

Highly Emissive Hexanuclear Rhenium(III) Clusters Containing the Cubic Cores $[\text{Re}_6\text{S}_8]^{2+}$ and $[\text{Re}_6\text{Se}_8]^{2+}$ Thomas G. Gray,[‡] Christina M. Rudzinski,[†] Daniel G. Nocera,^{*,†} and R. H. Holm^{*,‡}

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Substantial current interest^{1,2} attends hexanuclear rhenium(III) chalcogenide clusters with cubic $[\text{Re}_6(\mu_3\text{-Q})_8]^{2+}$ cores^{3,4} (inset, Figure 1), lately available in soluble molecular form by the protocol of dimensional reduction.^{5,6} Oxidized anions $[\text{Re}_5^{\text{III}}\text{Re}^{\text{IV}}\text{S}_8\text{Br}_6]^{3-}$ and $[\text{Re}_6\text{Se}_8\text{I}_6]^{3-7}$ sustain reductive dehalogenation by Ag^{I} reagents or phosphines, affording cluster solvates $[\text{Re}_6\text{Se}_8(\text{solv})_6]^{2+}$ and phosphine-substituted $[\text{Re}_6\text{Q}_8(\text{PET}_3)_{6-n}\text{X}_n]^{(2-n)+}$ ($n = 4-6$; $\text{Q} = \text{S}, \text{X} = \text{Br}; \text{Q} = \text{Se}, \text{X} = \text{I}$).⁸⁻¹⁰ Diversely ligated clusters are now readily accessible, with adjustable microsymmetries secured using nonlabile phosphines as protecting groups. These clusters are isoelectronic with $[\text{M}_6(\mu_3\text{-X})_8\text{X}'_6]^{2-}$ ($\text{M} = \text{Mo}, \text{W}; \text{X}, \text{X}' = \text{Cl}, \text{Br}, \text{I}$), which phosphoresce with established photoredox and energy-transfer capabilities.¹¹⁻¹⁶ Although their terminal ligand substitution reactions are extensive, spectroscopic investigations have emphasized perhalogenated species.¹⁷ Photophysical understanding of cluster-based luminescence hinges upon identifying consequences of altered core compositions, peripheral ligand spheres, and local symmetries, ideally suiting $[\text{Re}_6\text{Q}_8]^{2+}$ clusters for detailed experimentation. We report that these clusters emit vivid red phosphorescence upon UV-visible excitation, with microsecond-scale emissive lifetimes. Luminescence maxima and nonradiative decay constants are correlated through the energy gap law.

Collected in Table 1 are luminescence data at 296 K for compounds **1–16**.¹⁸ Depicted in Figure 1 are absorption and emission spectra of $[\text{Re}_6\text{Se}_8(\text{Me}_2\text{SO})_6]^{2+}$ (**9**) in dimethyl sulfoxide solution, selected as a representative example. Ill-resolved LMCT

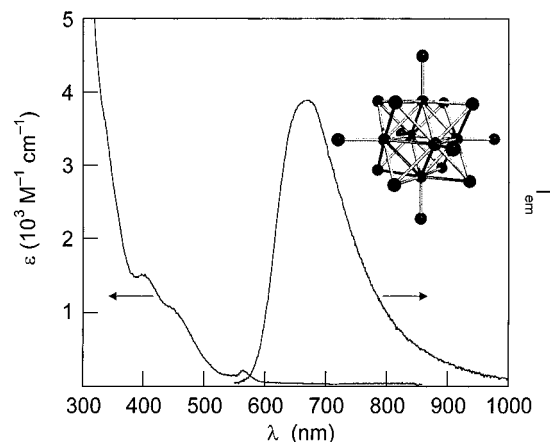


Figure 1. Absorption and corrected emission spectra (436 nm excitation, 296 K) of **9** in neat dimethyl sulfoxide. Inset: depiction of $[\text{Re}_6\text{Q}_8\text{L}_6]^{2+}$ clusters.

Table 1. Excited-State Parameters for Hexanuclear Rhenium(III) Chalcogenide Clusters^a

