# **Electronic and relativistic contributions to ion-pairing in polyoxometalate model systems – Supplementary Information**

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A spreadsheet with calculated molecular orbital energies, orbital populations, and electron transitions with oscillation strengths is also available.

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#### **S1** *T*<sub>1</sub> **Relaxation – A Brief Overview**



Fig. S1 A model relaxation curve for a theoretical solution ( $T_1 = 5.0$  seconds) with a line denoting the point at which  $T_1$  is reached.

At time  $\tau = 0$ , a 180° pulse inverts the magnetization vector  $M_z$  such that it lies along the negative-z axis (i.e.  $M_0 = -M_0$ ). The spin-lattice relaxation causes  $M_z$  to increase from its inverted value  $-M_0$ , through 0, and asymptotically approach its initial value  $M_0$  (Figure 1). Thus,  $M_z$  can be found at any time  $\tau$  by using the formula:

$$\frac{M_z}{M_0} = I[0] - Pe^{-\frac{\tau}{T_1}} = I[0] - Pe^{\tau R_{QR}}$$
(S1)

where P denotes a pre-exponential factor typically close in value to 2 (complete inversion of  $M_z$  to  $-M_z$ ), I[0] is the asymptote of the graph (thermodynamic equilibrium) as a fraction of  $M_0$  (typically close in value to 1), and  $\tau$  is time in seconds.

This longitudinal relaxation can be halted by applying a 90° pulse at some time  $\tau$  after the 180° pulse. This pulse rotates  $M_z$  so that it now lies in the transverse plane. By measuring the magnitude of the signal (appearing as a single peak) at a set of values of  $\tau$  and fitting the data to Equation S1,  $T_1$  (the time at which  $M_z$  has returned to  $1 - \frac{2}{e} \approx 26.4\%$  of its positive equilibrium value) can be obtained.

The electric field gradient  $q_z$  is provided by an asymmetric distribution of electron density around a quadrupolar nucleus. It is expressed as the second spatial derivative of the electrostatic potential (V), namely:

$$q_z = \frac{\partial^2 V(x)}{\partial x_z^2} \tag{S2}$$

and thus has a  $x^{-3}$  dependence, where  $x_z$  is the distance between the source of negative charge and the cesium nucleus. Because the electric field gradient term in the quadrupolar relaxation rate expression is the only distance-dependent term and is squared,  $R_{QR}$  has a  $x^{-6}$  distance dependence, making it especially sensitive to relative degrees of contact ion-pairing while being less sensitive to solvent-separated ion-aggregation.



Fig. S2 Sample 1D  $^{133}$ Cs sprectrum (60 mM Cs<sub>8</sub>Nb<sub>6</sub>O<sub>19</sub>). The single peak arises from rapid exchange of free and bound Cs<sup>+</sup>.

# S2 T<sub>1</sub> Relaxation Fits

Each reported  $T_1$  value was obtained from a fit from a 16-membered variable delay ( $\tau$ ) list. Delay time ( $d_1$ ) values were at least five times longer than the  $T_1$  for each solution to ensure complete relaxation before proceeding to the next 180° pulse. Each species is reported as the set of parameters I[0], P, and  $R_{QR}$ , along with the standard deviation of the fit (Tables S1-S3).

Table S1 Fitting parameters for  ${}^{133}$ Cs  $T_1$  Inversion-Recovery NMR for 5 mM solutions of mixed metal clusters

Species	I[0]	Р	$R_{QR}(\mathrm{s}^{-1})$	St. Dev
Cs <sub>5</sub> NbW <sub>9</sub> O <sub>32</sub>	1.014	1.873	0.1087	$3.229 \times 10^{-3}$
Cs5TaW9O32	1.003	1.894	0.2414	$3.784 \times 10^{-3}$
$Cs_4Nb_2W_4O_{19}$	1.001	1.874	0.1257	$2.792 \times 10^{-3}$
Cs5NbW9O32	0.9983	1.932	0.5708	$4.666 \times 10^{-3}$

