0.83127	0.073(1)
H34	0.45269	0.47994	0.85649	0.073(1)
H35	0.57202	0.41766	0.87384	0.073(1)
H36	0.46625	0.39411	0.90672	0.073(1)

Crystallographic data of $(TBA)_2[W_6I_8(CF_3COO)_6]$

Table 9. Crystal data and structure refinement for $[W_6I_8(CF_3COO)_6](TBA)_2$.

Empirical formula	C44 H72 F18 I8 N2 O12 W6	
Formula weight	3281.33	
Temperature	243(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 1308.62(4) pm	α= 114.963(2)°.
	b = 1321.46(4) pm	β= 102.910(3)°.
	c = 1335.44(4) pm	γ = 102.138(3)°.
Volume	1.9157(1) nm^3	
Z	1	
Density (calculated)	2.844 g/cm^3	
Absorption coefficient	12.285 mm^{-1}	
F(000)	1476	
Crystal size	0.2 x 0.1 x 0.1 mm^3	
Theta range for data collection	2.877 to 25.026°	
Index ranges	$-15 \le h \le 15$, $-15 \le k \le 15$, $-15 \le l \le 15$	
Reflections collected	17913	
Independent reflections	6690 [R(int) = 0.0188]	
Completeness to theta = 25.026°	98.8 %	
Absorption correction	Numerical	
Max. and min. transmission	0.4031 and 0.1180	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6690 / 2 / 462	
Goodness-of-fit on F^2	1.186	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0348, wR2 = 0.0763	
R indices (all data)	R1 = 0.0398, wR2 = 0.0786	
Largest diff. peak and hole	0.667 and -0.592 e.Å-3	

Table 10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for $[W_6I_8(CF_3COO)_6](TBA)_2$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
W(1)	899(1)	1206(1)	-138(1)	45(1)
W(2)	1270(1)	-335(1)	557(1)	45(1)
W(3)	216(1)	1099(1)	1548(1)	44(1)
I(1)	2072(1)	-244(1)	-1198(1)	54(1)
I(2)	2509(1)	2068(1)	2074(1)	54(1)
I(3)	-163(1)	2782(1)	911(1)	55(1)
I(4)	-626(1)	463(1)	-2373(1)	55(1)
O(1)	1910(5)	2474(5)	-402(5)	61(2)
C(1)	2503(8)	3553(9)	229(9)	63(2)
O(2)	2561(7)	4242(7)	1217(7)	92(2)
C(2)	3202(11)	3985(11)	-343(13)	87(3)
F(1)	2659(10)	3712(12)	-1404(11)	183(5)
F(2)	3959(10)	3543(13)	-454(15)	211(7)
F(3)	3698(12)	5088(8)	186(12)	210(6)
O(3)	2671(5)	-812(6)	1060(5)	61(2)
C(3)	3391(7)	-568(8)	2022(8)	57(2)
O(4)	3538(6)	129(7)	3024(6)	85(2)
C(4)	4132(8)	-1319(9)	1791(9)	66(2)
F(4)	4598(6)	-1388(7)	2754(7)	102(2)
F(5)	3605(5)	-2416(5)	925(6)	93(2)
F(6)	4976(5)	-837(6)	1565(7)	92(2)
O(5)	393(5)	2261(5)	3303(5)	58(1)
C(5)	960(8)	3350(8)	4049(8)	60(2)
O(6)	1585(6)	4087(6)	3927(7)	82(2)
C(6)	788(9)	3728(9)	5202(9)	73(3)
F(7)	-222(7)	3699(10)	5118(8)	153(4)
F(8)	1397(9)	4798(9)	5993(7)	167(5)
F(9)	919(13)	3060(11)	5637(9)	200(6)
N(1)	3207(6)	7401(7)	4694(6)	61(2)
C(7)	3342(9)	8681(9)	5126(9)	69(3)
C(8)	2380(12)	9049(12)	5397(13)	83(3)
C(9)	2602(11)	10343(11)	5721(13)	86(4)
C(10)	1672(13)	10774(14)	6001(14)	118(5)
C(11)	3020(8)	7037(9)	5588(8)	63(2)
C(12)	3971(9)	7682(11)	6769(9)	84(3)
C(13)	3711(11)	7243(13)	7585(10)	99(4)
C(14)	4577(14)	7811(19)	8717(14)	156(8)

