Energy Transfer in Supramolecular [Crypt-*RE*]-[W_6I_{14}] Solids

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Table S1. Single crystal structure refinement data for **(1)K, (1)Rb, (1)Cs, (1)Sr,** and **(2)Na**

Compound	**(1)K**	**(1)Rb**	**(1)Cs**	**(1)Sr**	**(2)Na**
Empirical formula	$[\{C_{18}H_{36}N_2O_6\}K]_2[W_6I_{14}]$	$[\{C_{18}H_{36}N_2O_6\}Rb]_2[W_6I_{14}]$	$[\{C_{18}H_{36}N_2O_6\}Cs]_2[W_6I_{14}]$	$[\{C_{18}H_{36}N_2O_6\}Sr][W_6I_{14}]$	$[\{C_{24}H_{35}N_4O_4\}Na]_2[W_6I_{14}]$
CSD	1937039	1937051	1937550	1937593	1937034
Exact formula	$[\{C_{18}H_{36}N_2O_6\}K]_2[W_6I_{14}]$ $\cdot$ 2 C_3H_6O	$[\{C_{18}H_{36}N_2O_6\}Rb]_2[W_6I_{14}]$ $\cdot$ 0.5 $C_4H_{12}O_2S_2$	$[\{C_{18}H_{36}N_2O_6\}Cs]_2[W_6I_{14}]$ $\cdot$ 0.82 C_3H_6O $\cdot$ 0.58 H_2O	$[\{C_{18}H_{36}N_2O_6\}(H_2O)(C_3H_7NO)Sr][W_6I_{14}]$ $\cdot$ 2 C_3H_7NO $\cdot$ 0.701 C_3H_7NO $\cdot$ 0.299 H_3CCN	$[\{C_{24}H_{35}N_4O_4\}Na]_2$[W6I14]
Formula weight	3826.97	3881.68	3956.52	3643.94	3810.78
Temperature / K	100(2)	100(2)	293(2)	100(2)	100(2)
Wavelength / Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$
Unit cell dimensions					
a /Å	16.2061(6)	10.863(1)	14.8492(4)	17.4169(5)	11.5824(2)
b / Å	16.5636(6)	13.777(2)	15.1634(5)	19.2144(6)	11.7282(2)
c /Å	17.6306(6)	13.879(2)	22.2020(8)	20.5070(7)	14.5135(3)
α / °	72.864(2)	74.868(5)	72.954(3)		106.396(1)
β / °	66.933(2)	85.696(5)	87.373(3)		91.055(1)
γ / °	68.017(1)	79.503(5)	59.816(2)		95.029(1)
Volume / Å³	3976.5(3)	1970.7(4)	4100.2(2)	6862.8(4)	1882.15(6)
Z	2	1	2	4	1
Density (calculated) / g·cm^{-3}	3.196	3.271	3.205	3.527	3.362
Absorption coefficient / mm^{-1}	14.233	15.504	14.574	17.128	14.933
F(000)	3398	1714	3480	6377	1684
Crystal size / mm³	0.14 x 0.13 x 0.11	0.259 x 0.084 x 0.055	0.170 x 0.06 x 0.06	0.022 x 0.02 x 0.02	
Theta range for data collection / °	1.650 to 25.026	1.880 to 27.769	2.690 to 25.500	1.865 to 27.103	1.767 to 27.501
Index ranges	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18	-17 ≤ h ≤ 17, -18≤ k ≤ 18, -26 ≤ l ≤ 26	-21≤ h ≤ 22, -24 ≤ k ≤ 24, -26 ≤ l ≤ 26	-15<=h<=15, -15<=k<=15, -18<=l<=18
Reflections collected	59772	65904	17545	51859	88555
Independent reflections	14000 [R(int) = 0.0285]	9207 [R(int) = 0.0171]	7542 [R(int) = 0.0753]	15131 [R(int) = 0.0237]	8601 [R(int) = 0.0224]
Completeness to theta = 25.242° / %	99.7	99.9	48.7	99.9	100.0
Absorption correction	Semi-empirical from equivalents	Numerical	Numerical	Numerical	Numerical
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	14000 / 0 / 743	9207 / 0 / 370	7542 / 246 / 649	15131 / 0 / 597	8601 / 6 / 490
Goodness-of-fit on F2	1.010	1.095	1.047	1.033	1.045
Final R indices [I>2sigma(I)]	R_1 = 0.0219, wR_2 = 0.0393	R_1 = 0.0123, wR_2 = 0.0245	R_1 = 0.0477, wR_2 = 0.1052	R_1 = 0.0193, wR_2 = 0.0409	R_1 = 0.0150, wR_2 = 0.0316
R indices (all data)	R_1 = 0.0367, wR_2 = 0.0430	R_1 = 0.0140, wR_2 = 0.0249	R_1 = 0.0769, wR_2 = 0.1204	R_1 = 0.0212, wR_2 = 0.0416	R_1 = 0.0176, wR_2 = 0.0323
Largest diff. peak and hole / e·A^{-3}	1.050 and -0.896	0.777 and -0.651	1.072 and -1.056	1.900 and -1.268	0.743 and -1.413

