Electronic Supplementary Information (*Dalton Transaction*)

A Study on the Redox, Spectroscopic, and Photophysical Characteristics of a Series of Octahedral Hexamolybdenum(II) Clusters: $[\{Mo_6X_8\}Y_6]^{2-}$ (X, Y = Cl, Br, or I)

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Characterizations of 1 – 9: ESI-MS (CH_3CN)

For $C_{32}H_{72}N_2Mo_6Cl_8Y_6$.

Y = Cl (**1**): m/z 535 (M–2TBA). Y = Br (**2**): m/z 669 (M–2TBA). Y = I (**3**): m/z 810 (M–2TBA).

For $C_{32}H_{72}N_2Mo_6Br_8Y_6$.

Y = Cl (**4**): m/z 713 (M–2TBA). Y = Br (**5**): m/z 847 (M–2TBA). Y = I (**6**): m/z 988 (M–2TBA).

For $C_{32}H_{72}N_2Mo_6I_8Y_6$.

Y = Cl (**7**): m/z 901(M–2TBA). Y = Br (**8**): m/z 1035 (M–2TBA). Y = I (**9**): m/z 1176 (M–2TBA).

Characterizations of 1 – 9: Elemental Analysis

Anal. Calcd for $C_{32}H_{72}N_2Mo_6Cl_8Y_6$.

Y = Cl (**1**): C, 24.69; H, 4.67; N, 1.80. Found: C, 25.05; H, 4.88; N, 1.20. Y = Br (**2**): C, 21.08; H, 3.99; N, 1.54. Found: C, 20.99; H, 3.66; N, 1.32. Y = I (**3**): C, 18.25; H, 3.45; N, 1.33. Found: C, 18.26; H, 3.55; N, 1.28.

Anal. Calcd for $C_{32}H_{72}N_2Mo_6Br_8Y_6$.

Y = Cl (**4**): C, 20.01; H, 3.80; N, 1.47. Found: C, 20.12; H, 3.63; N, 1.66. Y = Br (**5**): C, 17.64; H, 3.33; N, 1.29. Found: C, 17.42; H, 3.11; N, 1.18. Y = I (**6**): C, 15.62; H, 2.95; N, 1.14. Found: C, 15.66; H, 3.01; N, 1.22.

Anal. Calcd for $C_{32}H_{72}N_2Mo_6I_8Y_6$.

Y = Cl (**7**): C, 16.80; H, 3.17; N, 1.22. Found: C, 16.91; H, 3.19; N, 1.26. Y = Br (**8**): C, 15.04; H, 2.84; N, 1.10. Found: C, 15.22; H, 2.81; N, 0.99. Y = I (**9**): C, 13.55; H, 2.56; N, 0.99. Found: C, 13.42; H, 2.36; N, 0.91.

Table S1. Absorption maximum wavelengths and molar absorption coefficients of $[\{Mo_6X_8\}Y_6]^{2-}$ in CH_3CN at 298 K.

X = Cl	$[\{Mo_6Cl_8\}Y_6]^{2-}$		
	1 (Y = Cl)	**2** (Y = Br)	**3** (Y = I)
λ_a (ε) / nm (10^3 $M^{-1}cm^{-1}$)	222 (157.0), 241 (6.8), 342 (2.3)	242 (100.0), 292 (2.9), 366 (2.3)	209 (59.2), 224 (122.3), 241 (55.7), 280 (76.0), 377 (5.9)
$\tilde{\nu}_a$ / 10^3 cm^{-1} a)	29.2	27.3	26.5

X = Br	$[\{Mo_6Br_8\}Y_6]^{2-}$		
	4 (Y = Cl)	**5** (Y = Br)	**6** (Y = I)
λ_a (ε) / nm (10^3 $M^{-1}cm^{-1}$)	233 (137.1), 292 (3.6), 335 (4.2), 386 (3.5)	221 (34.9), 251 (61.9), 302 (2.5), 333 (2.2), 388 (2.1)	221 (63.6), 233 (118.0), 259 (58.3), 289 (72.5), 326 (21.3), 397 (6.1)
$\tilde{\nu}_a$ / 10^3 cm^{-1} a)	25.9	25.8	25.2

X = I	$[\{Mo_6I_8\}Y_6]^{2-}$		
	7 (Y = Cl)	**8** (Y = Br)	**9** (Y = I)
λ_a (ε) / nm (10^3 $M^{-1}cm^{-1}$)	207 (58.6), 229 (41.2), 255 (51.7), 286 (10.0), 322 (6.6), 363 (3.6), 419 (3.3)	214 (86.2), 224 (86.0), 267 (76.7), 325 (7.3), 339 (8.4), 371 (4.7), 421 (5.1)	212 (62.9), 224 (58.1), 245 (82.6), 282 (46.0), 304 (39.0), 354 (17.2), 429 (6.1), 500 (3.1)
$\tilde{\nu}_a$ / 10^3 cm^{-1} a)	23.9	23.8	20.0

a) The energy of the lowest-wavelength absorption band.

Table S2. Photophysical properties of $[\{Mo_6X_8\}Y_6]^{2-}$ (X, Y = Cl, Br, or I) in deaerated crystalline phases at 298 K.

