

Photoredox Ability of a Hexarhenium(III) Cluster $[\text{Re}_6(\mu_3\text{-S})_8\text{Cl}_6]^{4-}$

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The photoredox ability of a hexarhenium(III) cluster, $(n\text{-Bu}_4\text{N})_4^{4+}[\text{Re}_6(\mu_3\text{-S})_8\text{Cl}_6]^{4-}$, was examined in acetonitrile on the basis of emission quenching experiments of the cluster by several neutral electron acceptors. The quenching rate constants and the relevant activation parameters indicated that the hexarhenium(III) cluster acted as a useful photoredox sensitizer towards various electron acceptors.

We found recently that hexarhenium(III) clusters, $[\text{Re}_6(\mu_3\text{-S})_8\text{X}_6]$ where $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$ or CN^- (abbreviated hereafter as $[\text{Re}_6]^{4-}$), showed strong room temperature emission in the visible region (600-1000 nm) with the emission lifetime (τ) and quantum yield in acetonitrile of 4-11 μs and 0.015-0.056, respectively.^{1,2} It is worth noting that the τ value of $[\text{Re}_6]^{4-}$ is much longer than that of tris(2,2'-bipyridine)ruthenium(II) (Ru^{2+} , $\tau = 850$ ns in CH_3CN at 298 K), which is known as a photoredox sensitizer.³ As another unique characteristics, $[\text{Re}_6]^{4-}$ possesses a strong reducing ability; as a typical example, the oxidation potential of $[\text{Re}_6(\mu_3\text{-S})_8\text{Cl}_6]^{4-}$ in acetonitrile is +0.27 V (vs. SCE).⁴ Since the oxidation potential of Ru^{2+} is as positive as +1.27 V (vs. SCE),³ the redox ability of the hexarhenium(III) cluster is remarkable. Owing to the long excited-state lifetime and the strong redox ability, $[\text{Re}_6]^{4-}$ is expected to act as a new photoredox sensitizer in various systems. A study on photoinduced electron transfer (PET) quenching of $[\text{Re}_6]^{4-}$ by electron acceptors would thus contribute to further progresses in the photoredox chemistry of transition metal complexes. In this letter, we demonstrate, for the first time, that $[\text{Re}_6(\mu_3\text{-S})_8\text{Cl}_6]^{4-}$ undergoes PET with several organic electron acceptors in acetonitrile.

$[\text{Re}_6(\mu_3\text{-S})_8\text{Cl}_6]^{4-}$ used in this study was the same sample reported earlier.¹ Organic electron acceptors (A: pyromellitic dianhydride, 1,3-dinitrobenzene, methyl 4-nitrobenzoate, methyl 3-nitrobenzoate, 3-nitroanisole, and 2,3,5,6-tetramethyl-1,4-dinitrobenzene) and acetonitrile as a solvent were purified prior to the use. Steady-state emission quenching experiments were per-

formed with a Hitachi F-4500 spectrofluorometer, while lifetime quenching experiments were conducted by using a Nd:YAG laser (355 nm, 6 ns pulse width; Continuum, Surelite) as an excitation light source and a streak camera as a photodetector (monitoring wavelength = 700 nm: Hamamatsu Photonics, C4334). Sample solutions were deaerated thoroughly by purging an Ar-gas stream over 20 min prior to the experiments and sealed at the constriction of a cell. The temperature of the solution was controlled within 1 °C (13 - 58 °C) by using a thermo-electronic equipment. For analyzing quenching data, temperature dependencies of the emission lifetime⁵ of $[\text{Re}_6]^{4-}$ and the solvent properties (dielectric constant and viscosity)^{3a} were considered. The diffusional effects of the solutes on the quenching rate constant (k_q) were also taken into account by using the equation;^{3a} $k_q^{-1} = k_o^{-1} - k_d^{-1}$, where k_o and k_d are the bimolecular quenching rate constant (determined by a Stern-Volmer plot) and the diffusion-limited rate constant (calculated by the Smoluchowski equation) in acetonitrile, respectively.