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Table S2. Single crystal structure refinement data for **(3)Nd·DMSO, (3)Yb·DMSO** and **(3)Lu·DMSO**

Compound	**(3)Nd·DMSO**	**(3)Yb·DMSO**	**(3)Lu·DMSO**

Empirical formula	$[\{C_{36}H_{26}D_4N_8O_2\}Nd\cdot DMSO]_2[W_6I_{14}]_3$	$[\{C_{36}H_{26}D_4N_8O_2\}Yb\cdot DMSO]_2[W_6I_{14}]_3$	$[\{C_{36}H_{26}D_4N_8O_2\}Lu\cdot DMSO]_2[W_6I_{14}]_3$
CSD	1939598	1938653	1940624
Exact formula	[illegible] $D_4N_8O_2$ [illegible] DMSO$]_2$ [illegible] 7 [illegible] SO · 1.58 [illegible] $_{10}$O· 1. [illegible] · 3.04 H_2 [illegible]	[{C$_{36}$ [illegible] $D_4N_8O_2\}$Y [illegible] SO$]_2$ [W$_6$ [illegible] 3.78 C [illegible] O · 0.79 C [illegible] O · 0.72 C_6H_{14} [illegible]	$[\{C_{36}H_{26}D_4N_8O_2\}Lu\cdot DMSO]_2$ $[W_6I_{14}]_3$ · 7.42 C_2H_6SO · 2 $C_4H_{10}O$ · 1.56 C_6H_{14} [illegible] $_2$O
Formula weight	11183.63	113 [illegible]	11239.12
Temperature / K	100(2)	[illegible] 00(2)	100(2)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal system	Monocli [illegible]	[illegible] onoclinic	Monoclinic
Space group	[illegible] c	[illegible]	$P2_1/c$
Unit cell dimensions			
a / Å	14.560(3)	[illegible] 5137(6)	14.576(6)
b / Å	24. [illegible]	24.5673(8)	24.51(1)
c / Å	30.796(6)	30.292(1)	30.76(1)
β / °	10 [illegible] 3)	100.75 [illegible]	101.658(5)
Volume / Å³	10726([illegible]	[illegible] 0611.1([illegible]	10763(8)
Z	2	2	2
Density (calculated) / g·cm^{-3}	3.462	3.537	3.468
Absorption coefficient / mm^{-1}	16. [illegible]	16.857	16.640
F(000)	9768.6	9862.5	9807
Crystal size / n	[illegible]	[illegible]	0.002
Theta range fo	[illegible]	[illegible]	27
Index ranges	[illegible]	[illegible]	$-29 \le k \le 29$, $-36 \le l \le 36$
Reflections col	[illegible]	[illegible]	[illegible]
Independent re	[illegible]	[illegible]	= 0.0887]
Completeness	[illegible]	[illegible]	[illegible]
Absorption cor	[illegible]	[illegible]	[illegible]
Refinement me	[illegible]	[illegible]	ast-squares on F^2
Data / restraint	[illegible]	[illegible]	995
Goodness-of-fi	[illegible]	[illegible]	[illegible]
Final R indices	[illegible]	[illegible]	$wR_2 = 0.1468$
R indices (all d	[illegible]	[illegible]	$wR_2 = 0.1722$
Largest diff. pe	[illegible]	[illegible]	94