C(15)	2172(9)	6611(9)	3585(8)	63(2)
C(16)	2100(11)	6897(11)	2587(10)	79(3)
C(17)	1019(11)	6079(11)	1546(10)	80(3)
C(18)	-41(10)	6104(11)	1799(11)	96(4)
C(19)	4251(10)	7236(12)	4463(11)	78(3)
C(20)	4364(12)	6033(13)	4117(13)	108(4)
C(21)	5580(20)	6020(30)	4080(20)	232(16)
C(22)	5650(30)	6060(30)	3150(30)	259(15)

Table 11. Bond lengths [pm] and angles [°] for $[W_6I_8(CF_3COO)_6](TBA)_2$.

W(1)-O(1)	211.2(6)
W(1)-W(3)	264.67(4)
W(1)-W(3)#1	264.88(5)
W(1)-W(2)	265.57(5)
W(1)-W(2)#1	265.80(5)
W(1)-I(2)	279.81(6)
W(1)-I(3)	280.30(7)
W(1)-I(4)	281.00(6)
W(1)-I(1)	281.92(7)
W(2)-O(3)	212.2(6)
W(2)-W(3)#1	265.31(5)
W(2)-W(3)	265.41(5)
W(2)-W(1)#1	265.80(5)
W(2)-I(2)	278.48(6)
W(2)-I(3)#1	279.42(6)
W(2)-I(4)#1	279.60(6)
W(2)-I(1)	280.94(6)
W(3)-O(5)	211.4(6)
W(3)-W(1)#1	264.88(5)
W(3)-W(2)#1	265.30(5)
W(3)-I(3)	279.09(6)
W(3)-I(2)	279.71(6)
W(3)-I(4)#1	280.77(6)
W(3)-I(1)#1	282.24(6)
I(1)-W(3)#1	282.24(6)
I(3)-W(2)#1	279.41(6)
I(4)-W(2)#1	279.61(6)
I(4)-W(3)#1	280.76(6)
O(1)-C(1)	125.4(11)
C(1)-O(2)	121.9(12)
C(1)-C(2)	148.5(14)
C(2)-F(3)	125.5(14)
C(2)-F(2)	125.7(15)
C(2)-F(1)	128.6(16)
O(3)-C(3)	127.5(10)
C(3)-O(4)	120.2(11)
C(3)-C(4)	151.7(13)
C(4)-F(5)	131.2(11)
C(4)-F(6)	131.6(11)
C(4)-F(4)	134.4(11)

O(5)-C(5)	127.5(11)
C(5)-O(6)	122.6(11)
C(5)-C(6)	149.2(14)
C(6)-F(9)	126.3(14)
C(6)-F(8)	128.0(12)
C(6)-F(7)	129.3(13)
N(1)-C(7)	149.3(13)
N(1)-C(19)	150.4(14)
N(1)-C(11)	151.2(11)
N(1)-C(15)	152.4(11)
C(7)-C(8)	150.5(17)
C(8)-C(9)	151.8(18)
C(9)-C(10)	150.4(18)
C(11)-C(12)	151.8(13)
C(12)-C(13)	150.2(15)
C(13)-C(14)	143.3(18)
C(15)-C(16)	152.1(14)
C(16)-C(17)	152.1(15)
C(17)-C(18)	150.2(18)
C(19)-C(20)	150.7(18)
C(20)-C(21)	160(2)
C(21)-C(22)	128(2)

O(1)-W(1)-W(3)	138.87(17)
O(1)-W(1)-W(3)#1	131.27(17)
W(3)-W(1)-W(3)#1	89.857(14)
O(1)-W(1)-W(2)	134.06(18)
W(3)-W(1)-W(2)	60.074(12)
W(3)#1-W(1)-W(2)	60.020(12)
O(1)-W(1)-W(2)#1	135.44(18)
W(3)-W(1)-W(2)#1	60.016(12)
W(3)#1-W(1)-W(2)#1	60.017(12)
W(2)-W(1)-W(2)#1	90.252(14)
O(1)-W(1)-I(2)	90.30(17)
W(3)-W(1)-I(2)	61.750(15)
W(3)#1-W(1)-I(2)	121.352(18)
W(2)-W(1)-I(2)	61.344(15)
W(2)#1-W(1)-I(2)	121.755(18)
O(1)-W(1)-I(3)	91.31(18)
W(3)-W(1)-I(3)	61.531(15)
W(3)#1-W(1)-I(3)	121.489(18)
W(2)-W(1)-I(3)	121.588(18)

