

## Gondola-Shaped Luminescent Tetrarhenium Metallacycles with Crown-Ether-like Multiple Recognition Sites

Malaichamy Sathiyendiran,<sup>†</sup> Rong-Tang Liao,<sup>†</sup> P. Thanasekaran,<sup>†</sup> Tzuoo-Tsair Luo,<sup>†</sup> N. S. Venkataramanan,<sup>†</sup> Gene-Hsiang Lee,<sup>‡</sup> Shie-Ming Peng,<sup>‡</sup> and Kuang-Lieh Lu<sup>\*†</sup>

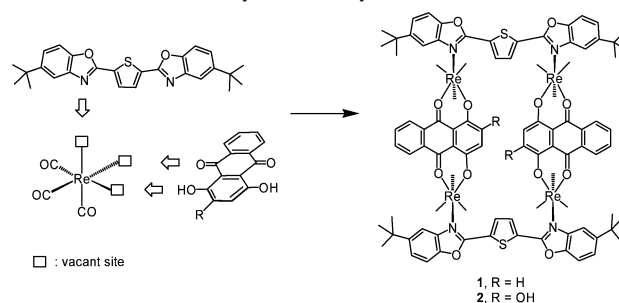
Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan, and Department of Chemistry, National Taiwan University, Taipei 107, Taiwan

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The self-assembly of gondola-shaped tetrarhenium metallacyclophanes was achieved in near quantitative yield from  $\text{Re}(\text{CO})_3$  corners, a ditopic heterocyclic clip, and a bischelating-bridging unit using an orthogonal-bonding approach. The highly luminescent metallacycles contain crown-ether-like recognition sites, which are capable of selectively recognizing metal ions and planar aromatic molecules.

Large cavity-containing metallacycles are currently attracting a great deal of attention because of their potential applications in separation materials, as components in nanoelectronics, and as recognition elements in chemical and biological sensors.<sup>1–3</sup> Several general synthetic approaches toward the preparation of discrete supramolecular complexes have emerged, which include directional-bonding,<sup>1b–f</sup> symmetry interaction,<sup>1i–j</sup> and weak-link approach.<sup>2a</sup> Recent emphasis in this field has shifted from preparing aesthetically pleasing structures to the design of functional metallacycles

Scheme 1. Self-Assembly of Metallacycles 1 and 2



with unusual molecular sensing or catalytic properties. Examples include the development of fluorescent sensors and allosteric catalysts that mimic the properties of allosteric enzymes.<sup>2</sup> Herein we report on a new *orthogonal-bonding approach* for assembling functional molecules. This approach, which is an offshoot of the directional-bonding approach, involves the simultaneous introduction of a bis(chelating) dianion to coordinate to two equatorial sites of two *fac*-( $\text{CO}$ )<sub>3</sub>Re cores and a ditopic nitrogen-donor ligand to the remaining orthogonal axial site, leading to the generation of a new, hitherto unexplored class of metallacycles (Scheme 1).

As proof-of-concept, 2,5-bis(5-*tert*-butyl-2-benzoxazolyl)-thiophene (tpbb) and 1,4-dihydroxy-9,10-anthraquinone (H<sub>2</sub>-dhaq) or 1,2,4-trishydroxy-9,10-anthraquinone (H<sub>2</sub>-thaq) were chosen for use as basic building units. The presence of two nitrogen donors should permit the tpbb ligand to act as a neutral bifunctional molecular clip. We rationalized that the use of the bischelating ligands H<sub>2</sub>-dhaq and H<sub>2</sub>-thaq would result in a macrocycle host with a large internal cavity.<sup>4</sup> Although both ligands are important in dye chemistry,