The emission of $[\text{Re}_6]^{4-}$ was quenched efficiently in the presence of A. It is noteworthy that, since the k_q values determined by both the emission intensity and lifetime agree very well with each other, the quenching is concluded to proceed via a dynamic pathway. As the data summarized in Table 1 show, k_q increased from 10^7 to $10^{10} \text{ M}^{-1}\text{s}^{-1}$ ($\text{M} = \text{mol}/\text{dm}^3$) in the decreasing order of the reduction potential of A. The results are readily understood by PET quenching of the $[\text{Re}_6]^{4-}$ cluster, since the reduction potential of A ($E(A/A^-)$) is related directly to the free energy change of PET (ΔG) via the following equation,⁶

$$\Delta G = E([\text{Re}_6]^{3-}/[\text{Re}_6]^{4-}) - E(A/A^-) - E_{00} - w_p$$

where $E([\text{Re}_6]^{3-}/[\text{Re}_6]^{4-})$ and E_{00} are the oxidation potential and the excited-state (triplet) energy of $[\text{Re}_6]^{4-}$ (1.61 eV, determined from the emission maximum at room temperature)¹, respectively. w_p is the electrostatic work necessary for separating the products ($[\text{Re}_6]^{3-}$ and A^-) from the ion pair (+0.12 eV at

Table 1. Rate constants and activation parameters for PET quenching of $[\text{Re}_6(\mu_3\text{-S})_8\text{Cl}_6]^{4-}$ by electron acceptors in acetonitrile

Quencher (reduction potential, V vs. SCE)	ΔG^c kJ/mol	k_q^c $\text{M}^{-1}\text{s}^{-1}$	ΔH^* kJ/mol	ΔS^* J/mol K	ΔG^* kJ/mol
2,3,5,6-Tetramethyl-1,4-dinitrobenzene (-1.22) ¹⁰	-23.2	4.4×10^7	21.6	-34.7	31.9
3-Nitroanisole (-1.14) ^a	-30.9	1.0×10^9	12.6	-38.4	24.0
Methyl 3-nitrobenzoate (-1.04) ^b	-40.5	3.1×10^9	8.0	-45.0	21.4
Methyl 4-nitrobenzoate (-0.95) ^b	-49.2	6.4×10^9	6.2	-44.4	19.4
1,3-Dinitrobenzene (-0.90) ^b	-54.0	2.6×10^{10}	5.6	-33.1	15.5
Pyromellitic dianhydride (-0.51) ^b	-91.7	1.3×10^{10}	8.3	-35.8	19.0

^a R. Obata, Ms. Thesis, Tokyo Institute of Technology, (1986). ^b The data taken from Ref. 3b. ^c At 298 K.

298 K).⁷ Since ΔG is sufficiently negative for all quenchers, PET between $[\text{Re}_6]^{4+}$ and A is thermodynamically favorable. At the present stage of the investigation, we have not yet conducted transient absorption spectroscopy, so that there is no direct evidence for PET. Nonetheless, energy transfer from the excited triplet state of $[\text{Re}_6]^{4+}$ to A does not contribute to the quenching, since the excited triplet state energy of A is predicted to be much higher than that of the $[\text{Re}_6]^{4+}$ cluster.⁸ On the basis of these discussions, we conclude that the emission quenching is essentially due to PET from the $[\text{Re}_6]^{4+}$ cluster to A , and the cluster acts as an efficient photoredox sensitizer.

In order to obtain further information about the PET mechanism, we studied the temperature (T) dependence of k_q . The T dependence of k_q always fall on a straight line in the T range studied, and we determined the activation parameters (activation enthalpy (ΔH^*), entropy (ΔS^*), and free energy (ΔG^*)) of the quenching on the basis of the Eyring equation,^{3a}