W(2)#1-W(1)-I(3)	61.480(15)
I(2)-W(1)-I(3)	90.157(19)
O(1)-W(1)-I(4)	85.80(17)
W(3)-W(1)-I(4)	121.434(17)
W(3)#1-W(1)-I(4)	61.822(15)
W(2)-W(1)-I(4)	121.829(18)
W(2)#1-W(1)-I(4)	61.433(15)
I(2)-W(1)-I(4)	176.10(2)
I(3)-W(1)-I(4)	89.728(19)
O(1)-W(1)-I(1)	84.54(18)
W(3)-W(1)-I(1)	121.716(18)
W(3)#1-W(1)-I(1)	62.059(15)
W(2)-W(1)-I(1)	61.661(15)
W(2)#1-W(1)-I(1)	122.058(18)
I(2)-W(1)-I(1)	89.451(19)
I(3)-W(1)-I(1)	175.83(2)
I(4)-W(1)-I(1)	90.382(19)
O(3)-W(2)-W(3)#1	131.12(17)
O(3)-W(2)-W(3)	139.27(17)
W(3)#1-W(2)-W(3)	89.605(14)
O(3)-W(2)-W(1)	135.46(17)
W(3)#1-W(2)-W(1)	59.861(12)
W(3)-W(2)-W(1)	59.794(12)
O(3)-W(2)-W(1)#1	134.50(17)
W(3)#1-W(2)-W(1)#1	59.778(12)
W(3)-W(2)-W(1)#1	59.819(12)
W(1)-W(2)-W(1)#1	89.748(14)
O(3)-W(2)-I(2)	91.08(17)
W(3)#1-W(2)-I(2)	121.697(18)
W(3)-W(2)-I(2)	61.842(15)
W(1)-W(2)-I(2)	61.849(15)
W(1)#1-W(2)-I(2)	121.643(19)
O(3)-W(2)-I(3)#1	84.80(17)
W(3)#1-W(2)-I(3)#1	61.577(15)
W(3)-W(2)-I(3)#1	121.626(18)
W(1)-W(2)-I(3)#1	121.419(18)
W(1)#1-W(2)-I(3)#1	61.815(16)
I(2)-W(2)-I(3)#1	175.88(2)
O(3)-W(2)-I(4)#1	90.28(17)
W(3)#1-W(2)-I(4)#1	121.724(18)
W(3)-W(2)-I(4)#1	61.951(15)
W(1)-W(2)-I(4)#1	121.725(18)

W(1)#1-W(2)-I(4)#1	61.962(15)
I(2)-W(2)-I(4)#1	89.813(19)
I(3)#1-W(2)-I(4)#1	90.192(19)
O(3)-W(2)-I(1)	85.07(17)
W(3)#1-W(2)-I(1)	62.143(15)
W(3)-W(2)-I(1)	121.809(18)
W(1)-W(2)-I(1)	62.033(16)
W(1)#1-W(2)-I(1)	121.902(17)
I(2)-W(2)-I(1)	89.920(19)
I(3)#1-W(2)-I(1)	89.741(19)
I(4)#1-W(2)-I(1)	175.34(2)
O(5)-W(3)-W(1)	138.32(16)
O(5)-W(3)-W(1)#1	131.54(16)
W(1)-W(3)-W(1)#1	90.142(14)
O(5)-W(3)-W(2)#1	134.44(17)
W(1)-W(3)-W(2)#1	60.204(12)
W(1)#1-W(3)-W(2)#1	60.119(12)
O(5)-W(3)-W(2)	134.96(17)
W(1)-W(3)-W(2)	60.132(12)
W(1)#1-W(3)-W(2)	60.163(12)
W(2)#1-W(3)-W(2)	90.394(14)
O(5)-W(3)-I(3)	89.89(16)
W(1)-W(3)-I(3)	61.994(16)
W(1)#1-W(3)-I(3)	121.801(18)
W(2)#1-W(3)-I(3)	61.701(15)
W(2)-W(3)-I(3)	122.110(18)
O(5)-W(3)-I(2)	90.53(16)
W(1)-W(3)-I(2)	61.788(15)
W(1)#1-W(3)-I(2)	121.521(19)
W(2)#1-W(3)-I(2)	121.982(18)
W(2)-W(3)-I(2)	61.376(16)
I(3)-W(3)-I(2)	90.427(19)
O(5)-W(3)-I(4)#1	85.62(16)
W(1)-W(3)-I(4)#1	121.620(18)
W(1)#1-W(3)-I(4)#1	61.911(15)
W(2)#1-W(3)-I(4)#1	122.017(18)
W(2)-W(3)-I(4)#1	61.507(15)
I(3)-W(3)-I(4)#1	175.50(2)
I(2)-W(3)-I(4)#1	89.326(19)
O(5)-W(3)-I(1)#1	85.12(16)
W(1)-W(3)-I(1)#1	121.833(17)
W(1)#1-W(3)-I(1)#1	61.935(16)

