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Direct Observation of a $\{Re_6(\mu_3\text{-}S)_8\}$ Core-to-Ligand Charge-Transfer Excited State in an Octahedral Hexarhenium Complex

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S *Supporting Information*

ABSTRACT: A new complex, $[Re_6S_8Cl_5ppy]^{3-}$ (ppy = 4-phenylpyridine), was synthesized and characterized. The complex showed red emission at 296 K in both the crystalline phase and CH_3CN. The transient absorption spectrum of $[Re_6S_8Cl_5ppy]^{3-}$ revealed that the emissive excited state involved the $\{Re_6(\mu_3\text{-}S)_8\}$ core-to-ligand charge-transfer character.

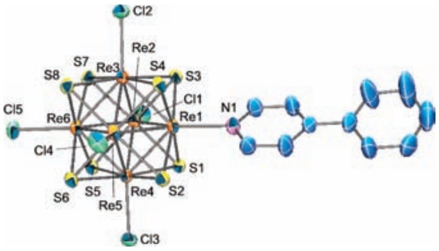

Figure 1. ORTEP drawing of $[Re_6S_8Cl_5ppy]^{3-}$. Hydrogen atoms are omitted for clarity. The bond distances were Re−Re = av. 2.598(1), Re−S = av. 2.408(6), Re−N = 2.254(5), and Re−Cl = av. 2.440(4) Å.

The nature of the lowest-energy electronic transition in a metal complex is determined by the combination of a metal ion and a ligand, and the lowest-energy excited state of the complex takes either the metal-to-ligand charge-transfer (CT), ligand-to-metal CT, metal-centered, or ligand-centered (LC) excited state.[1] For example, mononuclear iridium(III) polyimine complexes possess LC and CT excited states.[1b] In the case of square-planar dinuclear platinum(II) complexes and linear gold(I) complexes, furthermore, the excited states induced by metal−metal interactions play important roles in determining their photophysical properties.[1b] Control of the excited-state characteristics is significantly important to realize a desirable compound for a light-driven system. In contrast to mononuclear metal complexes and their metal−metal-interacted complexes, the number of metal−metal-bonded polynuclear complexes more than trinuclei having various types of ligands hitherto reported is very limited. Therefore, control of the excited-state characteristics of a polynuclear metal complex is worth exploring. As a representative metal−metal-bonded polynuclear complex, an octahedral hexanuclear rhenium complex with a $Re_6(\mu_3\text{-}Q)_8$ (Q = chalcogenide or halide) core and six terminal ligands, in general, shows photoluminescence.[2,3] The emission arises from the cluster-core ($\{Re_6Q_8\}$)-centered (CC) excited triplet state, in which the excited electron is primarily localized on the d orbitals of the metal atoms.[3a,c,d,h−k] As an exceptional case, we recently reported that *trans*- and *cis*-$[Re_6S_8Cl_4L_2]^{2-}$ [L = 4,4′-bipyridine (bpy) or pyrazine (pz)] exhibited $\{Re_6S_8\}$-to-ligand CT (MLCT)-type emission, as demonstrated by temperature-controlled spectroscopic and photophysical experiments.[4] However, the emissions from both *trans*- and *cis*-$[Re_6S_8Cl_4L_2]^{2-}$ were very weak in solution because the excited electron on the bpy^- or pz^- ligand(s) interacted with solvent molecules at the noncoordinate nitrogen site of L. Moreover, we previously reported that the excited states of *trans*/*cis*-$[Re_6S_8Cl_4(ppy)_2]^{2-}$ and *mer*-$[Re_6S_8Cl_3(ppy)_3]^-$ (ppy = 4-phenylpyridine) were in the marginal cases between MLCT and CC excited states, as demonstrated by the spectroscopic/redox properties and density functional theory calculations.[4] To realize intense MLCT-type emission in a $Re_6(\mu_3\text{-}Q)_8$ complex, it is important to finely control the energy difference between the Re_6S_8 core-centered highest occupied molecular orbital (HOMO) and the π^* orbital of the N-heteroaromatic ligand and to reduce the thermal deactivation efficiency arising from interactions of the complex with solvent molecules. In the present study, we newly synthesized a ppy ligand-coordinated hexarhenium complex, $(Bu_4N)_3[Re_6S_8Cl_5ppy]$ ($(Bu_4N)_3[\mathbf{1}]$) and found that the complex showed intense MLCT-type emission. Also, we succeeded in observing direct evidence of the participation of the MLCT excited state to the emission from $(Bu_4N)_3[\mathbf{1}]$, as revealed by transient absorption spectroscopy.