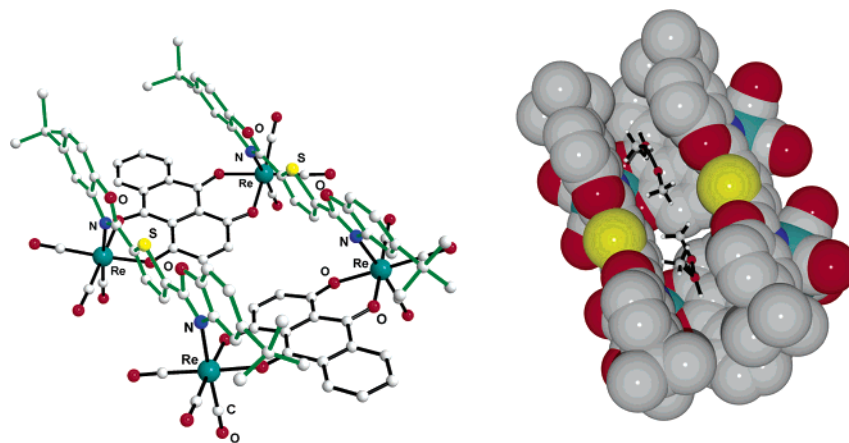
\* To whom correspondence should be addressed. E-mail: lu@chem.sinica.edu.tw.

<sup>†</sup> Academia Sinica.

<sup>‡</sup> National Taiwan University.

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**Figure 1.** Crystal structure of the metallacycle **1**; ball and stick representation (left); space-filling representation (right) with four methanol guests (shown in ball and stick model) occupied in the intramolecular cavity of **1**.

electroluminescent devices, biology, and pharmaceutical chemistry,<sup>5</sup> their use as building units in the construction of supramolecular assemblies has not been previously investigated. The combination of the above-mentioned new building blocks and the novel orthogonal-bonding approach permits the preparation of unique gondola-shaped structures with crown-ether-like recognition sites, highly fluorescent properties, and selective binding capabilities. This approach is so effective that the products can be prepared in near quantitative yield.

The assembly of compounds **1** and **2** was achieved by reacting equimolar amounts of  $\text{Re}_2(\text{CO})_{10}$ , tpbb, and  $\text{H}_2$ -dhaq or  $\text{H}_2$ -thaq in refluxing mesitylene. The resulting dark-green products were air and moisture stable and are slightly soluble in polar solvents. The IR spectrum of **1** in acetone exhibited strong bands at 2014 and 1900  $\text{cm}^{-1}$ , characteristic of *fac*- $\text{Re}(\text{CO})_3$ . The  $^1\text{H}$  NMR spectrum of **1** showed well-resolved signals for each of the protons. Compared to the free ligands, the signals corresponding to the tpbb protons remained nearly unchanged, while those of the dhaq proton of  $\text{H}^2$  was shifted upfield by 0.16 ppm after complexation with the Re(I) centers. A similar pattern was observed for **2** with an additional singlet at 10.99 ppm corresponding to the uncoordinated hydroxyl hydrogen ( $\text{C}^2\text{-OH}$ ) atoms. The ESI-MS spectrum of **1** showed a molecular ion peak at  $m/z$  2418.1.

A single-crystal X-ray diffraction analysis shows that compound **1** adopts an unusual gondola-shaped structure (Figure 1).<sup>6</sup> The structure can be regarded as a special type of grid. The two tpbb ligands serve as molecular clips, utilizing the benzoxazoline N atoms to bridge two doubly bridged dirhenium units. The bishydroxy anthraquinone (dhaq) acts as a doubly bridging unit using the adjacent phenolate and quinone oxygens. Interestingly, the hydrophobic internal cavity of the metallacycle is sufficiently large (size:  $5.6 \text{ \AA} \times 7.0 \text{ \AA} \times 17.8 \text{ \AA}$ ) to accommodate four MeOH

molecules. Compound **2** is *isostructural* with respect to **1** but contains two additional uncoordinated hydroxyl groups. It is noteworthy that compounds **1** and **2** possess multiple-recognition sites. The arrangement of heteroatoms may be considered as the structural framework of 1,10-dithio-(18-crown-6) (see Supporting Information).<sup>7</sup>