W(2)#1-W(3)-I(1)#1	61.648(15)
W(2)-W(3)-I(1)#1	122.081(18)
I(3)-W(3)-I(1)#1	89.54(2)
I(2)-W(3)-I(1)#1	175.65(2)
I(4)#1-W(3)-I(1)#1	90.364(19)
W(2)-I(1)-W(1)	56.306(14)
W(2)-I(1)-W(3)#1	56.210(14)
W(1)-I(1)-W(3)#1	56.006(14)
W(2)-I(2)-W(3)	56.782(14)
W(2)-I(2)-W(1)	56.807(14)
W(3)-I(2)-W(1)	56.462(14)
W(3)-I(3)-W(2)#1	56.721(14)
W(3)-I(3)-W(1)	56.475(14)
W(2)#1-I(3)-W(1)	56.703(14)
W(2)#1-I(4)-W(3)#1	56.540(14)
W(2)#1-I(4)-W(1)	56.605(14)
W(3)#1-I(4)-W(1)	56.266(14)
C(1)-O(1)-W(1)	135.1(6)
O(2)-C(1)-O(1)	127.8(9)
O(2)-C(1)-C(2)	119.2(10)
O(1)-C(1)-C(2)	113.0(10)
F(3)-C(2)-F(2)	105.0(13)
F(3)-C(2)-F(1)	105.2(13)
F(2)-C(2)-F(1)	103.4(14)
F(3)-C(2)-C(1)	115.2(12)
F(2)-C(2)-C(1)	112.9(12)
F(1)-C(2)-C(1)	114.0(11)
C(3)-O(3)-W(2)	136.8(6)
O(4)-C(3)-O(3)	129.9(9)
O(4)-C(3)-C(4)	119.1(9)
O(3)-C(3)-C(4)	111.0(8)
F(5)-C(4)-F(6)	108.3(9)
F(5)-C(4)-F(4)	106.6(9)
F(6)-C(4)-F(4)	105.3(8)
F(5)-C(4)-C(3)	113.9(8)
F(6)-C(4)-C(3)	111.5(8)
F(4)-C(4)-C(3)	110.7(9)
C(5)-O(5)-W(3)	134.8(6)
O(6)-C(5)-O(5)	128.9(9)
O(6)-C(5)-C(6)	118.6(9)
O(5)-C(5)-C(6)	112.5(9)
F(9)-C(6)-F(8)	108.0(12)

F(9)-C(6)-F(7)	102.7(12)
F(8)-C(6)-F(7)	104.4(11)
F(9)-C(6)-C(5)	114.3(10)
F(8)-C(6)-C(5)	113.9(10)
F(7)-C(6)-C(5)	112.6(10)
C(7)-N(1)-C(19)	107.5(8)
C(7)-N(1)-C(11)	111.1(8)
C(19)-N(1)-C(11)	110.7(8)
C(7)-N(1)-C(15)	110.4(8)
C(19)-N(1)-C(15)	111.6(8)
C(11)-N(1)-C(15)	105.6(7)
N(1)-C(7)-C(8)	116.8(9)
C(7)-C(8)-C(9)	110.3(11)
C(10)-C(9)-C(8)	113.3(12)
N(1)-C(11)-C(12)	115.3(8)
C(13)-C(12)-C(11)	111.2(9)
C(14)-C(13)-C(12)	114.2(12)
C(16)-C(15)-N(1)	115.8(8)
C(17)-C(16)-C(15)	111.1(9)
C(18)-C(17)-C(16)	116.0(11)
N(1)-C(19)-C(20)	117.8(11)
C(19)-C(20)-C(21)	112.9(14)
C(22)-C(21)-C(20)	107(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z