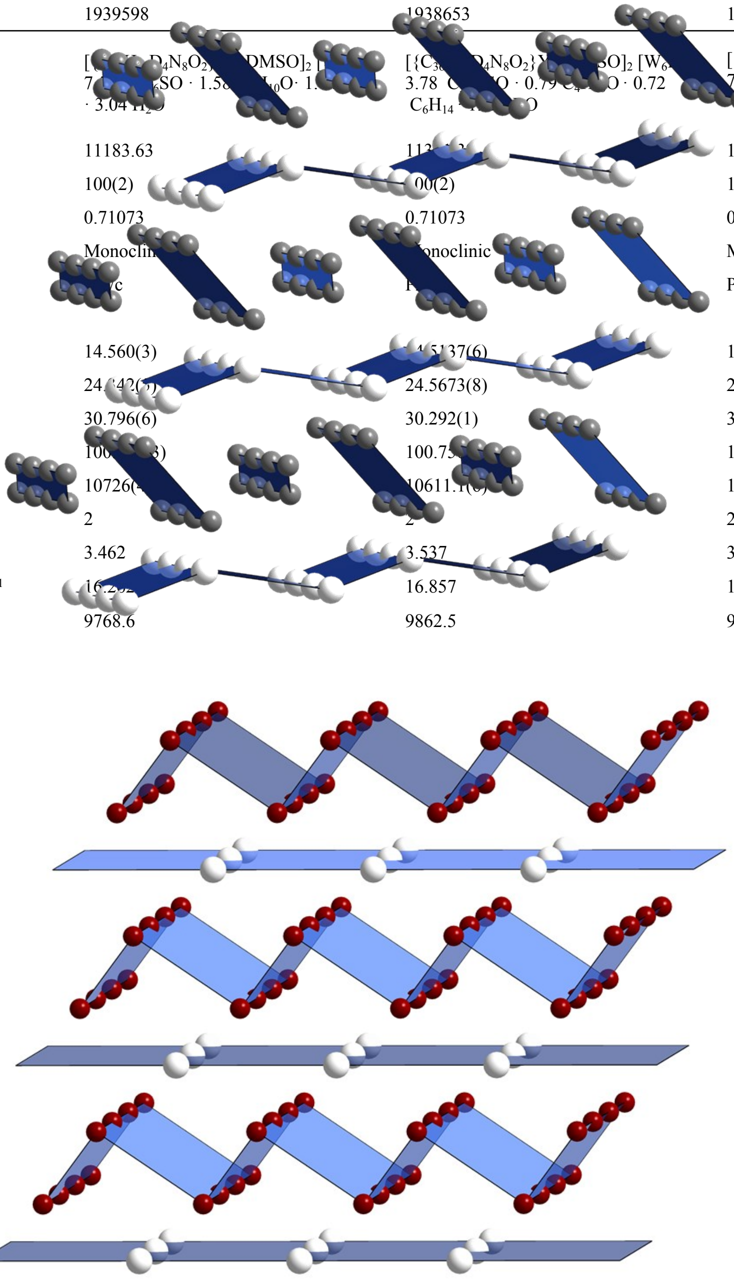

Figure S1. Layered structure arrangement in $[\{C_{18}H_{36}N_2O_6\}A]_2[W_6I_{14}]$ **(1)*A*** on the example of *A* = K, (top) and *A* = Rb (bottom). Only the centers of gravity of $\{C_{18}H_{36}N_2O_6\}A]^+$ represented by the alkaline ion (grey spheres for K and red spheres for Rb) and the center of gravity of the $[W_6I_{14}]^{2-}$ cluster ions (white spheres) are shown for clarity.

