Supramolecular Host-Guest Assemblies of $[M_6Cl_{14}]^{2-}$, M = Mo, W Clusters with γ-Cyclodextrin for the Development of CLUSPOMs

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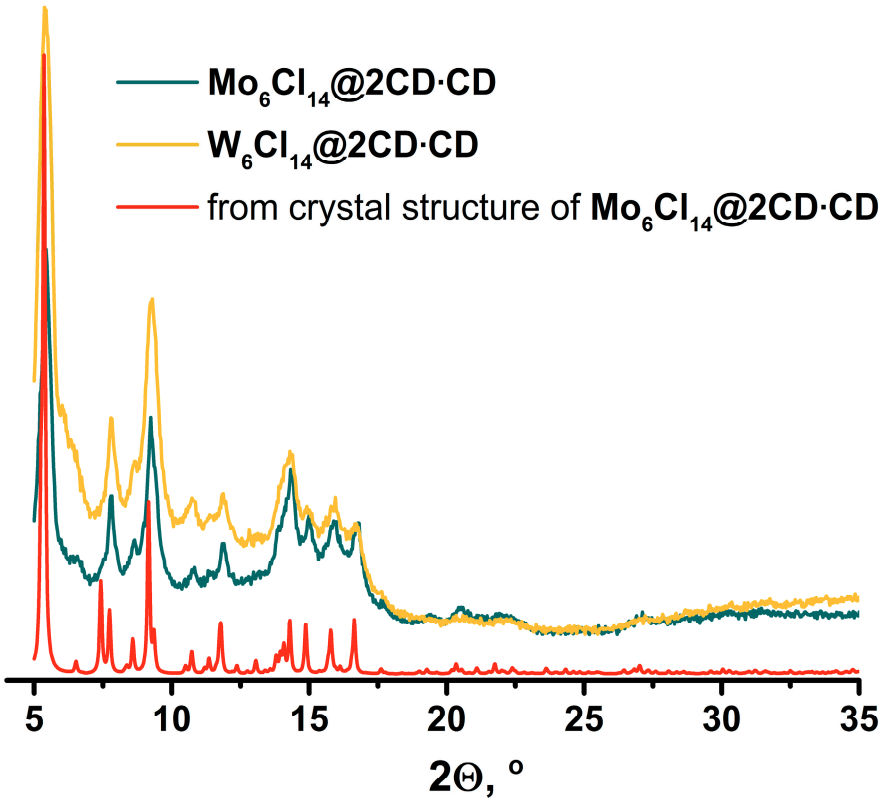

Figure S1. Powder patters of **Mo_6Cl_{14}@2CD·CD** and **W_6Cl_{14}@2CD·CD** in comparison with theoretical one constructed from SCXRD data for **Mo_6Cl_{14}@2CD·CD**.