Table 12. Anisotropic displacement parameters ($pm^2 x\ 10^{-1}$) for $[W_6I_8(CF_3COO)_6](TBA)_2$. 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}
W(1)	42(1)	44(1)	44(1)	22(1)	13(1)	7(1)
W(2)	40(1)	47(1)	43(1)	22(1)	11(1)	11(1)
W(3)	42(1)	43(1)	40(1)	19(1)	11(1)	8(1)
I(1)	46(1)	60(1)	53(1)	26(1)	20(1)	14(1)
I(2)	43(1)	53(1)	50(1)	20(1)	8(1)	5(1)
I(3)	58(1)	45(1)	57(1)	24(1)	18(1)	15(1)
I(4)	58(1)	60(1)	48(1)	32(1)	15(1)	16(1)
O(1)	59(4)	51(3)	62(4)	26(3)	22(3)	2(3)
C(1)	55(5)	65(6)	68(6)	34(5)	22(5)	14(5)
O(2)	91(5)	64(4)	86(6)	19(4)	33(4)	0(4)
C(2)	73(7)	79(8)	115(10)	55(8)	45(7)	7(6)
F(1)	171(10)	240(13)	167(10)	144(10)	80(9)	11(9)
F(2)	161(10)	259(15)	400(20)	245(16)	204(13)	118(10)
F(3)	271(14)	87(6)	233(13)	56(7)	150(12)	-24(8)
O(3)	48(3)	68(4)	62(4)	32(3)	12(3)	20(3)
C(3)	47(5)	61(5)	53(5)	22(5)	15(4)	13(4)
O(4)	72(5)	97(6)	59(4)	23(4)	8(4)	32(4)
C(4)	51(5)	72(6)	74(6)	42(6)	15(5)	11(5)
F(4)	79(4)	133(6)	113(5)	82(5)	15(4)	44(4)
F(5)	85(4)	62(4)	107(5)	30(4)	20(4)	22(3)
F(6)	69(4)	94(5)	126(6)	57(4)	53(4)	28(3)
O(5)	60(4)	56(4)	49(3)	23(3)	15(3)	11(3)
C(5)	54(5)	60(6)	54(5)	22(5)	16(4)	17(4)
O(6)	90(5)	51(4)	85(5)	21(4)	40(4)	3(4)
C(6)	72(7)	64(6)	61(6)	16(5)	23(5)	13(5)
F(7)	100(6)	224(11)	116(7)	54(7)	65(5)	54(7)
F(8)	180(9)	125(7)	86(6)	-9(5)	57(6)	-32(7)
F(9)	410(20)	206(11)	116(7)	118(8)	153(10)	204(13)
N(1)	63(5)	57(4)	49(4)	23(4)	13(4)	10(4)
C(7)	60(6)	60(6)	59(6)	16(5)	11(5)	9(5)
C(8)	87(9)	81(8)	75(8)	29(7)	32(7)	33(7)
C(9)	75(8)	76(8)	78(8)	27(7)	3(7)	24(6)
C(10)	120(12)	122(12)	127(12)	62(10)	49(10)	64(10)
C(11)	59(5)	66(6)	58(5)	32(5)	14(4)	13(5)
C(12)	70(7)	100(8)	60(6)	39(6)	6(5)	6(6)
C(13)	95(9)	139(12)	56(6)	54(7)	14(6)	27(8)
C(14)	122(13)	220(20)	102(12)	87(14)	25(10)	21(14)

C(15)	66(6)	53(6)	50(5)	22(4)	6(5)	5(5)
C(16)	90(8)	64(7)	67(7)	37(6)	14(6)	0(6)
C(17)	96(9)	67(7)	58(6)	32(6)	10(6)	10(6)
C(18)	94(9)	85(8)	74(8)	33(7)	-4(7)	16(7)
C(19)	69(7)	94(9)	59(7)	31(7)	20(6)	25(6)
C(20)	133(12)	108(10)	104(10)	48(9)	64(9)	65(10)
C(21)	400(40)	290(30)	240(30)	190(30)	250(30)	270(30)
C(22)	230(30)	300(40)	260(40)	160(40)	90(30)	90(30)

Table 13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (pm^2x 10^{-1}) for $[W_6I_8(CF_3COO)_6](TBA)_2$.

