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Synthesis and Characterization of a Metal-to-Polyoxometalate Charge Transfer Molecular Chromophore

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S Supporting Information

ABSTRACT: $[P_4W_{35}O_{124}\{Re(CO)_3\}_2]^{16-}$ (**1**), a Wells−Dawson $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ polyoxometalate (POM)-supported $[Re(CO)_3]^+$ complex containing covalent $W^{VI}-O-Re^I$ bonds has been synthesized and characterized by several methods, including X-ray crystallography. This complex shows a high visible absorptivity ($\varepsilon_{470\text{ nm}} = 4000$ M^{-1} cm^{-1} in water) due to the formation of a Re^I-to-POM charge transfer (MPCT) band. The complex was investigated by computational modeling and transient absorption measurements in the visible and mid-IR regions. Optical excitation of the MPCT transition results in instantaneous (<50 fs) electron transfer from the Re^I center to the POM ligand.

Chromophores containing heterobinuclear groups linked by an oxo bridge (M−O−M′; M = Zr^{IV}, Ti^{IV}; M′ = Cu^I, Ce^{III}, Sn^{II}, etc.) and supported on mesoporous substrates have recently been shown to be promising in conjunction with photocatalytic solar fuel production.[1−10] These heterogeneous heterobinuclear units possess enhanced visible absorptivity and all-inorganic structures for oxidative stability. Their visible absorption properties originate from the photoinduced formation of long-lived metal-to-metal charge transfer (MMCT) excited states that can be effectively coupled with multielectron-transfer catalysts. In spite of the reported successes involving these heterobinuclear chromophores, molecular/homogeneous counterparts are sought because their geometrical and electronic structures as well as their chemical properties (e.g., interfacing with catalysts) can be more extensively altered and all of their properties can be studied and optimized more readily than for heterogeneous analogues.[11−15] Inspired by the heterogeneous bimetallic assemblies on mesoporous silica and the well-known metal-to-(organic) ligand charge transfer (MLCT) complex (bpy)$Re^I(CO)_3Cl$ (bpy = 2,2′-bipyridyl),[16−18] we have been seeking a new general type of charge transfer (CT) chromophore in which a polyoxometalate (POM) unit as a whole (delocalized orbitals involving many tungsten atoms) replaces the single metal center or bpy as the electron acceptor. POMs would be logical candidates for such an application because they are oxidatively, hydrolytically (over varying pH ranges) and thermally stable and can accommodate multiple metals with varying potentials, but they have not yet been systematically explored as tunable electron-accepting chromophores.[19,20] We report here a new complex comprising a $[Re(CO)_3]^+$ unit supported on the defect Wells−Dawson-type POM $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$, which exhibits an intense Re^I-to-POM CT transition. This is an example of a potentially general transition that we will call metal-to-POM charge transfer (MPCT). Unlike the well-documented MMCT heterobimetallic chromophores,[1−10] this study involves multimetal and delocalized orbitals in the acceptor (POM) unit. This complex, $[P_4W_{35}O_{124}\{Re(CO)_3\}_2]^{16-}$ (**1**), has been characterized by computational and multiple time-resolved spectroscopic studies as well as standard physical and X-ray crystallographic work.

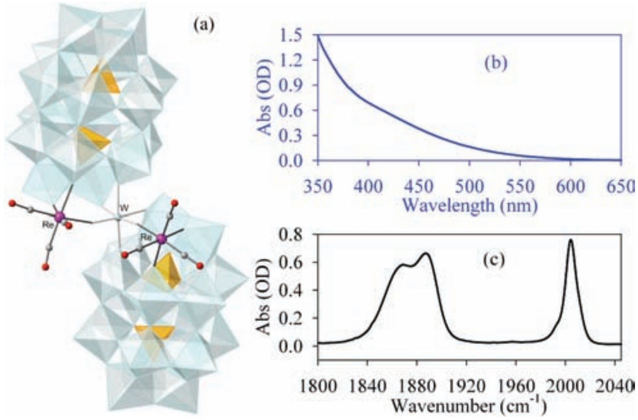

Figure 1. (a) X-ray structure of $[P_4W_{35}O_{124}\{Re(CO)_3\}_2]^{16-}$ (**1**) in combined polyhedral and ball-and-stick notation. Re, purple; O, red; C, gray; WO_6 octahedra, pale-blue; PO_4 tetrahedra, yellow. (b) UV−vis and (c) FTIR spectra of **1** in CH_2Cl_2.