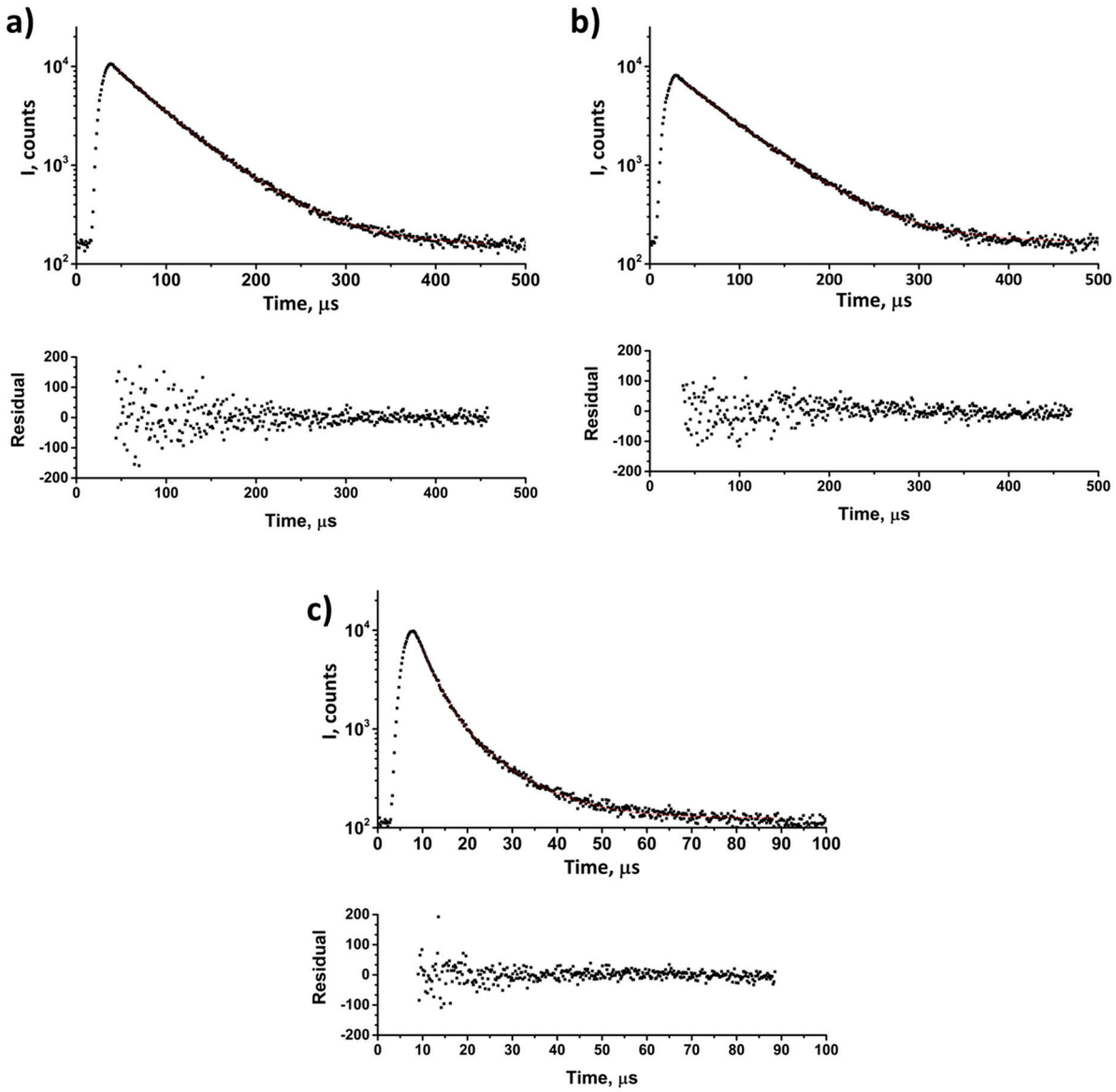

Figure S2. Luminescence decay curves of Mo_6Cl_{14} (a), Mo_6Cl_{14}**@2CD·CD** (b) and W_6Cl_{14} (c) in solid state. χ^2 = 0.99962, 0.99959 and 0.99964 correspondingly.

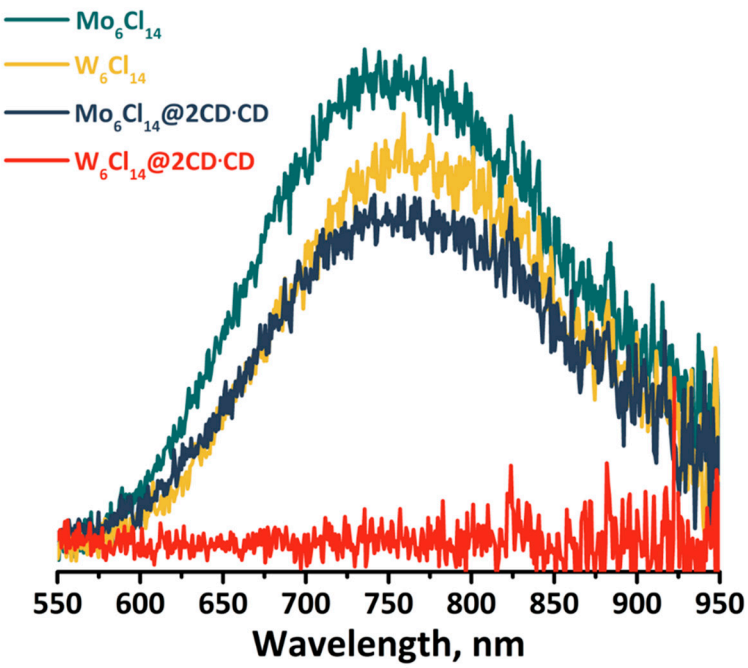

Figure S3. Emission spectra of compounds in solid state.