	clusters ^b	E_{em} (10^3 cm^{-1})	ϕ_{em}^d	τ_0 (μs)
1	$[\text{Re}_6\text{S}_8\text{Cl}_6](\text{Bu}_4\text{N})_4$	13.27	0.031	5.1
2	$[\text{Re}_6\text{S}_8\text{Br}_6](\text{Bu}_4\text{N})_4$	12.85	0.012	3.9
3	$[\text{Re}_6\text{S}_8\text{I}_6](\text{Bu}_4\text{N})_4^c$	12.50	0.011	2.6
4	$[\text{Re}_6\text{S}_8(\text{PET}_3)_6]\text{Br}_2$	13.90	0.044	10.0
5	$[\text{Re}_6\text{Se}_8(\text{PET}_3)_6]\text{I}_2$	13.70	0.068	10.8
6	$[\text{Re}_6\text{Se}_8(\text{MeCN})_6](\text{SbF}_6)_2^c$	14.40	0.100	14.8
7	$[\text{Re}_6\text{Se}_8(\text{pyridine})_6](\text{SbF}_6)_2^c$	14.50	0.163	14.0
8	$[\text{Re}_6\text{Se}_8(\text{DMF})_6](\text{SbF}_6)_2^c$	14.70	0.203	18.9
9	$[\text{Re}_6\text{Se}_8(\text{Me}_2\text{SO})_6](\text{SbF}_6)_2^c$	15.10	0.238	22.4
10	<i>trans</i> - $[\text{Re}_6\text{Se}_8(\text{PET}_3)_4\text{I}_2]$	13.40	0.037	5.4
11	<i>cis</i> - $[\text{Re}_6\text{Se}_8(\text{PET}_3)_4\text{I}_2]$	13.30	0.029	6.0
12	$[\text{Re}_6\text{Se}_8(\text{PET}_3)_5\text{I}]$	13.50	0.085	6.5
13	$[\text{Re}_6\text{S}_8(\text{PET}_3)_5\text{Br}]$	13.53	0.043	7.0
14	<i>trans</i> - $[\text{Re}_6\text{S}_8(\text{PET}_3)_4\text{Br}_2]$	13.48	0.008	5.7
15	<i>cis</i> - $[\text{Re}_6\text{S}_8(\text{PET}_3)_4\text{Br}_2]$	13.33	0.010	4.8
16	<i>(\text{Bu}_4\text{N})_3\text{mer}</i> - $[\text{Re}_6\text{S}_8(\text{PET}_3)_3\text{Br}_3]$	13.04	0.019	4.2

^a E_{em} is the corrected emission energy maximum, k_r is the radiative decay rate, k_{nr} is the nonradiative decay rate, ϕ_{em} is the quantum yield for emission, and τ_0 is the observed luminescence lifetime. ^b Parameters were measured in deoxygenated CH_2Cl_2 at $23 \pm 2^\circ\text{C}$ unless otherwise noted. ^c Parameters for compounds **3** and **6–9** were measured in neat or excess ligand. ^d $\pm 10\%$; absorbance of all solutions was ≤ 0.1 . ^e $\pm 0.1 \mu\text{s}$.

transitions^{5,19} dominate absorption spectra of $[\text{Re}_6\text{Q}_8]^{2+}$ clusters in the region 210–500 nm. Excitation of any such band elicits broad, structureless emission extending from ca. 600 to 1000 nm. Maximal quantum yields ϕ_{em} occur for **6–9**, with oxygen- or nitrogen-based terminal ligands; phosphine ligation in **5** reduces the $[\text{Re}_6\text{Se}_8]^{2+}$ yield by roughly a third. Sulfido clusters exhibit

(19) For a discussion of charge-transfer transitions within cyanide-bridged $[\text{Re}_6\text{Q}_8]^{2+}$ ($\text{Q} = \text{S}, \text{Se}, \text{Te}$) framework solids, cf. Shores, M. P.; Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 775.

[†] Massachusetts Institute of Technology.

[‡] Harvard University.

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- (18) Emission spectra were corrected for grating and detector sensitivity using the correction curve generated from an NBS standard lamp using the appropriate red-sensitive Hamamatsu R316–02 photomultiplier tube cooled to -40°C . Integrated emission quantum yields ϕ_{em} were determined in dry, deoxygenated solvents at $23 \pm 2^\circ\text{C}$ relative to $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Cl}_{14}]$ as a standard ($\phi_{\text{em}} = 0.19$, 436 nm excitation in acetonitrile).

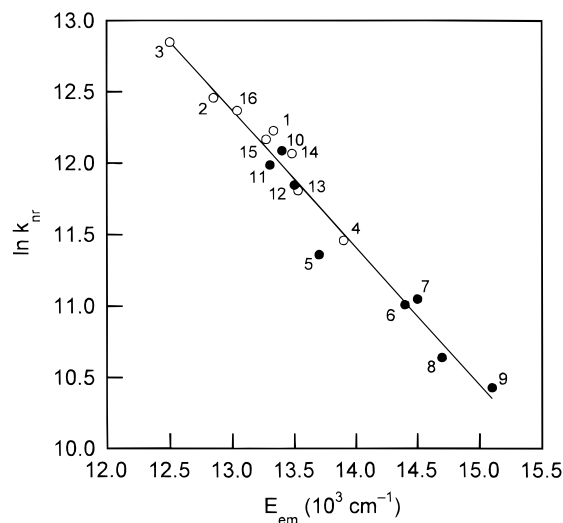


Figure 2. Energy gap plot of compounds 1–16; O, $[\text{Re}_6\text{S}_8]^{2+}$; ●, $[\text{Re}_6\text{Se}_8]^{2+}$. 1, 2, 4, 5, 10–16 in neat CH_2Cl_2 ; 3 in CH_2Cl_2 containing 10^4 -fold excess of Bu_4NI ; and 6–9 in neat terminal ligand.

attenuated sensitivity to heavy atom termini, with ϕ_{em} diminishing as $4 \approx 1 > 2 \approx 3$; progressive phosphine substitution of 2 exerts erratic effects. Luminescence from compounds 1, 2, 4, 5, and 10–16 decays monoexponentially with the lifetimes shown in Table 1.