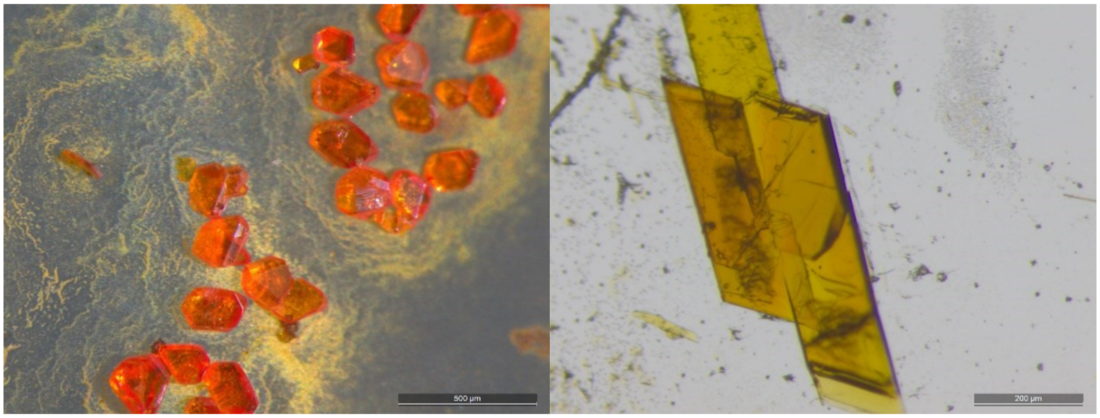

Figure S2. Light microscopy image of **(1)Cs** single crystals (left) and **(1)K** (right).

