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One-Dimensional Supramolecular Assemblies Based on a Re_2(III,III) Synthon and Their Solid-State Phosphorescence

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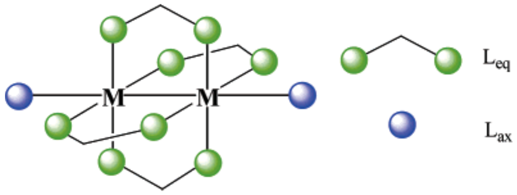
Reactions between $Re_2(DMBA)_4(NO_3)_2$ (**1**; DMBA is dimethylbenzamidinate) and a bidentate dianion, either tungstate (WO_4^{2-}) or terephthalte (1,4-$(O_2C)_2C_6H_4^{2-}$), resulted in the one-dimensional coordination polymers $[Re_2(DMBA)_4(\mu\text{-}O,O'\text{-}WO_4)]_\infty$ (**2**) and $[Re_2(DMBA)_4(\mu\text{-}O,O'\text{-}1,4\text{-}(O_2C)_2C_6H_4)]_\infty$ (**3**), respectively. Both polymers display phosphorescence from a $^3(\delta \rightarrow \delta^*)$ state, which is significantly blue shifted from the phosphorescence previously observed for $Re_2(DMBA)_4Cl_2$ type compounds.

The chemistry of dinuclear paddlewheel compounds has been of great interest to the inorganic community for the last 40 years because of its ubiquitous role in the understanding of metal−metal multiple bonds.[1] In addition to the continued interest in the fundamental understanding of paddlewheel species, recent years have seen a surge of activities on supramolecular assemblies of paddlewheel units.[2−4] Frequently, the paddlewheel species are organized into dimers, triangular trimers, and square tetramers using the linker ligands that coordinate at the equatorial positions (Chart 1). These discrete supermolecules can be further assembled into 1-D loops and intricate 2-D networks using bi- and tripyridines as the axial linkers.[2] Dinuclear units used for such assemblies include Mo_2, Rh_2, W_2, and Re_2, and equatorial linkers are typically carboxylates and oxoanions. By utilization of all available equatorial sites in dicopper tetracarboxylates, microporous solids with tunable pore sizes have been obtained, and these solids exhibit very interesting gas-uptake properties.[5,6] Another assembly strategy is to link the paddlewheel species through axial sites only, and earlier examples include halide- and phenazine-bridged diruthenium tetracarboxylate[7,8] and 2-D networks of $M_2(O_2CR)_4$ (M = Rh and Ru) linked by TCNE, TCNQ, and triazine.[9−11] $Rh_2(O_2CCF_3)_4$, a strong Lewis acid, has been assembled into 1-D chain and 2-D networks through the axial coordination of a variety of weak Lewis base ligands including unsaturated hydrocarbon compounds such as olefin, alkyne, and polycyclic aromatics.[12−17] While the above-mentioned work is by and large curiosity driven, a lateral nanoscale device built from the axially linked Rh_2 polymers exhibits negative differential resistance, an important signature of molecular memory devices.[18]

Chart 1. Paddlewheel Motif as the Building Block for Supramolecules



Interest in redox-rich diruthenium alkynyl compounds has led to the development of a host of $Ru_2(DMBA)_4X_2$ compounds, where DMBA is *N*,*N*′-dimethylbenzamidinate and axial ligand X is either chloride or an alkynyl ligand.[19−23]

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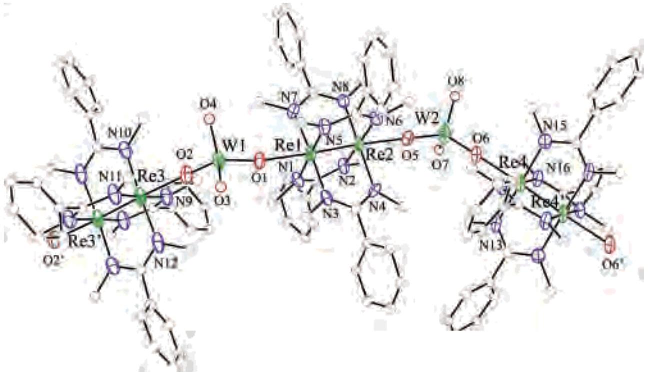