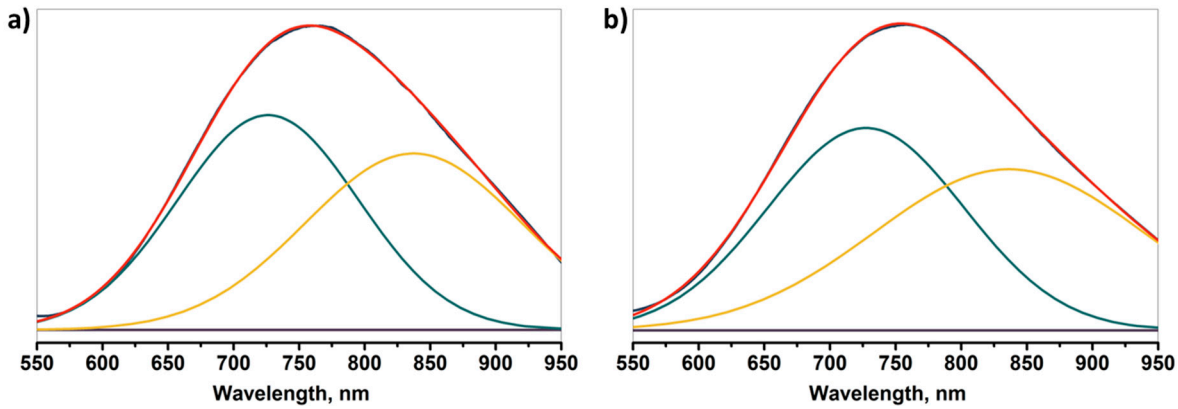

Figure S4. Deconvolution of the emission spectra of **Mo_6Cl_{14}** (a) and **Mo_6Cl_{14}@2CD·CD** (b) in solid state.

Table S1. Peak positions, relative contributions and coefficient of determination R^2 of **Mo_6Cl_{14}** and **Mo_6Cl_{14}@2CD·CD** of the two Voigt components of the fitted emission spectra in Fig. S4.

Compound	Peak, nm	Relative contribution	R^2
Mo_6Cl_{14}	726	0.522	0.9998
	837	0.478	
Mo_6Cl_{14}@2CD·CD	727	0.503	0.9998
	836	0.497	

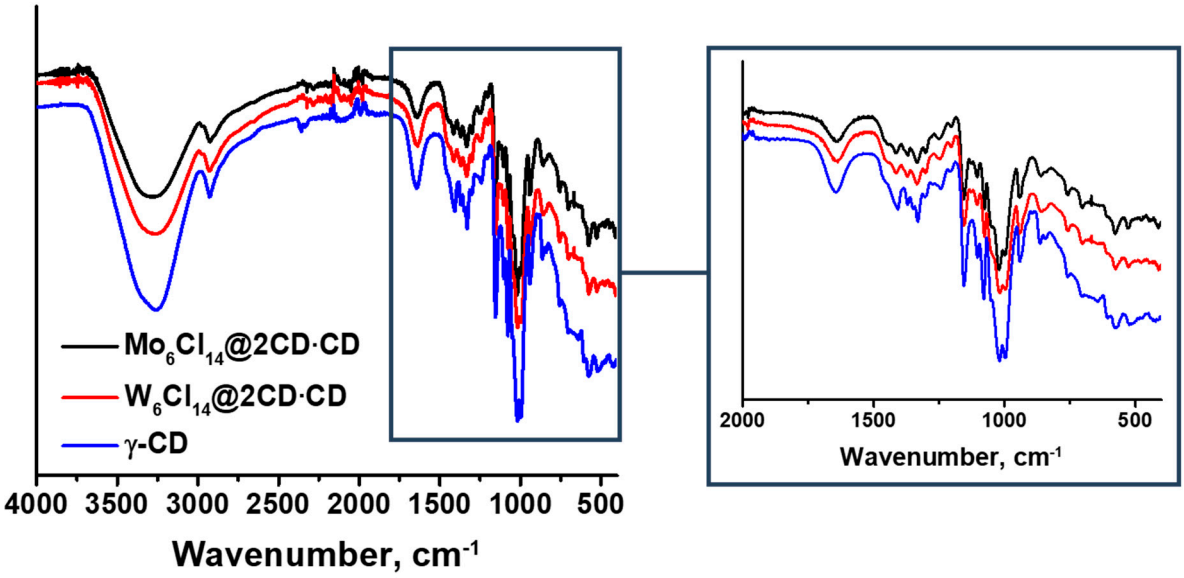

Figure S5. FTIR spectra of **Mo_6Cl_{14}@2CD·CD** and **W_6Cl_{14}@2CD·CD** in comparison with γ-CD.