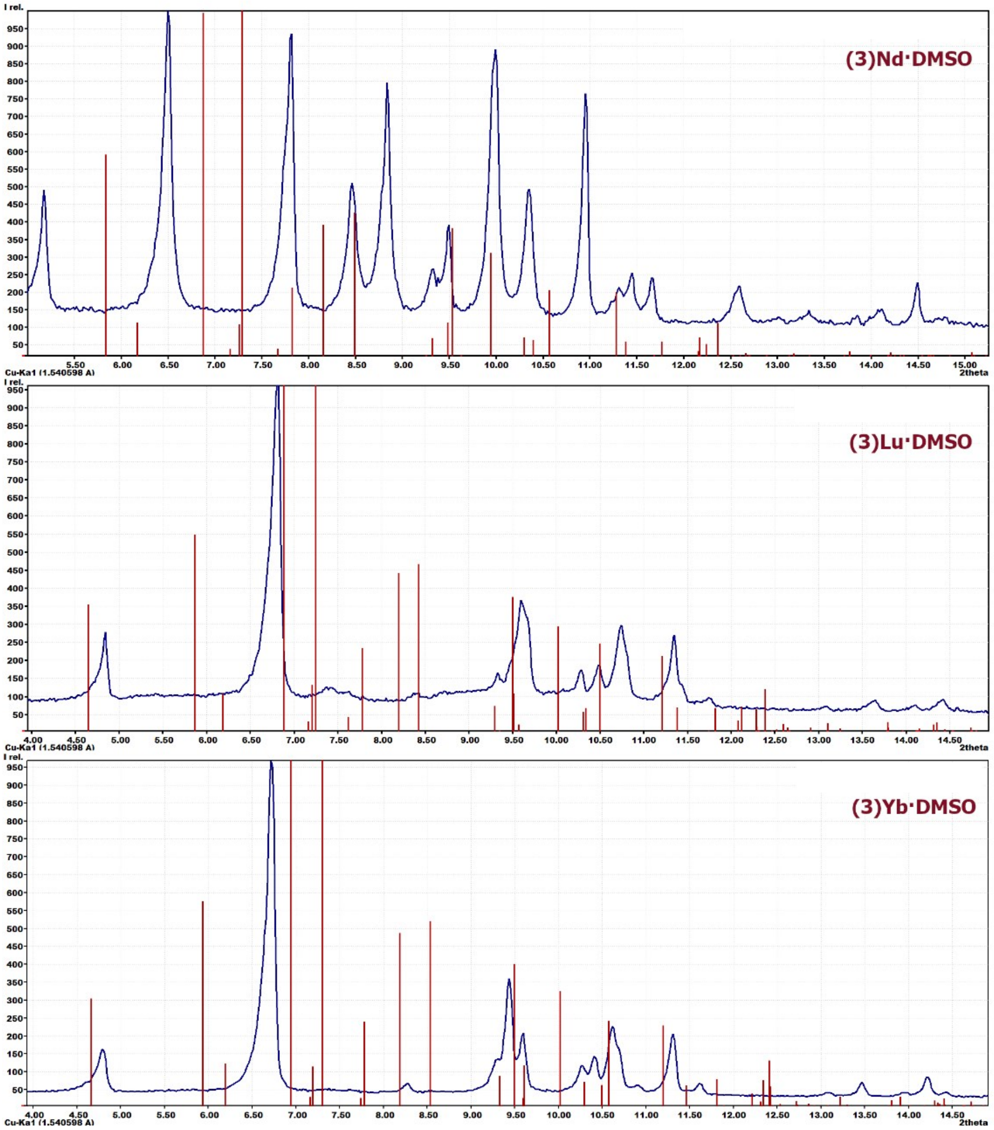

Figure S3. X-ray powder diffraction patters of the product from the reaction of $[\{C_{36}H_{26}D_4N_8O_2\}RE\cdot Cl]Cl_2$ with $Cs_2[W_6I_{14}]$. As the amount of solvents incorporated in the single crystals differ, the powder patterns are not expected to be in good agreement. Powder measurements of the supposed **(3)*RE*·Cl** do show the same pattern for *RE* = Yb and Lu. In red Bragg positions and intensities of the reference compounds $[\{C_{36}H_{26}D_4N_8O_2\}RE\cdot DMSO]_2[W_6I_{14}]_3$ obtained from single crystal data are shown.

Table S3. Energy-dispersive X-ray spectroscopy measurement of products resulting from the reaction of $Cs_2[W_6I_{14}]$ with $[\{C_{36}H_{26}D_4N_8O_2\}$*RE*$\cdot Cl]Cl_2$ with *RE* = Nd, Lu, Yb. Results are normalized to six tungsten atoms of $[W_6I_{14}]^{2-}$.

Element	Measured composition for **(3)Lu·Cl**	Measured composition for **(3)Nd·Cl**	Measured composition for **(3)Yb·Cl**
W	6	6	6
I	12.27 ± 2.67	13.78 ± 1.50	7.90 ± 1.76
RE	0.97 ± 0.06	0.95 ± 0.10	0.98 ± 0.10
Cl	0.92 ± 0.17	1.09 ± 0.29	1.07 ± 0.19