$(Bu_4N)_3[\mathbf{1}]$ was obtained by photoirradiation of a CH_3CN solution of $(Bu_4N)_4[Re_6S_8Cl_6]$ in the presence of 10 equiv of ppy at room temperature. Although photosubstitution reactions of the terminal ligands in a hexanuclear metal complex with solvent molecules (i.e., dimethyl sulfoxide) and so forth have been hitherto reported,[3h,5] the present photoreaction gives a ppy monocoordinate complex alone, $(Bu_4N)_3[\mathbf{1}]$. Figure 1 shows the X-ray structure of $[\mathbf{1}]^{3-}$. The bond distances and angles of $[\mathbf{1}]^{3-}$ are similar to those of the bis-ppy coordinate complex reported previously, *trans*-$[Re_6S_8Cl_4(ppy)_2]^{2-}$.[4] Figure 2 shows the emission spectra of $(Bu_4N)_3[\mathbf{1}]$ in the crystalline phase as well as in deaerated CH_2Cl_2, CH_3CN, C_6H_5CN, and *N*,

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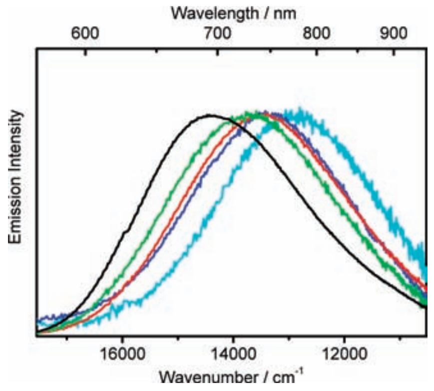

Figure 2. Normalized emission spectra of $(Bu_4N)_3[Re_6S_8Cl_5ppy]$ in the crystalline phase (black) and in CH_2Cl_2 (green), CH_3CN (red), C_6H_5CN (blue), and DMF (sky blue) at 296 K.

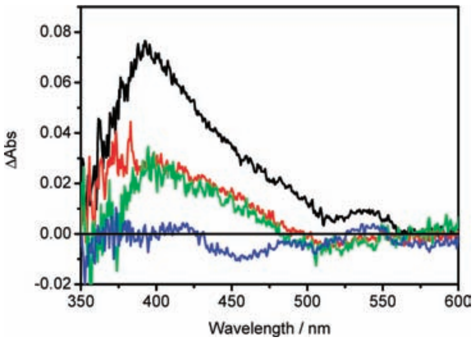

Figure 3. Transient absorption spectra of $(Bu_4N)_3[Re_6S_8Cl_5ppy]$ (black), $(Bu_4N)_2[$*cis*-$Re_6S_8Cl_4(ppy)_2]$ (red), $(Bu_4N)[$*mer*-$Re_6S_8Cl_3(ppy)_3]$ (green), and $(Bu_4N)_4[Re_6S_8Cl_6]$ (blue) in CH_3CN at 296 K. The sample absorbance at the excitation wavelength (266 nm) is set at a constant.