Compound **1** in  $\text{CH}_2\text{Cl}_2$  displayed intense absorption bands in the 230–395 nm region, which are assigned to  $\pi\text{-}\pi^*$  transitions of the dhaq and tpbb (357, 378, 397 nm) ligands, and a weak shoulder at 420 nm, assigned to the MLCT transition ( $\text{Re} \rightarrow \text{tpbb}$ ). In addition, weak absorption bands appeared at 585 and 632 nm, attributed to an intraligand transition of the dhaq unit. Compounds **1** and **2** show a high luminescence at room temperature with a quantum yield of 0.179 for **1** and 0.397 for **2** relative to  $\text{Ru}(\text{bpy})_3^{2+}$ . Upon excitation at  $\lambda_{\text{max}} = 378 \text{ nm}$ , compound **1** emits a set of structured bands centered at 438 nm with a lifetime of 1.4 ns. These emission bands are similar to that of the tpbb ligand. The small Stokes shift and very short lifetime of **1** indicate that the emission originates from the singlet  $\pi\text{-}\pi^*$  excited state. In the solid state, compound **1** exhibits two emission maxima at 448 and 518 nm when excited at 335 nm. The emission band at 448 nm is due to the decay of the  $\pi\text{-}\pi^*$  excited state of tpbb, while the band at 518 nm may be attributed to the decay of the  $d\text{-}\pi^*$   $\text{Re} \rightarrow \text{tpbb}$  excited state.

Preliminary studies were carried out on the host–guest chemistry of **1** using its absorption and luminescent features. The addition of metal ions such as  $\text{Li}^{\text{I}}$ ,  $\text{Sr}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Pb}^{\text{II}}$ , and  $\text{Ag}^{\text{I}}$  did not show noticeable effects on the absorption and emission bands of **1**. However, upon the

(4)  $[\text{M}-(\mu_2\text{-XR})_2\text{-M}]$  ( $\text{X} = \text{O}$  or  $\text{S}$ ),  $\sim 3.4 \text{ \AA}$ ;  $[\text{M}-(\mu_4\text{-bisbenzimidazole})\text{-M}]$ ,  $\sim 5.5 \text{ \AA}$ ;  $[\text{M}-(\mu_4\text{-2,2'-bipyrimidine})\text{-M}]$ ,  $\sim 5.85 \text{ \AA}$ , and  $[\text{M}-(\mu_4\text{-dhaq})\text{-M}]$ ,  $\sim 8.5 \text{ \AA}$ .

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addition of  $\text{Hg}^{\text{II}}$  ion, the absorption maximums of **1** at 357 and 378 nm decreased and a new absorption peak at 425 nm gradually became enhanced. Similarly, the emission maximum of **1** at 438 nm was quenched while the emission intensity at 490 nm gradually increased. A plot of  $1/(\Delta I)$  vs  $[G]^{-1}$  at 495 nm showed a good linear relationship,<sup>8</sup> indicating the formation of a 1:1 complex with a binding constant of  $1.3 \times 10^3 \text{ M}^{-1}$ . The binding constant did not change when different counterions ( $\text{CF}_3\text{SO}_3^-$ ,  $\text{NO}_3^-$ ) were used. The uncoordinated sulfur atoms of the tpbb ligands along with the flexibility of thiophene rings conferred by the  $\sigma$ -bond create a well-defined binding site for metal ion selective recognition. The adjacent hard (O atoms) Lewis base sites may exhibit a synergistic effect to strengthen the recognition capability. Another option is that each half of the macrocycle is occupied by one cation. Since the host/guest ratio is 1:1, the possibility that two macrocycles, with their cavities facing each other, are complexing two cations cannot be excluded. The emission enhancement of **1** may be attributed to the chelation of metal ions thereby leading to more rigid complexes, which reduces the nonradiative decay process.<sup>9,10</sup>

Furthermore, compound **1** was capable of specifically recognizing anthracene. Quenching of the emission intensity shows that **1** has a much higher affinity for anthracene ( $K = 3.8 \times 10^3 \text{ M}^{-1}$ ) than pyrene, naphthalene, or benzene ( $K$  not detectable). The contribution of  $\pi$  systems would be very important for the binding of aromatic molecules, and the preference found for anthracene may result from shape complementarity with the anthraquinone moiety.

In conclusion, a new class of neutral, luminescent Re-based metallacycles was designed and assembled in near quantitative yield using novel orthogonal-bonding strategy. The metallacycles are remarkable in terms of their structure, blue light-emitting property, multiple functional sites, and selective binding ability toward mercury cations and anthracene molecule. The orthogonal-bonding approach was found to be extremely effective toward the design of novel functional metallacycles. Further studies are underway to establish the full scope of this methodology.

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**Supporting Information Available:** Synthetic procedure and spectral data for compounds **1** and **2** (PDF). The crystallographic files for compounds **1** and **2** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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