Figure 1. Structural plot of $[Re_2(DMBA)_4(\mu\text{-}O,O'\text{-}WO_4)]_\infty$ at a 30% probability level. Hydrogen atoms and solvent water omitted for clarity. Selected bond distances (Å): Re1−O1, 2.225(8); Re2−O5, 2.248(9); Re3−O2, 2.272(10); Re4−O6, 2.265(9); W1−O1, 1.812(8); W1−O2, 1.792(9); W1−O3, 1.753(11); W1−O4, 1.722(11); W2−O5, 1.786(9); W2−O6, 1.766(9); W2−O7, 1.73(2); W2−O8, 1.69(2); Re1−N(av), 2.08[1]; Re2−N(av), 2.08[1]; Re3−N(av), 2.06[1]; Re4−N(av), 2.07[1].

Of particular interest is the axial affinity of the $[Ru_2(DMBA)_4]^{2+}$ unit toward monoanions (MAs) including putative counterions such as NO_3^- and BF_4^-, which lead to a series of $Ru_2(DMBA)_4(MA)_2$ type compounds.[23,24] One can easily envision that a 1-D chain, $[M_2(DMBA)_4(DA)]_\infty$, may be constructed from axially linking the $[M_2(DMBA)_4]^{2+}$ units with a properly selected dianion (DA) linker. This Communication describes assemblies based on the $[Re_2(DMBA)_4](NO_3)_2$ synthon (**1**)[25] as well as oxoanion and dicarboxylato linkers, the structural characterization of the resulting 1-D chains, and their solid-state emissive properties.

Slow diffusion of a CH_3CN solution of **1** into an aqueous solution of Na_2WO_4 resulted in orange blocks, which were identified as $[Re_2(DMBA)_4(\mu\text{-}O,O'\text{-}WO_4)]_\infty$ (**2**) through X-ray diffraction (Figure 1).[26] The asymmetric unit contains two Re_2 dimers: a complete dimer containing Re1 and Re2 centers and two half dimers based on Re3 and Re4 centers, respectively, where an inversion center bisecting the Re−Re′ vector relates each half to its symmetry equivalent. The three independent Re−Re bond lengths are 2.207(1), 2.202(1), and 2.206(1) Å for Re1−Re2, Re3−Re3′, and Re4−Re4′, respectively, which are the same within experimental error and slightly longer than that in **1** (2.173(1) Å).[25] The lengthening of Re−Re quadruple bonds in **2** is attributed to the stronger axial coordination of tungstate than nitrate. Two sets of W−O bond lengths can be easily identified with each tungstate (see the caption to Figure 1): the elongated one associated with the oxygen centers axially coordinated to Re and the shorter one with the noncoordinated oxygens. Examples of tungstate as ligands are rare: it was used as a tetradentate ligand to link two $Mo_2(DAniF)_3^+$ units at the equatorial positions[27] and a bidentate ligand in $[\{Cu^{II}L\}_2(\mu\text{-}WO_4)](WO_4)$ (L is a tetraazamacrocycle).[28] Compound **2** represents the first example of a $(WO_4)^{2-}$-based coordination polymer to the best of our knowledge.

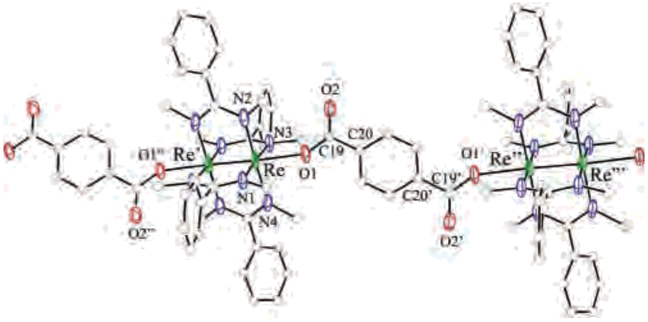

Figure 2. Structural plot of compound **3** at a 30% probability level. Hydrogen atoms and solvent water omitted for clarity. Selected bond distances (Å): Re−O1, 2.299(4); O1−C19, 1.281(9); O2−C19, 1.218(9); Re−N(av), 2.056[7].

