Supplementary Material (ESI) for Chemical Communications

Luminescence in Ce^{IV} Polyoxometalate $[Ce(W_5O_{18})_2]^{8-}$: A Combined Experimental and Theoretical Study

Supplementary Material

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Synthesis and Characterization. Sodium tungstate was used as obtained from Fisher. All other reagents were obtained from Acros and were used without further purification. The $Na_8[Ce(W_5O_{18})_2]$ cluster was synthesized following a known procedure.[1] UV-Vis measurements were performed in a Hewlett Packard 8453 UV-visible system. Photoluminescence measurements were performed in a PTI Photon Technology International instrument containing a motor driver MD-5020, lamp power system LPS 220B, and a Bryte box. The FT-IR measurements were performed on a Bruker Vertex 80v vacuum spectrometer using a Harrick Scientific MVP-ProTM ATR. The samples were place in a powder cell attachment to the ATR unit, and the entire system was evacuated to approximately 0.75 Torr (8 hPa) in order to eliminate water and CO_2 atmospheric absorption. For the far infrared region, a Hg arc lamp was used for stimulation with a 50μm Mylar® beamsplitter and a DLATGS (deuterated L-alanine doped triglycene sulphate) detector. For the mid infrared region, a high power globar was used for stimulation with a KBr beam splitter and a liquid N_2 cooled MCT detector. All spectra were measured with a resolution of 2 cm^{-1}, and spectral manipulation was performed with OPUS version 6.5 spectroscopy software. Raman spectroscopy experiments were performed in a Nicolet Magna IR 560 with FT Raman module. The accuracy was checked using a sulfur standard and was ± 4 cm^{-1}.

$Na_8[Ce(W_5O_{18})_2] \cdot 31H_2O$. $Na_2WO_4 \cdot 2H_2O$ (8.3g, 25 mmol) was dissolved in 20 mL of water. The pH was adjusted to pH= 7.0-7.5 by slow addition of acetic acid. The solution was heated to 90 ºC. Then, a solution containing $Ce(NO_3)_3 \cdot 6H_2O$ (1.08g, 2.47 mmol) in 2 mL of water was added to the hot tungsten solution with stirring. A cloudy solution formed that cleared instantly. After 10 minutes, the reaction mixture was allowed to cool to room temperature and crystallized by slow evaporation of the solvent. 6.37 g of the product was obtained. $Na_8[CeW_{10}O_{36}]\cdot 31H_2O$, M= 3297.04, monoclinic, a= 18.041(5), b= 18.497(5), c= 18.324(5), β= 95.941(3), V= 6082(3) $Å^3$, T= 120(1) K, space group C 2/c (No. 15), Z= 4, d_{calc}= 3.601 gcm^{-3}, μ(Mo-Kα) = 2.4 mm^{-1}, μ= 19.7 mm^{-1}, 32637 reflections measured ($2\theta_{max}$= 50.0º), and 7032 unique ($R_{int.}$= 0.0668). The final residuals were R(I>2σ; all data) = 0.0411; 0.0574, and wR(I>2σ; all data)= 0.0986; 0.1079.

[trihexyl(tetradecyl)phosphonium)$_8$][Ce(W$_5$O$_{18}$)$_2$]. [Trihexyl(tetradecyl)phosphonium chloride (1 g, 1.93 mmol) was dissolved in 20 mL of CH_2Cl_2. $Na_8[Ce(W_5O_{18})_2]$ (0.22 mmol) was dissolved in 20 mL of water. The solutions were mixed together and vigorously stirred for 1

h. Then, the phases were separated. The organic phase was concentrated under reduced pressure and freeze dried to obtained 1.06 g of product. IR data in cm^{-1}: 721, 780, 796, 823, 938, 1470, 2850, 2920, 2960.

Density Functional Calculations. All calculations were carried out using *Gaussian 03* (D.02 Version).[2] Geometry optimizations including solvation effects were performed using the hybrid B3LYP method, which incorporates Becke's three-parameter exchange functional (B3)[3] with the Lee, Yang, and Parr (LYP) correlation functional,[4] and the self-consistent reaction field (SCRF) approach based on the polarized continuum model (PCM) level of theory.[5] In PCM, the solvent is represented by a polarized dielectric medium characterized by the relative dielectric constant of the bulk, and a set of optimized radii are used to build an effective cavity occupied by the solute in the solvent. The solute-solvent boundary has been derived using a solvent excluding surface (SES).[6] This is the surface traced by the solvent sphere as it rolls over the molecular surface of the solute defined using the United Atom Universal Force Field topological model (UFF) for the radii of the solute atoms.[7] All SCRF calculations were performed with the default options implemented in *Gaussian 03*. Water solvent model was employed with a dielectric constant of 78.39 and the sphere radius of the solvent (R_{solv}) is 1.385 Å. For the solute interior, a dielectric constant of 1.0 is used throughout.