Species/Concentration	I[0]	Р	$R_{QR}(\mathrm{s}^{-1})$	St. Dev.
Cs <sub>8</sub> Nb <sub>6</sub> O <sub>19</sub>				
0.5 mM	0.7400	1.687	0.2939	$2.479 \times 10^{-2}$
1 mM	0.8659	1.849	0.4268	$1.372 \times 10^{-2}$
2 mM	1.001	1.919	0.5308	$5.344 \times 10^{-3}$
5 mM	0.9962	1.886	0.7289	$3.368 \times 10^{-3}$
10 mM	0.9985	1.889	0.9515	$2.477 \times 10^{-3}$
20 mM	0.9985	1.876	1.205	$8.623 \times 10^{-4}$
60 mM	0.9987	1.877	1.939	$9.025 \times 10^{-4}$
100 mM	0.9990	1.874	2.312	$8.962 \times 10^{-4}$
Cs <sub>8</sub> Ta <sub>6</sub> O <sub>19</sub>				
0.5 mM	0.8209	1.785	0.5473	$2.080 \times 10^{-2}$
1 mM	0.9981	1.962	0.8354	$8.080 \times 10^{-3}$
2 mM	0.9993	1.988	1.197	$5.965 \times 10^{-3}$
5 mM	0.9959	1.895	1.486	$1.982 \times 10^{-3}$
10 mM	1.000	1.904	1.714	$2.724 \times 10^{-3}$
20 mM	0.9986	1.887	2.125	$3.523 \times 10^{-3}$
60 mM	1.001	1.895	3.078	$1.014 \times 10^{-3}$
100 mM	0.9994	1.877	3.689	$1.324 \times 10^{-3}$

**Table S2** Fitting parameters for  ${}^{133}$ Cs  $T_1$  Inversion-Recovery NMR for solutions of Cs<sub>8</sub>M<sub>6</sub>O<sub>19</sub>

**Table S3** Fitting parameters for <sup>133</sup>Cs  $T_1$  Inversion-Recovery NMR for solutions of 20 mM TMA{M<sub>6</sub>} with added CsCl. All solutions are in 200 mM TMAOH.

Species/Concentration	I[0]	Р	$R_{QR}(\mathrm{s}^{-1})$	St. Dev.
$20 \mathrm{mM}\mathrm{TMA}\{\mathrm{Nb}_6\}$				
+10 mM CsCl	0.9954	1.881	3.499	$1.364 \times 10^{-2}$
+20 mM CsCl	0.9912	1.840	3.438	$4.559 \times 10^{-3}$
+40 mM CsCl	0.9953	1.839	3.124	$4.833 \times 10^{-3}$
+80 mM CsCl	0.9993	1.867	2.555	$2.365 \times 10^{-3}$
+120 mM CsCl	0.9970	1.857	2.100	$2.565 \times 10^{-3}$
+160 mM CsCl	0.9996	1.873	1.766	$2.253 \times 10^{-3}$
+200 mM CsCl	0.9996	1.869	1.544	$4.823 \times 10^{-4}$
+240 mM CsCl	0.9991	1.874	1.332	$1.030 \times 10^{-3}$
$20 \mathrm{mM}\mathrm{TMA}\{\mathrm{Ta}_6\}$				
+10 mM CsCl	1.001	1.785	4.434	$1.257 \times 10^{-2}$
+20 mM CsCl	0.9904	1.913	4.381	$7.615 \times 10^{-3}$
+40 mM CsCl	0.9957	1.888	4.170	$2.603 \times 10^{-3}$
+80 mM CsCl	0.9974	1.885	3.836	$2.094 \times 10^{-3}$
+120 mM CsCl	0.9973	1.883	3.436	$2.148 \times 10^{-3}$
+160 mM CsCl	0.9995	1.880	3.011	$9.399 \times 10^{-4}$
+200 mM CsCl	0.9988	1.886	2.684	$3.463 \times 10^{-3}$
+240 mM CsCl	0.9996	1.877	2.381	$1.624 \times 10^{-3}$