Similar to the synthesis of **2**, slow diffusion of **1** in CH_3CN into an aqueous solution of $(Bu_4N)_2(1,4\text{-}O_2CC_6H_4CO_2)$ yielded yellow plates, which were identified as $[Re_2(DMBA)_4(\mu\text{-}O,O'\text{-}1,4\text{-}O_2CC_6H_4CO_2)\cdot 2H_2O]_\infty$ (**3**, Figure 2) through X-ray diffraction.[26] The asymmetric unit of **3** consists of half a terephthalate and half a dirhenium unit because of the presence of inversion centers at the center of the Re−Re′ vector as well as the terephthalate group. The structure is a 1-D chain of alternating $Re_2(DMBA)_4$ and terephthalate groups, with the latter serving as the bidentate axial ligand (Figure 2). The Re−Re′ bond length (2.1944(6) Å) lies between those of **1** and **2**, and the order is consistent with the donor strength of axial ligands: $WO_4^{2-} > O_2CC_6H_4CO_2^{2-} > NO_3^{-1}$. Terephthalate, a versatile linker in metallosupramolecules, has been used to link Mo_2, Re_2, Ru_2, and Rh_2 units into dimers,[29−33] cyclic trimers,[34] and tetramers,[35−37]

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(26) X-ray diffraction data for crystals **2** and **3** were collected on a Bruker SMART1000 CCD diffractometer using Mo Kα at 300 K. *Crystal Data for* **2**: $C_{72}H_{88}N_{16}O_{13}Re_4W_2$, $M = 2498.08$, monoclinic, $P2_1/n$, $a = 12.5968(4)$ Å, $b = 19.5102(6)$ Å, $c = 34.6185(11)$ Å, $\beta = 93.8030(10)°$, $V = 8489.3(5)$ Å^3, $Z = 4$, $\rho = 1.955$ g cm^{-3}. Least-squares refinement based on 8431 reflections with $I = 2\sigma(I)$ and 964 parameters led to convergence with final R1 = 0.058 and wR2 = 0.122. *Crystal Data for* **3**: $C_{44}H_{48}N_8O_6Re_2$, $M = 1157.30$, monoclinic, $I2/a$, $a = 21.1694(16)$ Å, $b = 10.5140(8)$ Å, $c = 21.321(3)$ Å, $\beta = 104.4960(10)°$, $V = 4594.4(7)$ Å^3, $Z = 4$, $\rho = 1.673$ g cm^{-3}. Least-squares refinement based on 2579 reflections with $I = 2\sigma(I)$ and 271 parameters led to convergence with final R1 = 0.040 and wR2 = 0.071.

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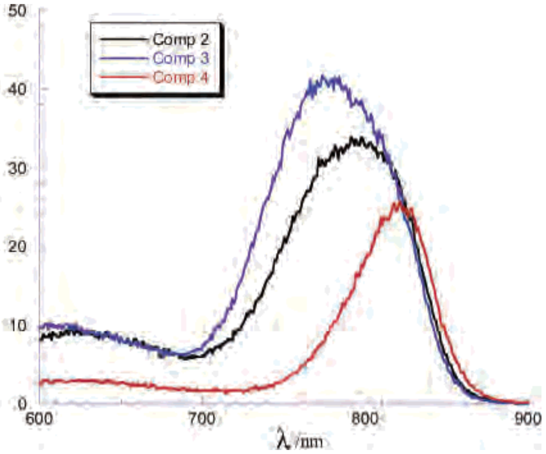

Figure 3. Solid-state emission spectra of compounds **2**−**4**.

all through equatorial coordination. Hence, compound **3** is a unique example where terephthalate facilitates the formation of a 1-D chain of paddlewheel species through axial coordination.