	x	y	z	U(eq)
H(7A)	3590(80)	8900(80)	4500(80)	60(30)
H(7B)	4120(80)	9120(90)	5720(90)	70(30)
H(8A)	1730(120)	8910(130)	4960(130)	130(60)
H(8B)	2280(110)	8900(120)	6000(120)	120(50)
H(9A)	3050(90)	10690(90)	6450(100)	70(30)
H(9B)	2670(80)	10470(80)	5050(90)	60(30)
H(10A)	1862	11602	6200	141
H(10B)	988	10302	5319	141
H(10C)	1567	10696	6664	141
H(11A)	2882	6182	5248	76
H(11B)	2343	7171	5727	76
H(12A)	4655	7557	6644	101
H(12B)	4103	8537	7133	101
H(13A)	3024	7366	7699	119
H(13B)	3569	6385	7207	119
H(14A)	4350	7483	9193	188
H(14B)	5256	7676	8617	188
H(14C)	4710	8658	9109	188
H(15A)	2220(80)	5820(90)	3250(80)	70(30)
H(15B)	1570(70)	6720(70)	3880(70)	50(20)
H(16A)	2150(80)	7650(90)	2780(80)	60(30)
H(16B)	2740(130)	6770(140)	2270(140)	150(60)
H(17A)	1070(90)	6350(90)	800(100)	90(30)
H(17B)	1030(70)	5330(80)	1330(80)	50(30)
H(18A)	-678	5555	1082	115
H(18B)	-60	5872	2395	115
H(18C)	-69	6902	2083	115
H(19A)	4240(80)	7270(90)	3860(90)	70(30)
H(19B)	4830(90)	7820(100)	5220(110)	90(40)
H(20A)	3804	5452	3336	130
H(20B)	4212	5785	4680	130
H(21A)	6160	6716	4789	278
H(21B)	5685	5302	4058	278
H(22A)	6376	6055	3106	311
H(22B)	5072	5370	2460	311
H(22C)	5545	6778	3189	311

Photoluminescence Measurements

Emission spectra and decay curves were collected with a fluorescence spectrometer FLS920 (Edinburgh Instruments) equipped with a 450 W ozone-free xenon arc lamp (OSRAM) for the emission scan and a µF920H flash lamp for the decay curve. The sample chamber was installed with a mirror optic for powder samples. For detection, a R2658P single-photon counting photomultiplier tube (Hamamatsu) was used. All luminescence spectra were recorded with a spectral resolution of 1 nm, a dwell time of 0.4 s in 1 nm steps, and three repeats. The sample was in a gas flow sample holder under ambient pressure (about 1 bar) and was perfused with nitrogen, air, oxygen and oxygen-nitrogen mixtures 50/50 and 75/25.

Decay Curves

Figure 2 and 3 show the measured decay curves and the monoexponential fits of both powder samples $(TBA)_2W_6I_8(CF_3COO)_6$ and $(TBA)_2Mo_6I_8(CF_3COO)_6$ under different oxygen concentrations, nitrogen, air, oxygen-nitrogen mixtures 50/50 and 75/25 and pure oxygen.

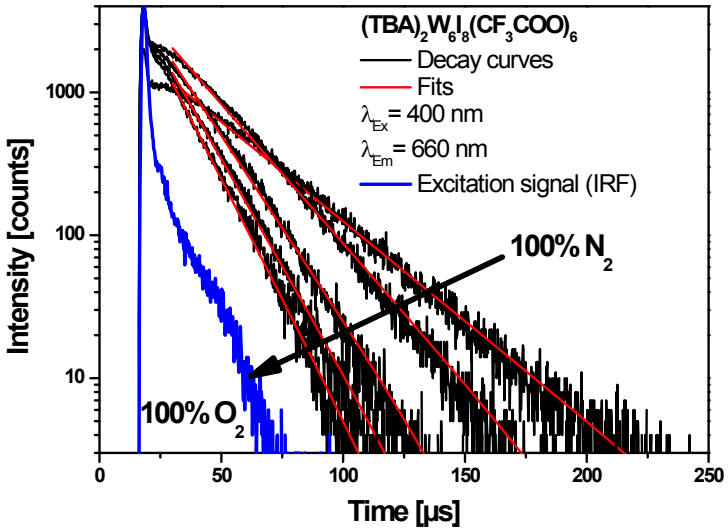

Figure 2: Decay curves of $(TBA)_2W_6I_8(CF_3COO)_6$ powder under different oxygen concentrations