Photophysical properties of five compounds (3 and 6–9) contrast with the remainder and are notably medium-sensitive. In the absence of excess ligand, these clusters display marginal quantum yields (<1%) and abbreviated lifetimes. These results indicate excited-state photolability, which inhibits emission. In support of this contention, addition of a 10^4 -fold excess of Bu_4NI to 3 in dichloromethane causes a 900 cm^{-1} emission red shift and restores monoexponential decay. Moreover, solvate clusters 7–9 in acetonitrile reproduce the emission profile of 6, with nearly equal quantum yields and lifetimes, also suggesting terminal ligand expulsion with attendant solvent coordination. Our experience in synthesis indicates the iodide is the most labile halide in ligand substitution reactions. Indeed, $[\text{Re}_6\text{Se}_8\text{I}_6]^{3-}$ is the precursor of choice for preparing clusters 5–9.^{7,9,10}

Figure 2 demonstrates a linear relationship between $\ln k_{\text{nr}}$, the nonradiative decay constant,²⁰ and the emission maximum E_{em} . Separate regression analyses of the sulfide and selenide series give parallel lines tightly spaced; an equally high correlation ($r^2 = 98.3\%$) results from fitting all data to a single line. In dichloromethane, labile clusters 3 and 6–9 lie above the line; remeasurement in the respective neat solvents or in an excess of iodide in dichloromethane (3) restores linearity. From radiationless decay theory, excited states of common parentage exhibit E_{em} and k_{nr} governed by the approximate energy gap law:^{21–23}

$$\ln k_{\text{nr}} = (\ln \beta - S) - \frac{\gamma E_{\text{em}}}{\hbar \omega_{\text{M}}}$$

Here, $\ln \beta$ incorporates the nuclear momentum matrix element and varies weakly as E_{em} ; S is the dimensionless Huang–Rhys parameter, which quantifies excited-state distortion; ω_{M} is the frequency of the deactivating mode(s), and $\gamma = \ln(E_{\text{em}}/S\hbar\omega_{\text{M}}) - 1$. The quantities E_{em} and $\ln k_{\text{nr}}$ are linearly related; the equation assumes validity in the low temperature ($k_{\text{B}}T \ll \hbar\omega_{\text{M}}$) and weak coupling ($E_{\text{em}} \gg \hbar\omega_{\text{M}}S$) limits.²⁴ We infer closely similar vibronic overlaps in $[\text{Re}_6\text{S}_8]^{2+}$ and $[\text{Re}_6\text{Se}_8]^{2+}$ species and conclude that $[\text{Re}_6\text{Q}_8]^{2+}$ lumophores discriminate little among core or apical ligands. Relaxation modes are similar in sulfides and selenides, validating the supposition that nonradiative decay from excited clusters is interpretable by the energy gap law.

The results presented here provide an affirmative reply to the recently raised question of whether these clusters are luminescent.^{2,25} Further, the photophysics of hexanuclear rhenium(III) chalcogenide clusters provides opportunities for syntheses and optical applications. $[\text{Re}_6\text{Q}_8]^{2+}$ clusters phosphoresce with microsecond-scale lifetimes and emission maxima spanning a 135-nm range. Quantitative, linear correlation between $\ln k_{\text{nr}}$ and E_{em} supports assignment of $[\text{Re}_6\text{Q}_8]^{2+}$ -predominated excited states. Terminal ligands modulate the energy gap between emissive and ground states, influencing quantum yields: those of *O*-bonded 8 and 9 surpass 20%. The energy gap law presupposes constant S , $\ln \beta$, and γ , a reasonable but inexact assumption. Rigorous studies of the parameters governing $[\text{Re}_6\text{Q}_8]^{2+}$ photoprocesses are underway. Core-confined excited states sustain emission with diminished influence from ligand-based vibrational de-excitation modes. Synthetic flexibility^{7–10} affords a range of clusters for developing innovative luminescent materials.²⁶ An available, rhomb-linked $[\text{Re}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]^{4+}$ dimer⁹ invites scrutiny of intercluster energy transfer. To date, these prospects are lacking for Group 6 $[\text{M}_6\text{X}_8]^{4+}$ clusters. Excited-state decomplexation suggests *photomediated* syntheses of species with yet unrealized ligand termini, a preparative strategy potentially applicable to analogous clusters and myriad ligands alike.

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(20) Definitions: $k_{\text{r}} = \phi_{\text{em}}/\tau_{\text{o}}$; $k_{\text{nr}} = (1 - \phi_{\text{em}})/\tau_{\text{o}}$.

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(24) E_{em} approximates ΔE , the internal energy gap between emissive and ground states. This substitution realizes that a medium dependence intrudes from contributions of collective solvent vibrations, cf. Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439.

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