N-dimethylformamide (DMF) solutions at 296 K. The complex $[\mathbf{1}]^{3-}$ showed the emission maximum wavelength (λ_{em}) at 690 nm in the crystalline phase. The λ_{em} values in the solutions shift to longer wavelength in the sequence of CH_2Cl_2 (726 nm) < CH_3CN (739 nm) < C_6H_5CN (747 nm) < DMF (772 nm). The emission lifetime (τ_{em}) of $[\mathbf{1}]^{3-}$ in the solution decreased in the order of CH_2Cl_2 (0.44 and 0.81 μs) > CH_3CN (0.33 μs) > C_6H_5CN (0.12 μs) > DMF (0.028 μs). The emission spectral band shape and λ_{em} of $[Re_6S_8Cl_6]^{4-}$ possessing the CC excited state are essentially the same in both the solution and crystalline phases. The maximum wavelength shift of $[\mathbf{1}]^{3-}$ in the solution relative to λ_{em} in the crystalline phase and the large solvent dependence of λ_{em} suggest that the excited state of the complex is not the CC character. The CT excited state of a molecule is stabilized in energy by solvation around the molecule in a polar solvent, and such a circumstance gives rise to a decrease in τ_{em} through an increase in k_{nr}. These experimental results clearly demonstrate that the excited state of $[\mathbf{1}]^{3-}$ is best characterized by $\{Re_6S_8\}$ core-to-ppy ligand CT (MLCT) in nature. In practice, the emission characteristics of $[\mathbf{1}]^{3-}$ are very similar to those of *trans*- and *cis*-$[Re_6S_8Cl_4L_2]^{2-}$ (L = bpy or pz) showing MLCT-type emission.[4] It is worth noting that the Φ_{em} (0.0089) and τ_{em} (0.33 μs) values of $[\mathbf{1}]^{3-}$ in CH_3CN at 296 K are much larger and longer, respectively, than the relevant values of *trans*- and *cis*-$[Re_6S_8Cl_4L_2]^{2-}$ (L = bpy or pz, Φ_{em} = 0.0010−0.0017, and τ_{em} = 0.0013−0.0029 μs).[3e] This is probably due to the absence of thermal deactivation through a solvent-accessible nitrogen site on ppy in the excited state of $[\mathbf{1}]^{3-}$, which is different from that in the bpy and pz complexes.

Direct evidence of the MLCT character in the excited state of $[\mathbf{1}]^{3-}$ has been obtained by nanosecond transient absorption spectroscopy. Figure 3 shows the transient absorption spectrum of $[\mathbf{1}]^{3-}$ in deaerated CH_3CN observed in 0−100 ns after 266 nm laser pulse excitation (shown by black), together with that of $[Re_6S_8Cl_6]^{4-}$ (blue). It is worth noting that no transient absorption can be observed for $[Re_6S_8Cl_6]^{4-}$ in the wavelength region studied except for the bleaching signal of the ground state of the complex in 430−530 nm. On the other hand, $[\mathbf{1}]^{3-}$ showed two absorption bands at 392 and 540 nm, whose spectral band shape agreed very well with that of a ppy^- anion or a MLCT excited state of $[Re(CO)_3(ppy)_3]^+$.[6a,b] The decay curve of the absorption band monitored at 400 nm shown in the Supporting Information (Figure S1) was fitted by a single-exponential function, and the decay time constant was determined to be 0.32 μs, which was in good agreement with the τ_{em} value of $[\mathbf{1}]^{3-}$: 0.33 μs. The results demonstrate explicitly that the electronic structure of the emissive excited state of $[\mathbf{1}]^{3-}$ is best characterized by the ppy^- anion and, thus, the excited state of the complex is $\{Re_6S_8\}$ core-to-ppy ligand CT. This is the first demonstration of direct evidence of participation of the MLCT character in the excited state of an octahedral hexanuclear metal cluster complex.