Table S2. Selected crystallographic parameters of the single-crystal X-ray diffraction structural analysis for $(H_3O)_2\{[Mo_6Cl_8Cl_6]@(\gamma\text{-CD})_2\}\cdot 2((H_3O)_2[Mo_6Cl_8Cl_6])\cdot 15H_2O$ (**Mo_6Cl_{14}@2CD·2Mo_6Cl_{14}**), $(H_3O)_2\{[Mo_6Cl_8Cl_6]@(\gamma\text{-CD})_2\}\cdot(\gamma\text{-CD})\cdot 15H_2O$ (**Mo_6Cl_{14}@2CD·CD**) and $(H_3O)_2\{[W_6Cl_8Cl_6]@(\gamma\text{-CD})_2\}\cdot 0.5((H_3O)_2[W_6Cl_8Cl_6])\cdot 15H_2O$ (**W_6Cl_{14}@2CD·0.5W_6Cl_{14}**)

	Mo_6Cl_{14}@2CD·2Mo_6Cl_{14}	**Mo_6Cl_{14}@2CD·CD**	**W_6Cl_{14}@2CD·0.5W_6Cl_{14}**
Chemical formula	$C_{96}H_{110}Cl_{42}Mo_{18}O_{97}$	$C_{144}H_{168}Cl_{14}Mo_6O_{140}$	$C_{192}H_{224}Cl_{42}O_{189.60}W_{18}$
M_r	6031.65	5210.71	10363.50
Crystal system, space group	Triclinic, *P*1	Tetragonal, $P42_12$	Tetragonal, *I*422
Temperature (K)	130	200	130
a, *b*, *c* (Å)	17.8167 (3), 17.9076 (3), 19.7519 (4)	23.806 (1), 23.806 (1), 22.831 (1)	35.7254 (5), 35.7254 (5), 34.3472 (12)
α, β, γ (°)	116.936 (2), 116.807 (2), 90.012 (1)	90, 90, 90	90, 90, 90
V (Å^3)	4846.01 (19)	12938.9 (12)	43837 (2)
Z	1	2	4
μ (mm^{-1})	1.79	0.52	5.04
Crystal size (mm)	0.25 × 0.20 × 0.20	0.1 × 0.1 × 0.02	0.25 × 0.25 × 0.25
Diffractometer	New Xcalibur, AtlasS2	Bruker D8 VENTURE	New Xcalibur, AtlasS2
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.41.123a (Rigaku Oxford Diffraction, 2022) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1213 before and 0.1053 after correction. The Ratio of minimum to maximum transmission is 0.8080. The l/2 correction factor is Not present.	Multi-scan *CrysAlis PRO* 1.171.41.123a (Rigaku Oxford Diffraction, 2022) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.977, 1.000	0.603, 0.746	0.479, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	85634, 44790, 42664	257159, 11500, 10490	45883, 16744, 10452
R_{int}	0.023	0.122	0.076
θ_{max} (°)	29.7	25.1	23.8
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.697	0.596	0.568

Range of h, k, l	$-24 \le h \le 24$, $-24 \le k \le 24$, $-26 \le l \le 25$	$-28 \le h \le 28$, $-28 \le k \le 28$, $-27 \le l \le 27$	$-40 \le h \le 40$, $-30 \le k \le 38$, $-30 \le l \le 39$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.144, 0.320, 1.09	0.075, 0.220, 1.04	0.066, 0.192, 1.03
No. of reflections, parameters, restraints	44790, 1314, 5	11500, 740, 0	16744, 958, 55
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 478.8877P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1333P)^2 + 49.8256P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0787P)^2 + 957.9431P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	4.98, -3.69	1.35, -1.15	3.18, -1.56
Absolute structure	Refined as an inversion twin.	Refined as an inversion twin.	Flack x determined using 3699 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	0.28 (11)	0.07 (7)	-0.023 (7)

Computer programs: *CrysAlis PRO* 1.171.41.123a (Rigaku OD, 2022), *SAINT* v8.37A (Bruker, 2015), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXT* (Sheldrick, 2015), *SHELXL2017*/1 (Sheldrick, 2017), *SHELXL* 2018/3 (Sheldrick, 2015), Olex2 1.5 (Dolomanov et al., 2009).