## S3 Viscometry

In order to normalize between solutions, we define an adjusted quadrupolar relaxation rate:

$$R_{adj} = \frac{R_{QR}}{\eta_{rel}} \tag{S3}$$

The viscosity of each solution was found relative to that of 10%  $D_2O/90\%$  H<sub>2</sub>O and are expressed as  $\eta_{rel}$ , such that:

$$\eta_{rel} = \frac{t_{soln} d_{soln}}{t_0 d_0} \tag{S4}$$

where  $t_{soln}$  is the efflux time of the solution in an Ostwald Viscosity Tube,  $d_{soln}$  is the density of the solution, and  $t_0$  and  $d_0$  are the efflux time and density of 10% D<sub>2</sub>O/90% H<sub>2</sub>O.

Viscosity measurements were taken with an Ostwald Viscosity Tube and a stopwatch at a constant temperature of 25 °C. A constant sample volume of 5.00 mL was held for each experiment. Five efflux times were recorded for each sample and the averages of these times are reported (Table S4) along with solution density and relative viscosity to 10% D<sub>2</sub>O/90% H<sub>2</sub>O.

Table S4 Relative viscosities of solutions found by Ostwald Viscometer. All solutions are in 10% D<sub>2</sub>O/90% H<sub>2</sub>O

Solution	Density $(gmL^{-1})$	Mean Efflux Time (s)	$\eta_{rel}$
D <sub>2</sub> O/H <sub>2</sub> O	1.016	58.52	1.000
5 mM Cs{Nb <sub>6</sub> }	1.023	58.94	1.014
20 mM Cs{Nb <sub>6</sub> }	1.040	58.86	1.030
$100 \text{ mM Cs}\{\text{Nb}_6\}$	1.161	58.50	1.112
$5 \text{ mM Cs}{Ta_6}$	1.025	58.93	1.016
$20 \text{ mM Cs}\{\text{Ta}_6\}$	1.048	58.66	1.034
$100 \text{ mM Cs}{Ta_6}$	1.206	57.19	1.160
$20 \text{ mM TMA}{Nb_6} + 200 \text{ mM TMAOH}$	1.030	64.74	1.122
+ 80 mM CsCl	1.036	62.36	1.087
+ 240 mM CsCl	1.051	61.02	1.079
$20 \text{ mM TMA}{Ta_6} + 200 \text{ mM TMAOH}$	1.044	63.03	1.107
+ 80 mM CsCl	1.057	62.54	1.112
+ 240 mM CsCl	1.073	62.45	1.127

Remaining values of  $\eta_{rel}$  were generated by linear approximations between the two nearest concentrations. *i.e.*, for the following set of solutions:

(A) 20 mM TMA{Nb<sub>6</sub>} + 200 mM TMAOH + 80 mM CsCl ( $\eta_{rel} = 1.087$ )

(B)  $20 \text{ mM TMA}{Nb_6} + 200 \text{ mM TMAOH} + 120 \text{ mM CsCl}$ 

(C) 20 mM TMA{Nb<sub>6</sub>} + 200 mM TMAOH + 240 mM CsCl (
$$\eta_{rel} = 1.079$$
)

we can obtain the approximate viscosity of (B) from the known values of (A) and (C)

$$\eta_B = \eta_A - \frac{120 - 80}{240 - 80} (\eta_A - \eta_C) = 1.085$$
(S5)

## S4 Syntheses

#### S4.1 Cs<sub>8</sub>Nb<sub>6</sub>O<sub>19</sub>

3.42 g of Nb<sub>2</sub>O<sub>5</sub>·xH<sub>2</sub>O were slowly added to 10.0 g of 50 wt% CsOH solution at 90 °C and stirred such that the solution was allowed to become fully transparent after each aliquot. After all of the solid had dissolved, the solution was microfiltered and allowed to crystallize at room temperature. Well-formed crystals formed after 2 days. These crystals were filtered under vacuum, washed with 2-propanol, and dried in air.