The transient absorption spectra of *cis*-$[Re_6S_8Cl_4(ppy)_2]^{2-}$ (shown by red) and *mer*-$[Re_6S_8Cl_3(ppy)_3]^-$ (green) observed in CH_3CN are included in Figure 3. These complexes showed absorption bands at around 390 nm similar to that of $[\mathbf{1}]^{3-}$, and the weak negative peaks at around 520 nm could be assigned to the bleaching signals of the ground states of the complexes. It is clear from the data in Figure 3 that the emissive excited states of these complexes also possess the ppy^- character. On the other hand, the Φ_{em} and τ_{em} values of *trans*/*cis*-$[Re_6S_8Cl_4(ppy)_2]^{2-}$ and *mer*-$[Re_6S_8Cl_3(ppy)_3]^-$ in CH_3CN at 298 K are similar to the relevant value of $[Re_6S_8Cl_6]^{4-}$ as reported previously, and these data are much different from those of $[Re_6S_8Cl_5ppy]^{3-}$.[4] Moreover, the radiative (k_r) and nonradiative (k_{nr}) decay rate constants of $[\mathbf{1}]^{3-}$ in CH_3CN ($k_r = 2.7 \times 10^4$ and $k_{nr} = 3.0 \times 10^6$ s^{-1}) were much larger than those of $[Re_6S_8Cl_6]^{4-}$, *trans*/*cis*-$[Re_6S_8Cl_4(ppy)_2]^{2-}$, and *mer*-$[Re_6S_8Cl_3(ppy)_3]^-$ [$k_r = (6.1{-}9.3) \times 10^3$ s^{-1} and $k_{nr} = (1.5{-}2.4) \times 10^5$ s^{-1}].[3c,v,4,7] On the basis of the transient absorption spectral feature and emission/photophysical data (see also Figures S2 and S3 in the Supporting Information), it is concluded that the excited states of *trans*/*cis*-$[Re_6S_8Cl_4(ppy)_2]^{2-}$ and *mer*-$[Re_6S_8Cl_3(ppy)_3]^-$ are the marginal case between the MLCT and CC excited states. Interestingly, these results suggest that the extent of the CC or MLCT character in the excited state is controlled by the number of terminal chlorides or ppy ligands.

The transient absorption spectrum of *trans*-$[Re_6S_8Cl_4(bpy)_2]^{2-}$ in CH_3CN was also measured, and the results are reported in Figure S4 in the Supporting Information. Unfortunately, because *trans*-$[Re_6S_8Cl_4(bpy)_2]^{2-}$ in CH_3CN was almost nonemissive at room temperature and the decay time of the transient absorption was too fast to be determined, we could not obtain one-to-one correspondence between the emission lifetime and the decay time of the transient absorption band observed for the complex. Nonetheless, the transient absorption spectral band shape observed for *trans*-$[Re_6S_8Cl_4(bpy)_2]^{2-}$ in 370−430 nm was similar to that of a bpy^- anion or bpy-coordinated metal complex,[6a,c−e] although the spectrum observed for *trans*-$[Re_6S_8Cl_4(bpy)_2]^{2-}$ was shifted slightly to a longer wavelength compared with that of a bpy$^-$ anion or bpy-coordinated metal complex.[8] Therefore, we suppose that the emissive excited state of *trans*-$[Re_6S_8Cl_4(bpy)_2]^{2-}$ could also be MLCT in nature, as concluded by our previous emission spectroscopy experiments.[4]

In the present study, we demonstrated that the photoreaction of $[Re_6S_8Cl_6]^{4-}$ with excess ppy in CH_3CN at room temperature gave $[Re_6S_8Cl_5ppy]^{3-}$, which was the first chalcogenide-capped hexarhenium complex with five terminal halides and one *N*-heteroaromatic ligand. The complex showed MLCT ($\{Re_6S_8\}$ core-to-ppy ligand) photoluminescence, as demonstrated by transient absorption and emission spectroscopy. The present results also indicate the important role of the π^* orbital of an N-heteroaromatic terminal ligand(s) (ppy or bpy) in a hexarhenium cluster complex and the energy difference between the Re_6S_8 core-centered HOMO and the π^* orbital of the ligand in determining the lowest-energy excited-state character. Further studies on the MLCT excited-state properties of the hexarhenium complexes with a variety of low-energy-lying π^* ligands are now in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic procedure, crystallographic data in CIF format, experimental details, and figures of transient absorption decay profiles and a transient absorption spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The radiative (k_r) and nonradiative (k_{nr}) decay rate constants were calculated by the equations $k_r = \Phi_{em}/\tau_{em}$ and $k_{nr} = (1 - \Phi_{em})/\tau_{em}$.

(8) It was reported that the proton-coupled electron-transfer reaction from *trans*-$[Re_6S_8Cl_4(bpy)_2]^{2-}$ to *trans*-$[Re_6S_8Cl_4(Hbpy)_2]^{4-}$ took place upon reduction of the bpy ligands in the ground state.[3e] Therefore, a proton originating from a trace amount of water in the solution might attach to the free nitrogen sites of bpy in the excited state of *trans*-$[Re_6S_8Cl_4(bpy)_2]^{2-}$.