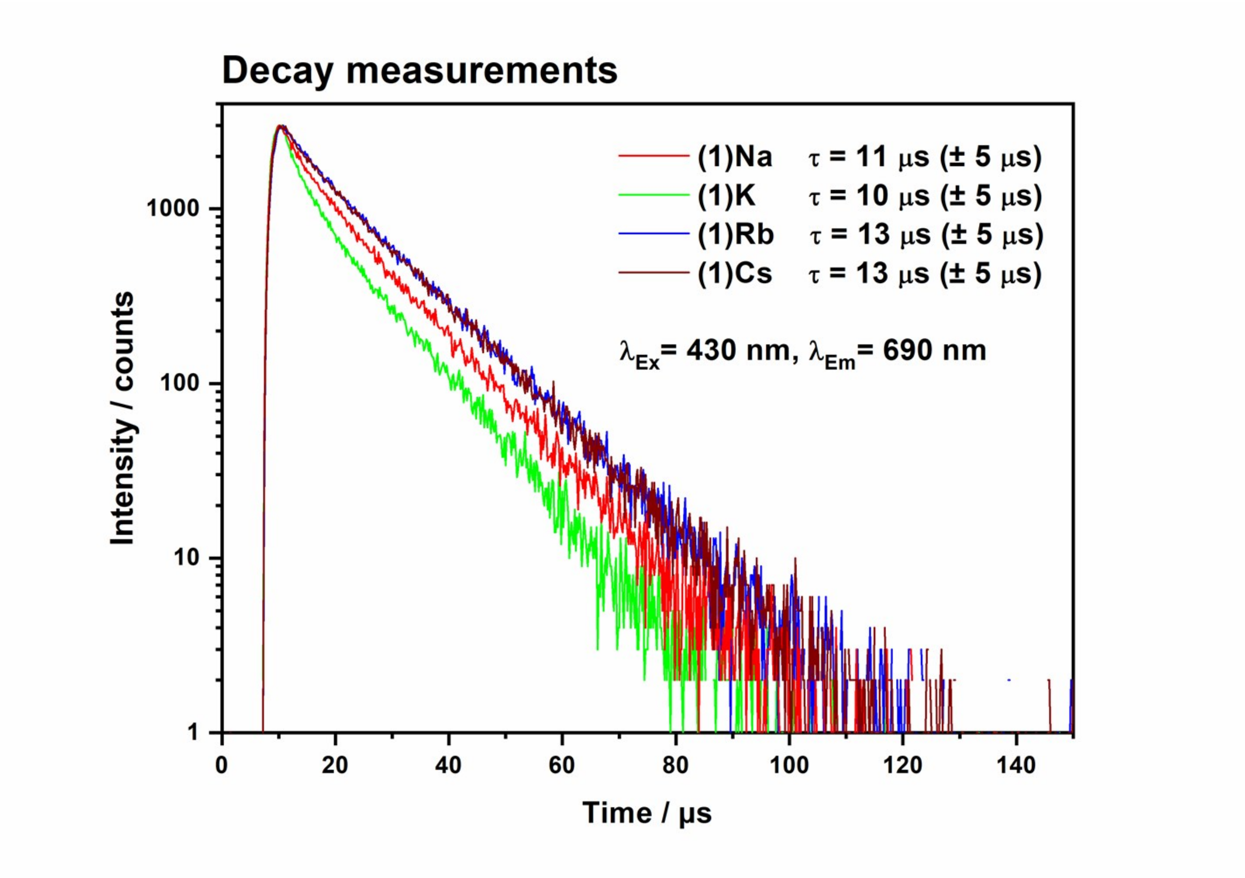

Figure S4. Decay measurements of **(1)*A*** with *A* = Na, K, Rb, Cs.

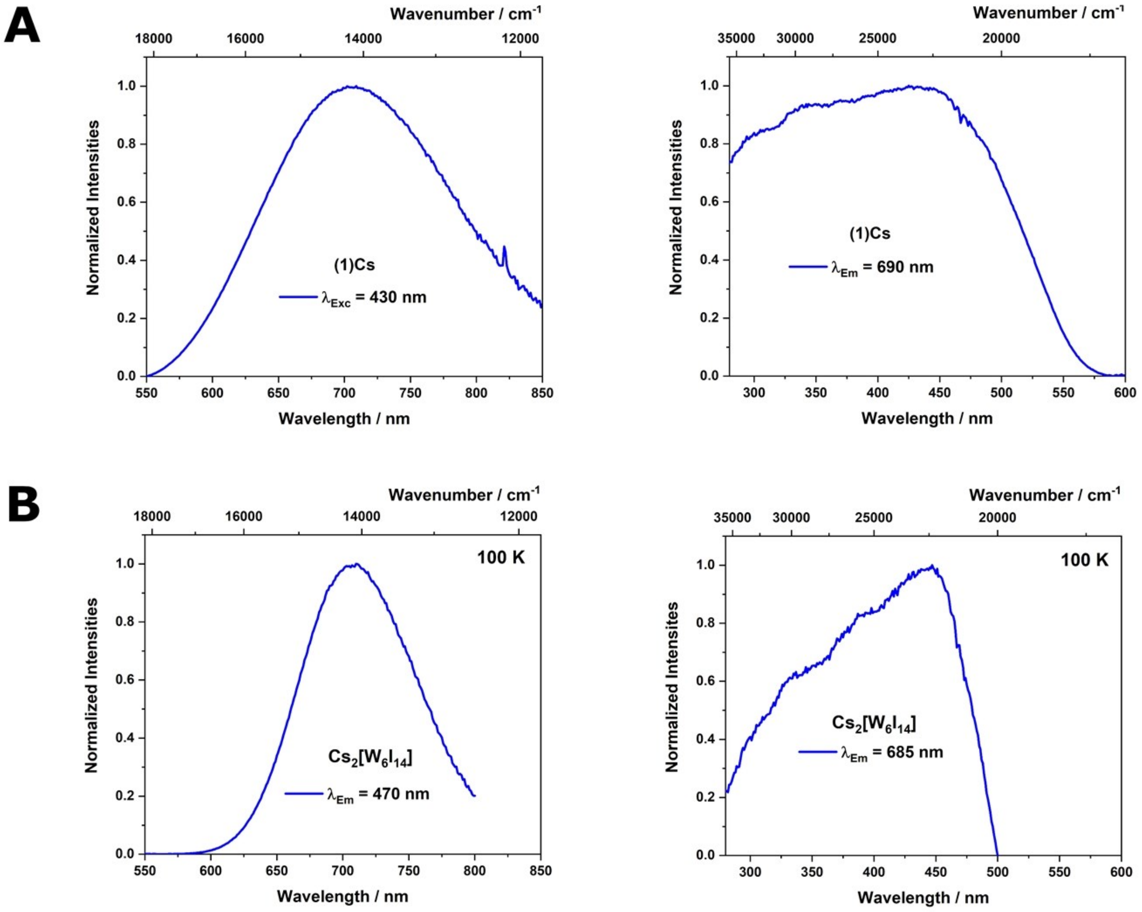

Figure S5. Maximum normalized emission spectra of solid **(1)Cs** (A, room temperature) and Cs$_2$[W$_6$I$_{14}$] (B, 100 K) displaying the [W$_6$I$_{14}$]$^{2-}$ emission upon excitation the cluster anion at 430 nm and 470 nm respectively. Excitation spectra are recorded by monitoring the 690 nm and 685 nm emission of [W$_6$I$_{14}$]$^{2-}$.