Table 14: Decay results from $(TBA)_2W_6I_8(CF_3COO)$

O_2 Partial Pressure	τ	Std.Dev. (τ)	Chi²
mbar	µs	µs	
0	29.2	0.1	1.028
210	20.2	0.1	0.988
500	14.4	0.1	1.03
750	11.8	0.1	0.921
1000	9.9	0.1	1.187

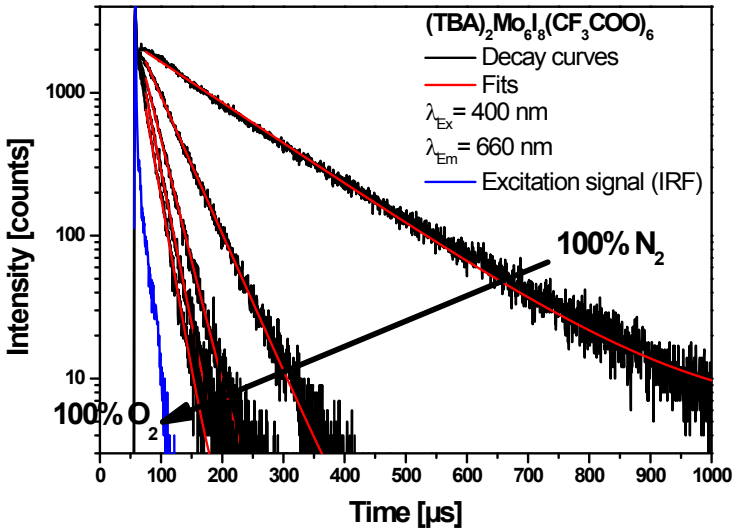

Figure 3: Decay curves of $(TBA)_2[Mo_6I_8(CF_3COO)_6]$ powder under different oxygen concentrations

Table 15: Decay results from $(TBA)_2[Mo_6I_8(CF_3COO)_6]$

O_2 Partial Pressure	τ_1	Std.Dev. (τ_1)	Rel. Ratio (τ_1)	τ_2	Std.Dev. (τ_2)	Rel. Ratio (τ_2)	Chi²	mean τ
mbar	µs	µs		µs	µs			µs
0	69.8	3.7	0.18	177.1	2.2	0.82	1.106	157.8
210	17.7	3.2	0.11	46	0.5	0.89	0.954	42.9
500	17.9	1.9	0.52	29.2	1.8	0.48	0.857	23.3
750	12.9	0.7	0.69	26	1.5	0.31	0.981	17.0
1000	0.8	0.54	19.1	0.7	0.46	1.174	13.214	8.2

Stern-Volmer parameter

The Stern-Volmer parameter given below are derived from the data as shown in figure 4.

Equation 1: Stern-Volmer equation [Otto Stern, Max Volmer: Über die Abklingzeit der Fluoreszenz. Physikalische Zeitschrift, 20, 183-188,(1919)]

$$F = \frac{F_0}{1 + K_{SV} * [O_2]} \qquad \tau = \frac{\tau_0}{1 + K_{SV} * [O_2]}$$

Table 16: Stern-Volmer parameter of $(TBA)_2[W_6I_8(CF_3COO)_6]$ und $(TBA)_2[Mo_6I_8(CF_3COO)_6]$.

	$(TBA)_2[W_6I_8(CF_3COO)_6]$		$(TBA)_2[Mo_6I_8(CF_3COO)_6]$	
	Emission integral	Decay time	Emission integral	Decay time
τ_0		29.1 µs		157.7 µs
K_{SV}	0.00266	0.0020	0.0116	0.0121
SD	0.00003	0.00005	0.00017	0.00046