Compound **1** was prepared by mixing equivalents of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 20H_2O$ and $Re(CO)_3(CH_3CN)_3(BF_4)$ in an acidic aqueous solution [see the Supporting Information (SI)]. The crystal structure of **1** shows idealized C_2 symmetry with one W atom as the symmetry center. This structural feature is consistent with the ^{31}P NMR spectrum of **1** in solution, which shows only two resonance peaks (Figure S3 in the SI). Each $[Re(CO)_3]^+$ moiety is stabilized by an $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ ligand in the "out-of-pocket" structural motif,[21−23] as shown in Figure 1a. The Re−C bond lengths in **1** range from 1.85 to 1.93 Å, while the C−O bond lengths range from 1.12 to 1.22 Å. Each half of **1** has C_s symmetry and shows three IR-active C−O stretching modes, two symmetric and one antisymmetric, at 1869, 1890, and 2006 cm^{-1}, respectively (Figure 1c).[24,25] These bond lengths and CO stretching frequencies are consistent with those

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Figure 2. Calculated HOMO and LUMO of the model complex $[\{P_2W_{18}O_{63}[Re(CO)_3]\}(H_2O)(OH)]^{8-}$ (**Model-1**). Color code: Re, purple; W, blue; P, yellow; O, red; C, gray. The two structures have the same orientation (Re centers at the left). See the SI for computational modeling details.

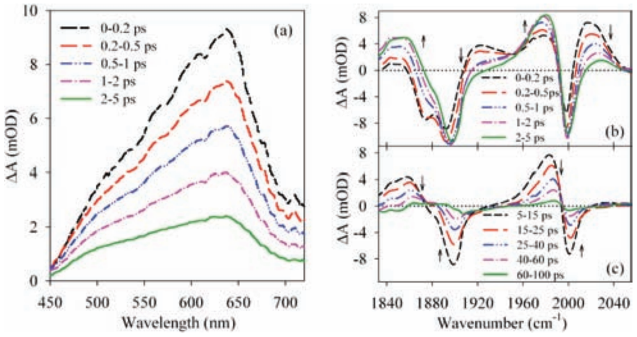

Figure 3. Average (a) visible and (b, c) mid-IR (b, 0−5 ps; c, 5−100 ps) transient absorption spectra of **1** in CH_2Cl_2 at indicated delay time windows after 400 nm excitation. Arrows in (b) and (c) indicate the directions of amplitude changes.

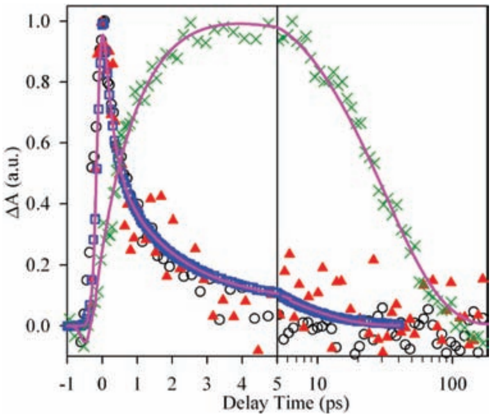

Figure 4. Transient kinetics of **1** in CH_2Cl_2 at 640 nm (blue □), 1927 cm^{-1} (red ▲), 1982 cm^{-1} (green ×) and 2020 cm^{-1} (black ○) after 400 nm excitation. Also shown are multiple-exponential fits to the kinetics at 640 nm and 1982 cm^{-1} (pink lines). The delay time is on a linear scale in the left panel (−1 to 5 ps) and a logarithmic scale in the right panel (5−200 ps).

observed for other Re(I) carbonyl complexes.[16−18,26,27] We note that several high-valent Re(V,VI,VII)-substituted POMs[28,29] and several nondefect (plenary) POMs with pendent $[M(CO)_3]^{n+}$ groups have been reported.[26,30−36] Unlike the preparations of other $[M(CO)_3]$−POM and closely related organometallic POM derivatives, **1** can be synthesized in aqueous solution under mild conditions in high yield and forms diffraction-quality crystals easily.

In contrast to its colorless components, $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]\cdot 20H_2O$ and $Re(CO)_3(CH_3CN)_3(BF_4)$, solid **1** is dark-red. The UV−vis spectra of **1** in CH_2Cl_2 (Figure 1b) and H_2O (Figure S1) show intense broad absorption (up to 700 nm) covering the entire UV and visible regions. The synthetic precursor $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ has O 2p → W 5d transitions that absorb only below 300 nm, and the ligand-to-metal CT band in the $[Re(CO)_3(CH_3CN)_3]^+$ precursor absorbs only below 380 nm (Figure S1). In addition, **1** has unexpectedly high visible absorptivity ($\varepsilon_{400\ nm} \approx 6200$ and 4500 $M^{-1}\ cm^{-1}$ in water and CH_2Cl_2, respectively). Importantly, while the wide spectral range and high extinction coefficients of **1** are comparable to those of many ruthenium polybipyridyl photosensitizers,[37,38] **1** is free of the oxidatively and hydrolytically unstable polypyridyl ligands.

We investigated the origin of the high visible absorptivity of **1** by computational modeling. As shown in Figure 2, the HOMO and LUMO of **Model-1** (a computational model of **1**) are very clearly $Re(CO)_3$- and POM-based orbitals, respectively. The lowest excited state of **Model-1** is a triplet that is 56.3 kcal/mol (2.45 eV, 506 nm) higher in energy than the singlet ground state. In this triplet state, almost one unpaired spin is located on the W and O atoms of the POM ligand, indicating a transfer of the electron density from the $Re(CO)_3$-based HOMO to the POM-based LUMO. Another unpaired spin (~1.02e) is located on the $-O_b-Re(CO)_3$ fragment, where O_b is the bridging oxygen atom between the $Re(CO)_3$ unit and the POM. Thus, the visible absorption spectrum of **1** (Figure 1b) can be attributed to the MPCT transition. Similar to previously reported MMCT chromophores, the CT interaction is enhanced by the formation of W−O−Re covalent bonds and occurs mostly among the metal centers. However, the electron in the CT excited state in **1** is delocalized among many W and O centers, a characteristic that resembles the MLCT states in Re and Ru bipyridyl complexes.