$$\ln(k_q/T) = \ln[k_B \kappa / h] + \Delta S^*/R - \Delta H^*/RT$$

where κ is the transmission coefficient of the PET step (assumed to be unity) and, k_B , h , and R are the usual meanings. The calculated parameters are included in Table 1. As seen in Table 1, a decrease in ΔG rendered the decrease in both ΔG^* and ΔH^* , while ΔS^* was remained almost constant irrespective of ΔG : $T\Delta S = -9.8$ - -13.4 kJ/mol. Such results remind us the T dependence of the reductive quenching of Ru^{2+} by aromatic amines (D), in which the analogous ΔG dependencies of the activation parameters with those determined in the present study have been observed.^{3a} In the case of the oxidative quenching of Ru^{2+} by A , on the other hand, a decrease in ΔG resulted in apparent negative ΔH^* and a large decrease in ΔS^* .^{3b} The results for PET quenching of Ru^{2+} have been explained in terms of the electrostatic interaction between the product ions in the intermediate state. For an $\text{Ru}^{2+} - D$ system, namely, the electrostatic interaction between the product ions is repulsive ($\text{Ru}^+ - D^+$) and, this usually leads to the ΔG dependencies of the activation parameters as described above. On the other hand, PET of an $\text{Ru}^{2+} - A$ system produces an electrostatically-attractive ion pair ($\text{Ru}^{3+} - A^-$) so that reverse electron transfer from the ion-pair to the excited-state encounter complex proceeds very efficiently, rendering both apparent negative ΔH^* and a large decrease in ΔS^* of the quenching, as reported in detail previously.³ The oxidative quenching of the excited state $[\text{Re}_6]^{4+}$ cluster by A produces an electrostatically-repulsive product ion-pair ($[\text{Re}_6]^{3+} - A^-$), so that the analogous T dependencies of the activation parameters with those for the reductive quenching of Ru^{2+} is quite reasonable.

The excited state of $[\text{Re}_6(\mu_3\text{-S})_8\text{Cl}_6]^{4+}$ is a strong reducing agent compared to that of Ru^{2+} . For example, emission quenching of the $[\text{Re}_6]^{4+}$ cluster by methyl 3-nitrobenzoate (3NB) proceeds with $k_q = 3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ($\Delta G = -40.5$ kJ/mol), while k_q for the $\text{Ru}^{2+} - 3\text{NB}$ system is 300 times slower (1×10^7

$\text{M}^{-1}\text{s}^{-1}$, $\Delta G = +8.8$ kJ/mol).^{3b} For a given electron acceptor, therefore, PET of $[\text{Re}_6]^{4+}$ is more favorable as compared to that of Ru^{2+} . Furthermore, electrostatic repulsion within the product ion-pair in an $[\text{Re}_6]^{4+} - A$ system should lead to very efficient charge separation of the product ions. This is a very favorable condition for constructing efficient PET reaction systems. The oxidation potentials of $[\text{Re}_6(\mu_3\text{-S})_8\text{X}_6]^{4+}$ ($\text{X}^- = \text{Br}^-, \text{I}^-$) and a series of $[\text{Re}_6(\mu_3\text{-S})_8\text{Cl}_4(\text{L})_2]^{2+}$ clusters ($\text{L} =$ pyridine derivatives or pyrazine) have been reported to be $+0.31$ - $+0.36$ and $+0.68$ - $+0.86$ V (vs. Ag/AgCl)⁹, respectively. All these hexarhenium(III) clusters are also emissive^{1,9} and, thus, will probably act as a photoredox sensitizer as well. An appropriate choice of a hexarhenium(III) cluster as a photosensitizer could enable one to conduct efficient photoinduced electron transfer reactions of various substrates.

References and Notes

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- 7 For the calculation of w_p , the following values were used: static dielectric constant of $\text{CH}_3\text{CN} = 39.2$ (298 K) and the contact distance between the two product ions = 9 Å. See also Ref. 3a.
- 8 The electron acceptors shown in Table 1 are known to quench the excited state of Ru^{2+} via PET, but not by energy transfer.^{3b} The excited triplet state energy of Ru^{2+} is 2.1 eV, and the value is much higher than that of $[\text{Re}_6]^{4+}$ (1.6 eV). Therefore, energy transfer quenching of $[\text{Re}_6]^{4+}$ by A is convincingly denied.
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