## S4.2 Cs<sub>8</sub>Ta<sub>6</sub>O<sub>19</sub>

5.5 g of  $Cs_3TaO_8$  was added to 50 g of 50 wt% CsOH solution and heated to reflux until complete dissolution was observed. The solution was cooled and microfiltered with a  $0.45 \mu m$  syringe filter. The solution was allowed to evaporate and after several days, a large crop of colorless well-formed crystals is observed.

## S4.3 Cs5NbW9O32

 $K_3[Nb(O_2)_4]$  (1.1 g, 3.3 mmol) was dissolved in 25 mL of H2O at 70 degreeCelsius. In a separate beaker, Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (3.6 g, 11 mmol) was dissolved in a mixture of H<sub>2</sub>O (11.9 mL) and aqueous H<sub>2</sub>O<sub>2</sub> (0.65 mL, 30% v/v). The contents of the two beakers were then combined and stirred for 30 min at 70°C to afford a clear solution. The pH of this solution was adjusted to 2.0 (3M H<sub>2</sub>SO<sub>4</sub>) and the resulting mixture was first refluxed for 2 h and then centrifuged at room temperature. CsCl (5.6 g, 33 mmol) was added to the supernatant under vigorous stirring and the thick yellow suspension thus obtained was stirred for 3 min and filtrated under vacuum. The isolated yellow precipitate was finally washed with cold water (2 mL) and dried under suction. Analytically pure crystals of Cs{NbW<sub>9</sub>} were obtained by recrystallizing this crude product twice from the minimum amount of boiling water.

## S4.4 Cs<sub>5</sub>TaW<sub>9</sub>O<sub>32</sub>

 $K_3[Ta(O_2)_4]$  (2.0 g, 4.7 mmol) was added to a stirred solution of  $Na_2WO_4 \cdot 2H_2O$  (6.6 g, 20.0 mmol) in 40 mL of hot (60 degreeCelsius)  $H_2O$ . The pH of the resulting mixture was carefully adjusted to 2.0 by the dropwise addition of HCl (37% w/w). The yellow suspension was refluxed for 2 h and centrifuged at room temperature. CsCl (10.0 g, 59.4 mmol) was added to the isolated bright yellow supernatant and a mass of light orange solids was isolated from the resulting suspension by centrifugation, washed twice with 5 mL of water, twice with 20 mL of 2-propanol and finally dried under vacuum. This crude product was dissolved in 30 mL of boiling H2O and yellow crystal plates formed overnight at 4 °C.

## S4.5 Cs<sub>4</sub>Nb<sub>2</sub>W<sub>4</sub>O<sub>19</sub>

Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (3.3 grams, 10.0 mmol) was added to 40 mL of H2O at room temperature and stirred until dissolution. K<sub>3</sub>[Nb(O<sub>2</sub>)<sub>4</sub>] (1.6 grams, 4.7 mmol) was added to the solution, which was further stirred for 10 minutes. The suspension was then slowly acidified dropwise with 12 M HCl, during which a white precipitate formed and redissolved until the pH reached a value of 7. Upon continued dropwise addition of HCl, the solution grew increasingly opaque and yellow until the pH reached a value of 2. The yellow suspension was then refluxed for 2 hours. The resulting solution was allowed to cool to room temperature and was then centrifuged. The supernatant was separated and microfiltered with a 0.45 µm nylon syringe filter. 6.0 grams of CsCl were then added to the supernatant and a cream-colored precipitate formed. This precipitate was isolated by centrifugation and removal of the supernatant liquid. The solid was dissolved in the minimum amount of boiling water ( $\approx 120 \text{ mL} \cdot \text{g}^{-1}$ ) and allowed to recrystallize at 4 °C. After a day, small needle-like colorless crystals formed. The crystals were washed in 2-propanol and dried under vacuum.