The CT dynamics were investigated by femtosecond visible pump/probe spectroscopy. The transient visible absorption spectra (Figure 3a) of **1** show a new broad absorption with maximum at ~640 nm. This absorption feature can be attributed to W(V) d−d transitions and W(V)−W(VI) intervalence charge transfer (IVCT) transitions in the reduced Wells−Dawson anionic ligand, generally known as "heteropoly blues".[39−44] In addition, for a Wells−Dawson POM anion, the polar and equatorial sites have different electron affinities, and the reduction preferentially occurs at the equatorial sites.[40−42,45,46] This is also the case for **1**, in which the electron density in the LUMO is distributed among the 12 equatorial WO_6 octahedrons, as shown in Figure 2. The kinetics of the formation and decay of this photoinduced absorption feature were monitored at 640 nm. As shown in Figure 4 and Table S2 in the SI, the best fit yielded a formation time of 35 ± 15 fs, which can be considered as instantaneous within the time resolution of this measurement (~150 fs), consistent with the nature of the MPCT transition. However, this CT excited state is short-lived, decaying with an average lifetime of 1.4 ps.

In addition to the formation of the reduced POM ligands discussed above, the MPCT excited state of **1** should also generate oxidized Re(II) centers. The latter can be most unambiguously probed by monitoring the CO stretching bands, the frequencies of which are sensitive to the charge density on the Re center because of the Re-to-CO $d\pi-\pi^*$ back-bonding.[47] For this reason, the dynamics of the CO stretching modes of **1** were investigated using femtosecond visible-pump/IR-probe spectroscopy. Following 400 nm excitation, bleaches of the CO stretching bands in the ground electronic state (~1870, 1890, and ~2000 cm^{-1}) and two new absorption bands at ~1925 and 2020 cm^{-1} (blue-shifted from the ground-state positions) were formed instantaneously. This is consistent with the formation of the MPCT excited state, in which the electron density at the Re center is reduced, shifting the CO stretching to higher frequencies.[47] Because of the spectral overlaps, only one broad feature at ~1925 cm^{-1} (instead of two peaks) was observed. The transient kinetics of the excited-state CO stretching bands are compared in Figure 4, which shows the same decay kinetics as the transient visible feature assigned to the reduced POM ligand. This agreement further confirms the assignment of the Re-to-POM CT transition in **1**.

The decay of the MPCT excited state leads to the formation of two positive absorption bands at ~1850 and 1980 cm^{-1}, which are red-shifted from the ground-state bleaches, as shown in Figure 3c. This can also be clearly seen in Figure 4, which shows that the formation kinetics of these features agrees well with the decay of the MPCT excited-state bands (in the visible and mid-IR). We attribute these features to the formation of "hot" ground state molecules, in which the energy of the excitation is converted into vibrational energy of the complex in the ground electronic state. The broadened and red-shifted CO bands undergo a continuous blue shift and narrowing with a time constant of 32 ps (Table S2), consistent with the vibrational cooling processes in related molecules.[48−53] The red-shifted CO stretching bands can result from the vibrational excitation of the CO stretching modes as well as anharmonically coupled low-frequency modes. To clarify further the nature of the hot ground state, we conducted transient IR-pump/IR-probe experiments in which only the CO stretching mode in the electronic ground state was excited. In this case (Figure S7), a red-shifted CO band assignable to the 1−2 transition was also observed, and it decayed with a similar time constant. However, this feature did not undergo continuous blue-shifting and narrowing. This comparison suggests that the hot ground state (shown in Figure 3b,c) contains both the excitation of the CO stretching mode (to the $v = 1$ state) and anharmonically coupled low-frequency modes.

In conclusion, we have synthesized a molecular metal-to-polyoxometalate charge transfer (MPCT) chromophore through a facile approach. Comprehensive computational and spectroscopic studies have shown that the high visible absorption in this complex can be attributed to a MPCT transition involving CT from the Re(I) center to the POM. The orbitals and transition addressed in this study are distinct from those in the well-documented heterobimetallic systems because the acceptor orbitals are delocalized and multimetal. In contrast, the heterobimetallic systems exhibit fairly localized orbitals that reside primarily on a single acceptor metal.[1−10] The photoactivities of this CT complex in some solar-conversion devices are under investigation. In addition, structural modifications to introduce electron-trapping centers in this MPCT chromophore for lengthening the lifetime of the CT excited states are ongoing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Materials, instrumentation, synthesis, crystallographic procedures and data (CIF), transient spectroscopic studies, and computational procedures and modeling This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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