			X		
			Cl	**Br**	**I**
$\tilde{\nu}_{em}$ / 10^3 cm^{-1} (*fwhm* / cm^{-1}) [λ_{em} / nm]	**Y**	**Cl**	13.2 (3830) [758]	13.5 (4210) [742]	14.1 (2320) [707]
		Br	12.9 (4040) [778]	12.9 (4030) [773]	14.0 (2850) [713]
		I	12.3 (3820) [810]	12.3 (3840) [812]	13.6 (4530) [735]
Φ_{em}	**Y**	**Cl**	0.20	0.21	0.57
		Br	0.17	0.15	0.24
		I	0.08	0.10	0.13
τ_{em} / μs	**Y**	**I**	130	115	170
		Br	105	85	130
		I	55	50	50
k_r / 10^3 cm^{-1}	**Y**	**Cl**	1.5	1.8	3.4
		Br	1.6	1.8	1.9
		I	1.5	2.0	2.6
k_{nr} / 10^3 cm^{-1}	**Y**	**Cl**	6.2	6.9	2.4
		Br	7.9	10	5.9
		I	17	18	17

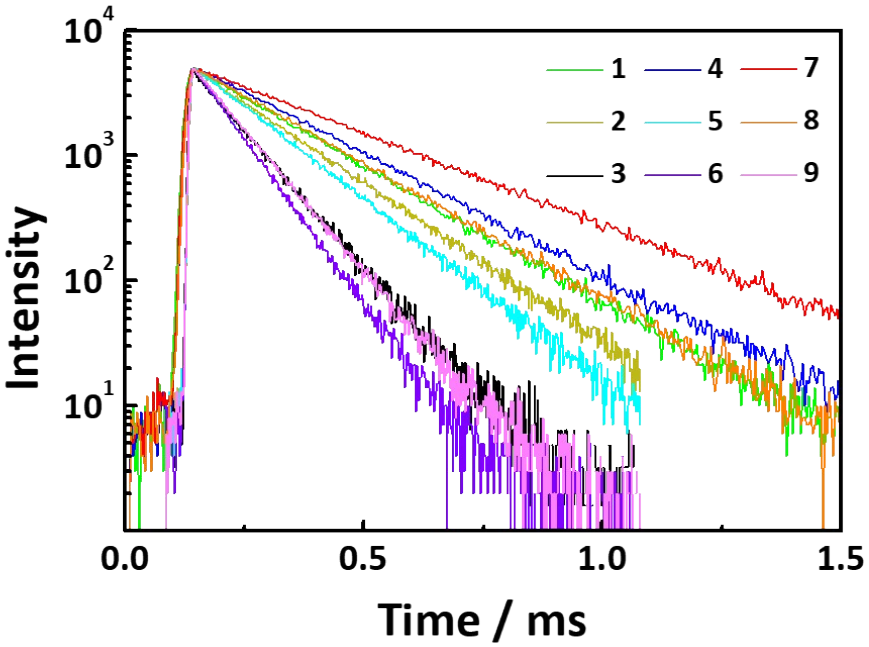

Figure S1. Emission decay profiles of **1** – **9** in deaerated CH_3CN at 298 K.

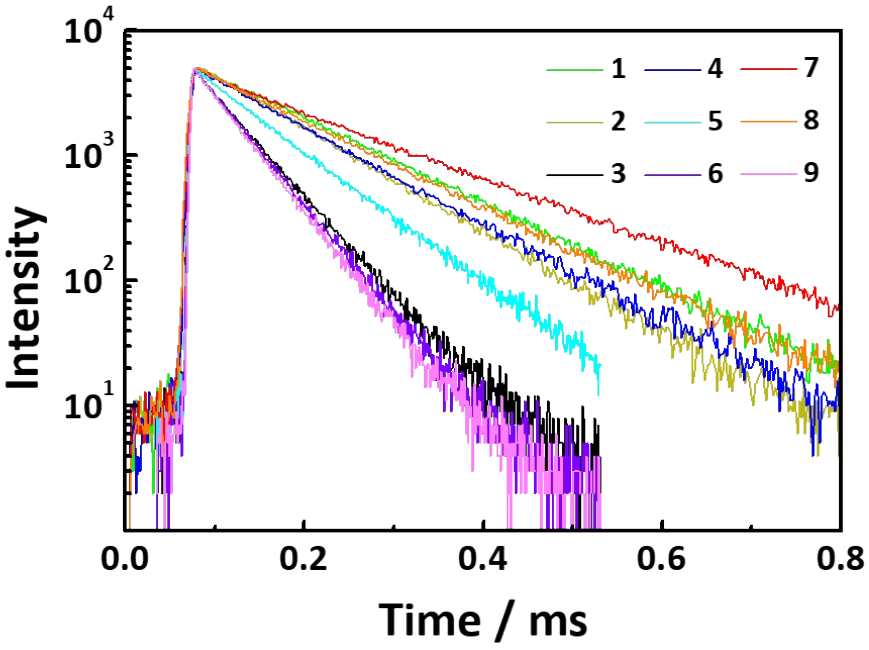

Figure S2. Emission decay profiles of **1** – **9** in deaerated crystalline phases at 298 K.