## S4.6 Cs<sub>4</sub>Na<sub>2</sub>Nb<sub>4</sub>W<sub>2</sub>O<sub>19</sub>

 $Na_2WO_4 \cdot 2H_2O(3.3 \text{ grams}, 10.0 \text{ mmol})$  was added to 40 mL of  $H_2O$  at room temperature and stirred until dissolution.  $Cs_3[Nb(O_2)_4]$ (2.9 grams, 4.7 mmol) was added to the solution, which was further stirred for 10 minutes. The suspension was then slowly acidified dropwise with 12 M HCl until the pH reached a value of 9, during which a white precipitate formed and redissolved. The solution was then refluxed for 4 h, microfiltered with a 0.45 µm nylon syringe filter, cooled to room temperature, and allowed to crystallize at 4 °C. Macroscopic colorless block-like crystals formed after 60 hours. The mother liquor was removed and the crystals were washed in 2-propanol and dried under vacuum.

## S4.7 [(CH<sub>3</sub>)<sub>4</sub>N]<sub>5</sub>H<sub>3</sub>Nb<sub>6</sub>O<sub>19</sub>

A 150 mL beaker was charged with tetramethylammonium hydroxide solution (2.8 M, 100 mL) and heated to 90 °C. Hydrous Nb<sub>2</sub>O<sub>5</sub> (20 g) was added in small aliquots, allowing full dissolution before addition of new aliquots. After addition of all the niobium oxide, the solution was allowed to cool to room temperature. Isopropyl alcohol was added to precipitate the final product. After excessive washing with isopropyl alcohol, a white crystalline powder is obtained through vacuum filtration.

#### S4.8 $[(CH_3)_4N]_6H_2Ta_6O_{19}$

A 125 mL flask was charged with  $(NH_4)_3Ta(O_2)_4$  (1.32 g) and 1.4 M tetramethylammonium hydroxide (8.25 mL). The solution was refluxed for 5 h with the condensing column chilled to approximately 5°C. The resulting solution was filtered with a 0.45 µm nylon syringe filter. The filtered solution was agitated with isopropyl alcohol (~40 mL) and centrifuged to yield a small denser layer containing the product. Further agitation of the bottom layer with isopropyl alcohol (30 mL) yielded a white precipitate. The precipitate was washed with isopropyl alcohol and oven-dried under vacuum (60 °C).

# S5 Hexaniobate Total X-Ray Scattering Spectrum



Fig. S3 PDF analysis of X-ray total scattering on solutions of 100 mM TMA{ $Nb_6$ } in 200 mM TMAOH with added CsCl (0 to 12 molar equivalents), with a growing Ta-Cs peak at 4.1 Å providing structural information and atomic-level resolution of the ion-pair in solution.

# S6 Elemental Analysis



Fig. S4 Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CTAB to 5 mM Cs<sub>8</sub>Nb<sub>6</sub>O<sub>19</sub>.

Measurement #	Br%	Nb%	Cs%	$Cs/{Nb_6}$
1	56.65	36.37	6.97	1.15
2	59.15	35.38	5.47	0.93
3	58.93	34.60	6.47	1.12
4	65.38	29.10	5.52	1.14
5	49.03	42.02	8.95	1.28
6	47.30	43.84	8.86	1.21
Avg.				1.14
St. Dev				0.12

Table S5 At% values of the precipitate upon adding CTAB to 5 mM  $Cs_8Nb_6O_{19}$ .

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Fig. S5 Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CTAB to 5 mM  $Cs_8Ta_6O_{19}$ .

Measurement #	Ta%	Cs%	$Cs/{Ta_6}$
1	70.61	29.39	2.50
2	71.34	28.66	2.40
3	70.55	29.45	2.50
4	73.20	26.80	2.17
5	73.43	26.57	2.15
Avg.			2.36
St. Dev			0.16

Table S6 At% values of the precipitate upon adding CTAB to 5 mM  $Cs_8Ta_6O_{19}$ . Br was not measured.



Fig. S6 Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CTAB to 10 mM Cs<sub>8</sub>Nb<sub>6</sub>O<sub>19</sub>.