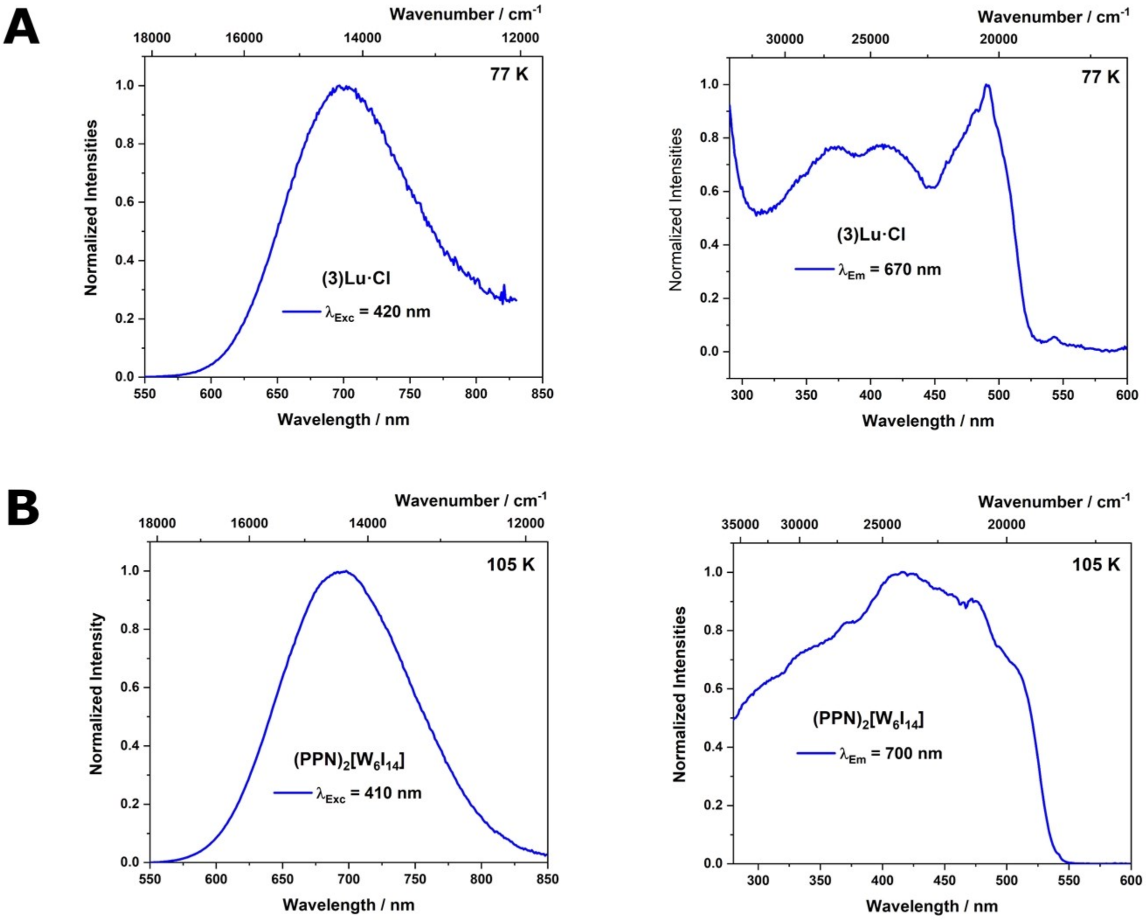

Figure S6. Maximum normalized emission spectra of solid **(3)Lu·Cl** (A, 77 K) and (PPN)$_2$[W$_6$I$_{14}$] (B, 105 K) displaying the [W$_6$I$_{14}$]$^{2-}$ emission upon excitation the cluster anion at 420 nm and 410 nm respectively. Excitation spectra are recorded by monitoring the 670 nm and 700 nm emission of [W$_6$I$_{14}$]$^{2-}$.