The basis sets LANL08[8], Stuttgart RSC 1997 ECP basis set (SDD)[9], and 6-311+G* were used for tungsten, cerium, and oxygen, respectively. All geometries were optimized without constraints and verified by vibrational analyses at the same level of theory to insure that they correspond to minima on the potential energy surface. The spin-unrestricted approach was employed for all calculations.

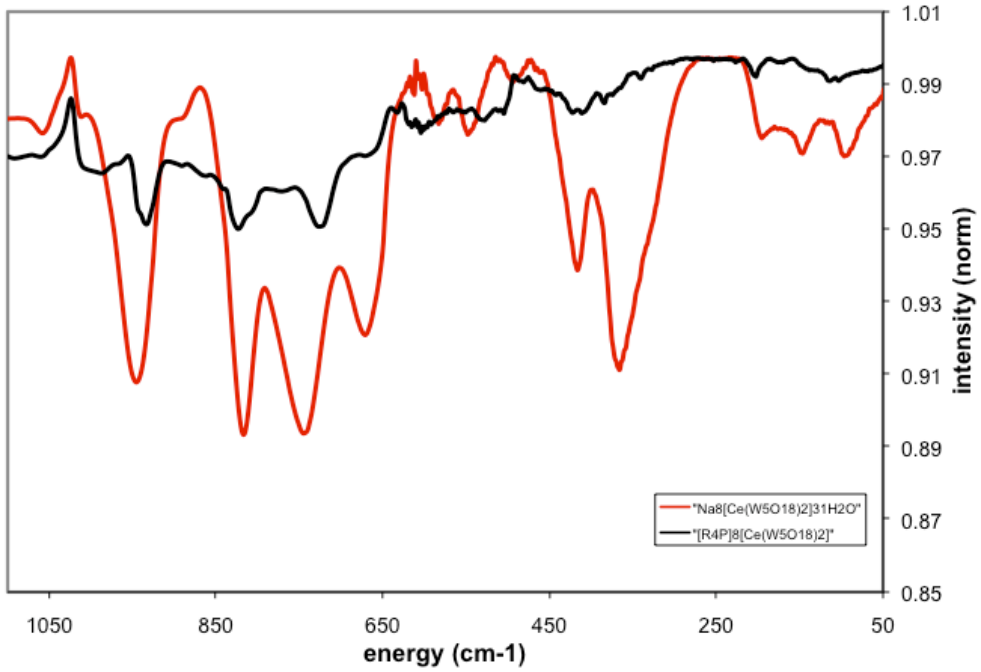

Figure S1. Infrared spectra of $Na_8[Ce(W_5O_{18})_2]$ (red) and $[R_4P]_8[Ce(W_5O_{18})_2]$ (black).

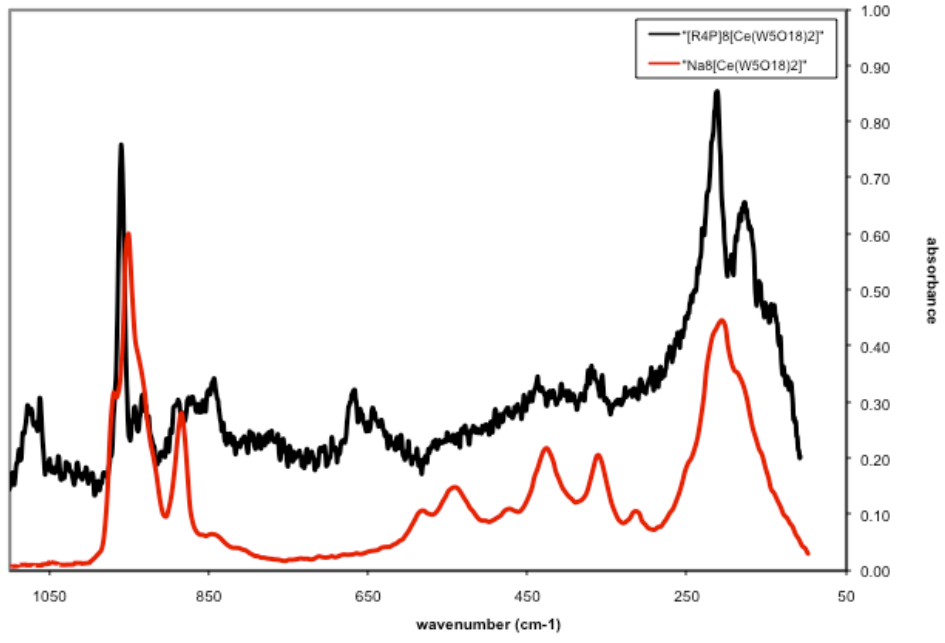

Figure S2. Raman spectra of $Na_8[Ce(W_5O_{18})_2]$ (red) and $[R_4P]_8[Ce(W_5O_{18})_2]$ (black).

Table S1. Optimized Geometry of $[Ce(W_5O_{18})_2]^{8-}$ in Cartesian Coordinates.