Measurement #	Br%	Nb%	Cs%	$Cs/{Nb_6}$
1	48.13	43.07	8.80	1.23
2	42.99	46.32	10.69	1.38
3	55.15	34.91	9.94	1.71
4	56.52	35.66	7.82	1.32
5	50.83	38.72	10.44	1.62
6	51.42	37.85	10.62	1.68
Avg.				1.49
St. Dev				0.21

Table S7 At% values of the precipitate upon adding CTAB to 10 mM  $\rm Cs_8Nb_6O_{19}.$ 



Fig. S7 Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CTAB to 10 mM Cs<sub>8</sub>Ta<sub>6</sub>O<sub>19</sub>.

Measurement #	Br%	Ta%	Cs%	$Cs/{Ta_6}$
1	50.19	33.83	15.98	2.83
2	43.67	37.95	18.38	2.91
3	43.93	36.95	19.13	3.11
4	42.79	38.95	18.25	2.81
5	62.43	24.63	12.94	3.15
Avg.				2.96
St. Dev				0.16

Table S8 At% values of the precipitate upon adding CTAB to 10 mM  $Cs_8Ta_6O_{19}$ .



Fig. S8 Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CTAB to 20 mM Cs<sub>8</sub>Nb<sub>6</sub>O<sub>19</sub>.

Measurement #	Nb%	Cs%	$Cs/{Nb_6}$
1	73.05	26.95	2.21
2	73.39	26.61	2.18
3	75.11	24.89	1.99
4	74.01	25.99	2.11
5	74.44	25.56	2.06
Avg.			2.11
St. Dev			0.09

Table S9 At% values of the precipitate upon adding CTAB to  $20 \text{ mM } \text{Cs}_8\text{Nb}_6\text{O}_{19}$ . Br was not measured.



Fig. S9 Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CTAB to 20 mM Cs<sub>8</sub>Ta<sub>6</sub>O<sub>19</sub>.

Measurement #	Ta%	Cs%	$Cs/{Ta_6}$
1	62.21	37.39	3.58
2	64.83	35.17	3.25
3	61.38	38.62	3.76
4	60.99	39.01	3.84
5	63.07	36.93	3.51
6	62.41	37.59	3.61
Avg.			3.60
St. Dev			0.21

Table S10 At% values of the precipitate upon adding CTAB to 20 mM  $Cs_8Ta_6O_{19}.$  Br was not measured.



Fig. S10 Sample Elemental Analysis spectrum of the resulting precipitate upon adding excess CsCl to 160 mM CsCl. Cs and Cl content was negligible (P/B < 0.6 in all cases).

#### **S7** Computational Details

#### **S7.1** Frontier MO energies

Molecular	$\{Nb_6\}$	$Cs{Nb_6}$	$Cs_4{Nb_6}$	$Cs_8{Nb_6}$
Orbital	OE (eV)	OE (eV)	OE (eV)	OE (eV)
HOMO-2	-5.633	-5.742	-6.041	-6.449
HOMO-1	-5.225	-5.361	-5.687	-6.150
HOMO	-4.844	-4.980	-5.442	-6.068
LUMO	0.544	0.054	-0.136	-0.354
LUMO+1	0.735	0.544	0.082	-0.109
LUMO+2	1.088	0.626	0.544	0.027
LUMO+3	1.197	0.898	0.571	0.163
H-L gap	5.388	5.034	5.306	5.714

**Table S11** Frontier molecular orbital energies of  $\{Nb_6\}$  with 0, 1, 4, and 8 associated Cs<sup>+</sup>, along with HOMO-LUMO gaps.

Table S12 Frontier molecular orbital energies of {Ta<sub>6</sub>} with 0, 1, 4, and 8 associated Cs<sup>+</sup>, along with HOMO-LUMO gaps

Molecular	${Ta_6}$	$Cs{Ta_6}$	$Cs_4{Ta_6}$	$Cs_8{Ta_6}$
Orbital	OE (eV)	OE (eV)	OE (eV)	OE (eV)
HOMO-2	-5.578	-5.687	-6.014	-6.422
HOMO-1	-5.361	-5.497	-5.823	-6.286
HOMO	-4.925	-5.061	-5.551	-6.177
LUMO	1.361	0.054	-0.136	-0.381
LUMO+1	1.469	0.789	0.082	-0.136
LUMO+2	1.796	0.898	0.599	0.163
LUMO+3	1.905	1.116	0.626	0.381
H-L gap	6.286	5.116	5.415	5.796