Despite the weak coordinating nature of tungstate and terephthalate, both 1-D chains **2** and **3** are quite stable because they are insoluble in common polar and nonpolar solvents. The insolubility thus prevents the characterization of **2** and **3** by typical solution techniques such as NMR, voltammetry, and absorption spectroscopy.

Prior studies revealed that Re_2(III,III) species supported by *N*,*N*′-bidentate ligands such as DpAniF (di(4-methoxyphenyl)formamidinate),[38] DMBA, and DEBA (*N*,*N*′-diethylbenzamidinate)[25] emit from their $^3(\delta \rightarrow \delta^*)$ excited states. Hence, we investigated the luminescence properties of the polymeric $Re_2(DMBA)_4$ species. Because of the insolubility of **2** and **3**, the emission measurements were performed on pure solid samples, and the spectra are shown in Figure 3. Included for comparison is the emission spectrum of $Re_2(DEBA)_4Cl_2$ (**4**), which is in accordance with previous results. We could detect no significant emission from compound **1** in the solid state at either room temperature or 77 K.

The emissions from **2** and **3** are broad and appear at somewhat shorter wavelengths compared to **4**. A previous report showed that the same type of shift also occurs in the $^1(\delta \rightarrow \delta^*)$ absorption when nitrate, which also binds via an oxygen atom, displaces chloride in the axial positions of $Re_2(DMBA)_4Cl_2$.[25] More specifically, the uncorrected emission maxima of **2** and **3** occur at about 795 and 780 nm, respectively, versus 825 nm for **4**. However, the detector efficiency falls off rapidly at wavelengths beyond 800 nm and probably distorts the spectrum of **4**. In line with the earlier results,[25] we assign the emissions to $^3(\delta \rightarrow \delta^*)$ excited states, and solid-state emission lifetimes at ambient temperatures (7.9 μs for **2** and 12.6 μs for **3**) are in accordance with the assignment. For comparison, a lifetime of 0.14 μs was measured for the emission from $[Et_4N]_2[Re_2Cl_8]$ under the same conditions, which is consistent with the $^1(\delta \rightarrow \delta^*)$ assignment by Gray[39] and Peacock.[40]

The change in the spin multiplicity of the emitting state is extremely interesting. In octachlorodirhenate, weak δ overlap results in a localized $^3(\delta \rightarrow \delta^*)$ excited state that lies relatively close to the ground state and well below the emitting $^1(\delta \rightarrow \delta^*)$ state. However, introduction of the bridging amidinate ($N{=}C(Ar){-}N^-$) group drastically changes the orbital overlap picture. One important change is the destabilization of the $\delta^*(Re_2)$ orbital by the donation from $\pi(N{=}C{-}N)$ orbitals and an increase in the HOMO(δ)−LUMO(δ^*) gap. This increase is reflected in the blue shift of $\lambda_{max}(\delta \rightarrow \delta^*)$ from 710 nm for $(Bu_4N)_2[Re_2Cl_8]$[1] to 440 nm for **4**,[25] as verified by both Xα and density-functional theory (DFT) calculations of related Re_2 species.[41,42] Understanding the triplet energies requires very high quality calculations such as time-dependent DFT and represents an important challenge.

In summary, $Re_2(DMBA)_4(NO_3)_2$ is a versatile synthon for 1-D polymers of dirhenium units axially linked by DAs such as tungstate and dicarboxylate. Given the propensity of potentially bridging DAs, many more 1-D polymers can be similarly prepared. Higher dimension assemblies are certainly possible with properly selected multidentate anions. Also noteworthy is the phosphorescence of these 1-D polymers because phosphorescence is preferred over fluorescence in electroluminecence devices. All of these aspects are being studied in our laboratories.

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Supporting Information Available: Syntheses and characterizations (PDF) and X-ray crystallographic files in CIF format for the structure determination of compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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