Examples of solution phase spectroscopic data

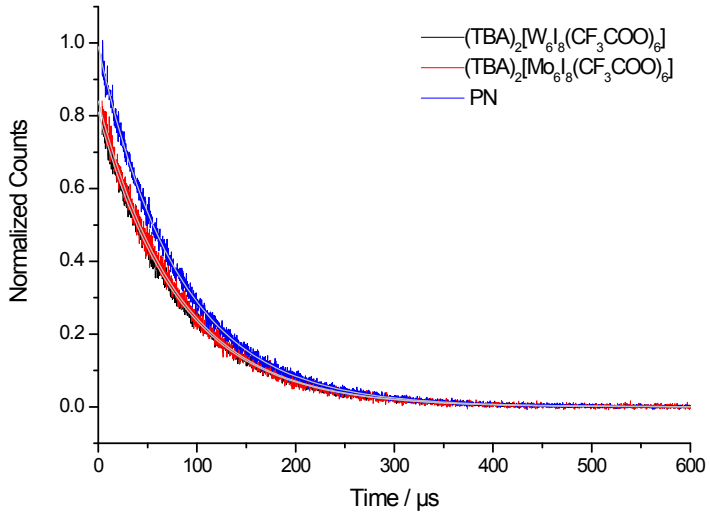

Figure 4. Representative traces of the time-resolved $O_2(a^1\Delta_g)$ phosphorescence signals from the hexanuclear clusters and phenalenone in acetonitrile. The traces for $(TBA)_2[W_8I_8(CF_3COO)_6]$ and $(TBA)_2[Mo_8I_8(CF_3COO)_6]$ overlap substantially. For the cluster solutions, points within the first 4 µs have been deleted since they contain fast decaying phosphorescence from the hexanuclear clusters. In all cases, the remaining data points can be fitted to a single exponential function (grey lines) with a lifetime, τ_Δ, of 81 ± 1 µs characteristic for $O_2(a^1\Delta_g)$ in acetonitrile.[1,2] This indicates that, under our conditions, the metal clusters do not quench $O_2(a^1\Delta_g)$. The signal intensities have been normalized relative to the intensity of the phenalenone sensitized signal by multiplication with the factor, $\phi_{\Delta,PN}P_{PN}(1-10^{-A_{PN}})\tau_{\Delta,PN} / I_{PN}P_X(1-10^{-A_X})\tau_{\Delta,X}$. Here P is the measured power incident on the samples, A is the absorbance at the excitation wavelength, and I is the integrated signal intensity. Thereby, the signal amplitude extrapolated to t = 0 µs is directly proportional to singlet oxygen quantum yield, ϕ_Δ.

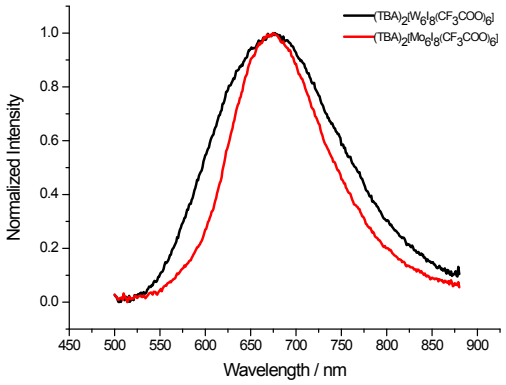

Figure 5. Emission spectra of hexanuclear cluster compounds in acetonitrile excited at 419 nm. Note that the phosphorescence spectra extend beyond 880 nm, which might result in a slight underestimation of the phosphorescence quantum yields.

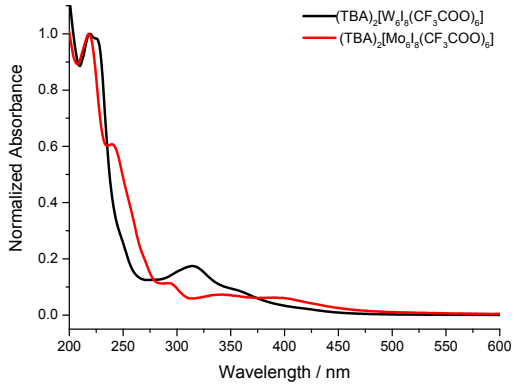

Figure 6. Normalized absorption spectra of the hexanuclear cluster compounds in acetonitrile.

1. Bregnhøj, M., Blazquez-Castro, A., Westberg, M., Breitenbach, T. & Ogilby, P. R. Direct 765 nm Optical Excitation of Molecular Oxygen in Solution and in Single Mammalian Cells. *J. Phys. Chem. B* **119,** 5422–5429 (2015).

2. Wilkinson, F., Helman, W. P. & Ross, A. B. Rate Constants for the Decay and Reaction of the Lowest Electronically Excited Singlet State of Molecular Oxygen in Solution. An Expanded and Revised Compilation. *J. Phys. Chem. Ref. Data* **24,** 663–1021 (1995).