#### S7.2 Graphical Orbital Renderings

#### S7.2.1 Oxo-Based MOs

#### S7.2.2 Other MOs

Included in spreadsheet

#### S7.3 Atomic Orbital Contributions to Frontier Molecular Orbitals

Included in spreadsheet

#### S7.4 Calculated Electronic Excitations

We also derived the theoretical UV-Vis spectra of the Cs-associated {M<sub>6</sub>} structures by calculating the oscillator strengths of their component electronic transitions. The significant reduction of the HOMO-LUMO gap due to stabilization of the LUMOs, especially seen in Cs{Ta<sub>6</sub>} (but also in Cs{Nb<sub>6</sub>} to a lesser extent), is evidently reflected in the spectra. In Cs{Nb<sub>6</sub>} (Figure S12) a charge transfer (CT) band prominently appears at 258 nm as an extra "hump" on the existing  $n(O_{2p}) \rightarrow \pi^*(Nb_{4d}-O_{2p})$  peak (247 nm). Remaining CT bands – always arising due to transitions from nonbonding  $n(O_{2p})$  orbitals to Cs<sup>+</sup>-mixed Nb<sub>4d</sub>, Nb<sub>5s</sub>, and Nb<sub>5p</sub> – are "covered" by bands already present in {Nb<sub>6</sub>}.

In Cs{Ta<sub>6</sub>}, on the other hand (Figure S13), a greater degree of Cs<sup>+</sup>-orbital admixture with Ta<sub>5d</sub>, Ta<sub>6s</sub>, and Ta<sub>6p</sub> gives rise to a larger number of low-lying LUMOs compared to Cs{Nb<sub>6</sub>}, and produces a visibly altered situation. In this case, CT transitions



**Fig. S11** Graphical renderings of the participating orbitals in the main charge transfer band (HOMO and LUMO+2) of {Nb<sub>6</sub>} and {Ta<sub>6</sub>}. The bridging oxygen  $O_{2p}$  contribution to the {Ta<sub>6</sub>} LUMO+2 is slightly smaller than it is for {Nb<sub>6</sub>}. Red spheres are oxygen, blue spheres are Nb/Ta.

give rise to two well-distinguishable peaks at 251 nm and 239 nm. Since metal-oxo  $\pi^*(Ta_{5d}-O_{2p})$  orbitals are higher in energy compared to their  $\pi^*(Nb_{4d}-O_{2p})$  counterparts, absorption of the  $n(O_{2p}) \rightarrow \pi^*(Ta_{5d}-O_{2p})$  is blueshifted (214 nm), and it is thanks to this that less interference occurs. There is, nonetheless, a third CT transition that, at 211 nm, overlaps with the  $n \rightarrow \pi^*$  band at 214 nm. Turning to the spectra of  $Cs_4\{M_6\}$  and  $Cs_8\{M_6\}$ , it is also evident that, upon association of additional  $Cs^+$  and steady re-increase of the HOMO-LUMO gap (this time due to stabilization of the HOMOs), CT bands become increasingly blueshifted, and eventually re-merge with the  $n \rightarrow \pi^*$  bands. Corroborating experimental UV-Vis spectra are not available, due to signal saturation from the excess base solution necessary to fully deprotonate  $\{Nb_6\}$  and  $\{Ta_6\}$  resulting in truncated spectra upon background subtraction.

A full list of transitions and oscillation strengths is included in the supporting spreadsheet.



Fig. S12 Simulated UV-Vis spectra of  $\{Nb_6\}$  with 0, 1, 4, and 8 associated  $Cs^+.$ 



Fig. S13 Simulated UV-Vis spectra of  $\{Ta_6\}$  with 0, 1, 4, and 8 associated Cs<sup>+</sup>.