Atom	X	Y	Z
Ce	-0.000859701	0.009074036	0.008406125
O	-3.175893667	-2.946359166	-2.857330344
O	3.209219703	-0.003588348	4.104437685
O	-3.236832272	2.919192754	2.881554471
O	3.206018636	-0.036052754	-4.096894086
O	-3.210241797	2.875285124	-2.928956364
O	3.224061508	4.106339902	-0.022926326
O	-3.208473124	-2.876608382	2.928783393
O	3.192901913	-4.101055088	0.021140747
O	-7.292222509	-0.016527723	-0.014607511
O	7.291118371	-0.010937567	-0.006650323
O	-3.255720547	0.002286603	0.003455145
O	3.256003377	-0.000538261	-0.003939172
O	-1.288578585	-1.411451517	-1.389220418
O	1.302793254	0.020451344	1.995379905
O	-1.305731154	1.432687074	1.410208105
O	1.293166494	-0.012045421	-1.99074321
O	-1.301510052	1.407000408	-1.412359315
O	1.304476797	2.004502222	-0.012394408
O	-1.295670784	-1.387433296	1.434866185
O	1.291272551	-1.976850295	0.024342465
O	-3.188718232	-0.0230227	-2.690144544
O	3.208363917	1.914042611	1.889671806
O	-3.211530049	2.687886239	-0.0225205
O	3.200807678	1.888762941	-1.911842344
O	-3.211626031	0.023489752	2.686063955
O	3.191917492	-1.920380232	-1.891377633
O	-3.186218121	-2.684891945	0.025010434
O	3.202405932	-1.884673831	1.907982227
O	-5.049315988	-1.343262869	-1.326534695
O	5.063897351	0.009469732	1.87626068
O	-5.074736706	1.336094333	1.309587137
O	5.057765532	-0.015558005	-1.882464313
O	-5.059988998	1.309628637	-1.347000009
O	5.065235642	1.874081972	-0.019082262
O	-5.061079543	-1.32154889	1.335394563
O	5.055668628	-1.883230816	0.009976959
W	-3.085796879	-1.667115237	-1.646772956
W	3.103267061	0.019753484	2.343940246
W	-3.106344396	1.669138163	1.642618425
W	3.090969462	-0.017038698	-2.337563957

W	-3.098140602	1.645067448	-1.670286172
W	3.102805146	2.3463591	-0.016539001
W	-3.09384587	-1.644839433	1.670971847
W	3.088490945	-2.340645149	0.014824944
W	-5.522450504	-0.006491434	-0.004413651
W	5.521394416	-0.006455413	-0.005219994

Table S4. Triplet Geometry of $[Ce(W_5O_{18})_2]^{8-}$ in Cartesian Coordinates.

Atom	X	Y	Z
Ce	-0.011799584	-0.006785942	-0.076402079
O	0.090390795	4.090122936	-3.290655478
O	2.906156212	-2.825048596	3.357125675
O	-0.082953329	-4.086451675	-3.328357267
O	-2.94889096	2.78333921	3.368144754
O	-4.086817477	0.087596766	-3.327970071
O	-2.837293668	-2.959442209	3.298200591
O	4.092359811	-0.083926662	-3.288628086
O	2.829851678	2.953163835	3.252399755
O	0.022726805	0.022355188	-7.341454106
O	0.110604163	0.107886198	7.398483103
O	0.003763631	0.001791545	-3.285264801
O	-0.012519605	-0.010669244	3.297412994
O	0.035483267	2.05338556	-1.353651229
O	1.46464793	-1.468942486	1.357027402
O	-0.043505211	-2.06645256	-1.374221847
O	-1.536000672	1.415680542	1.358808363
O	-2.069147024	0.038600555	-1.372303888
O	-1.481505021	-1.542754403	1.285200609
O	2.051517746	-0.057279865	-1.354635979
O	1.427902603	1.495111284	1.31728688
O	-1.853923525	1.939899745	-3.273790271
O	0.004920257	-2.676651577	3.30158978
O	-1.933939571	-1.855010722	-3.288360976
O	-2.675862871	-0.10767598	3.300441652
O	1.863070715	-1.936829726	-3.277092803
O	-0.070999767	2.65441286	3.275741988
O	1.940313723	1.858522323	-3.253965082
O	2.655972159	0.0439701	3.267412561
O	0.051481654	1.885600537	-5.1262444
O	1.294300748	-1.298858823	5.176932139
O	-0.029564684	-1.86388822	-5.144343684
O	-1.353405517	1.231833702	5.182283457
O	-1.862937575	0.050654946	-5.142223068

O	-1.288267327	-1.343430713	5.206866708
O	1.885932338	-0.029129845	-5.12597847
O	1.355186852	1.4126113	5.153615617
W	0.052089478	2.345674755	-3.142076719
W	1.659957138	-1.617976805	3.135596274
W	-0.045832671	-2.343227052	-3.163526129
W	-1.689617853	1.591439245	3.138784
W	-2.34376391	0.051151479	-3.163437005
W	-1.640542056	-1.710262325	3.050185467
W	2.347702538	-0.049028916	-3.142404986
W	1.625416507	1.697911289	3.092965334
W	0.013872685	0.012765952	-5.582618846
W	0.113469444	0.114240493	5.647101167

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