Rhenium-based molecular rectangular boxes with large inner cavity and high shape selectivity towards benzene molecule†

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The self-assembly of rhenium-based rectangular boxes with a large inner cavity can be achieved *via* a simple one-step synthetic route; these molecules selectively recognize planar aromatic molecules, benzene in particular.

Supramolecular metallacyclic hosts with inner cavities for guest inclusion have received considerable attention not only due to their aesthetic appeal, but also for their potential applications for selective recognition, to serve as model compounds that mimic biological systems, and to catalyze specific chemical transformations.[1–4] Among the reported metallacycles, the lower symmetry of a rectangle should lead to greater selectivity and binding, especially for planar aromatic guests.[5–8] Although a few methodologies are available for the preparation of rectangles, a simple one-step approach for preparing neutral rectangles with large inner cavities continues to remain a challenge.[5–8] We envision that the use of an orthogonal-bonding approach *i.e.* simultaneous incorporation of *fac*-$(CO)_3Re$-cores, neutral ditopic N-donors, and dianionic bis(chelating) ligands, may permit the preparation of a heterotopic rectangle rather than two molecular squares with homotopic bridging ligands (Scheme 1).

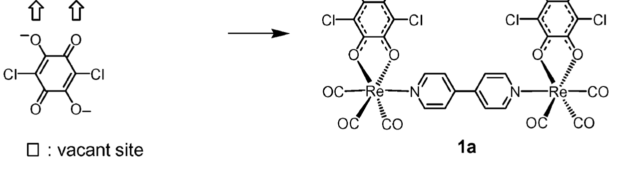
Rectangle $[\{(CO)_3Re(\mu\text{-}CA)Re(CO)_3\}_2(\mu\text{-}bpy)_2]\cdot$mesitylene (**1a**·mesitylene) was assembled by reacting equimolar amounts of $Re_2(CO)_{10}$, 4,4′-bipyridine (bpy) and chloranilic acid (H_2CA) in a one-pot method (eqn (1)). The products are air- and moisture-stable and are soluble in polar organic solvents. The IR spectrum of **1a** exhibited bands at 2023, 1923 and 1899 cm^{-1}, characteristic of *fac*-$Re(CO)_3$. The FAB-MS spectrum exhibited a molecular ion peak at *m*/*z* 1809.3.

$$2\,Re_2(CO)_{10} + 2\,H_2L^1 + 2\,L^2 \longrightarrow [\{(CO)_3Re(\mu\text{-}L^1)Re(CO)_3\}_2(\mu\text{-}L^2)_2] \qquad (1)$$

1a, L^1 = CA; L^2 = bpy
1b, L^1 = CA; L^2 = bpe
2a, L^1 = dhnq; L^2 = bpy
2b, L^1 = dhnq; L^2 = bpe

Rectangular box $[\{(CO)_3Re(\mu\text{-}CA)Re(CO)_3\}_2(\mu\text{-}bpe)_2]\cdot$2toluene (**1b**·2toluene) was synthesized following a similar procedure using *trans*-1,2-bis(4-pyridyl)ethylene (bpe) instead of bpy.A single-crystal X-ray diffraction analysis showed that compound **1a** adopts a tetranuclear rectangular architecture (Fig. 1).‡ Each Re center is coordinated in an octahedral fashion by three CO groups, one 4,4′-bipyridine and one dianionic chloranilate ligand. The pyridyl plane in bridging bpy is twisted by 18° which is close to the commonly observed twist angle for bpy in metallacycles. The dianion of chloranilic acid (CA^{2-}) chelates to the two rhenium(I) atoms through the four oxygen atoms, acting as a tetradentate ligand. The CA^{2-} unit is planar with π-electron delocalization confined to the two halves as shown in Scheme 1. The dimensions of the rectangular box were 11.4 × 8.1 × 6.3 Å. One mesitylene guest resides inside the cavity and interacts with the rectangular box with weak $\pi\cdots\pi$ (3.6–4.6 Å) and $C\text{–}H\cdots\pi$ interactions. The cage molecule lies about an inversion centre as does the mesitylene guest.

When the assembly unit was changed from H_2CA to 5,8-dihydroxy-1,4-naphthoquinone (H_2dhnq) with a slightly larger bridging length, compounds $[\{(CO)_3Re(\mu\text{-}dhnq)Re(CO)_3\}_2(\mu\text{-}L)_2]\cdot G$ (**2a**·G, L = bpy, G = 2benzene; **2b**·G, L = bpe, G = toluene) were formed. A single-crystal X-ray diffraction analysis showed that compound **2a** adopts a rectangular structure with dimensions of 11.4 × 8.5 × 6.5 Å (Fig. 2).§ One benzene is accommodated in the cavity which is stabilized by the $\pi\cdots\pi$ stacking interactions (3.5 Å) with the two coplanar bpy units. The two bpy units bow slightly inward reducing the cavity width from 8.5 to 7.1 Å at the centre thereby increasing the $\pi\cdots\pi$ interactions with the benzene guest. The distance (4.37 Å) between the plane of dhnq and the nearby carbon atom of the included benzene indicates the presence of weak $C\text{–}H\cdots\pi$ interactions.[8] The cage molecule and the entrapped benzene molecule have space group



Scheme 1 Orthogonal-bonding approach to molecular rectangular box **1a**.

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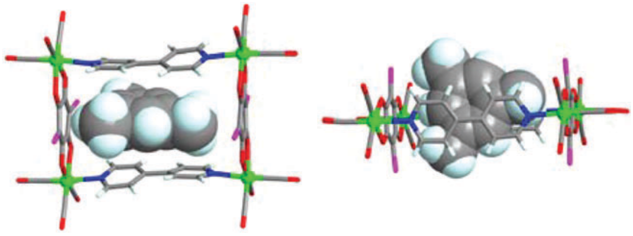

Fig. 1 Top and side views of the crystal structure for the **1a**·mesitylene (stick and space-filling representation). C gray, Cl pink, H lime, N blue, Re green.

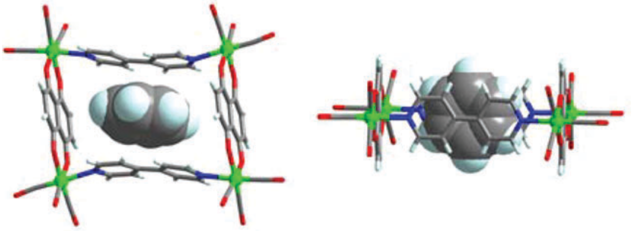

Fig. 2 Crystal structure for the **2a**·2benzene (stick and space-filling representation): C gray, H lime, N blue, Re green.

imposed *2*/*m* symmetry. In addition, one disordered guest benzene molecule filling the space between two rectangular boxes is also observed.

The UV-Vis absorption spectrum of **1a** in THF showed intense absorption bands (230, 262 and 276 nm) in the high-energy region, which are assigned to a ligand-centered π–π* transition, and two low energy bands (325 and 511 nm) corresponding to the MLCT- and intraligand transitions of the quinone unit. The red-shift of the lowest energy maximum at 325(sh) for **1a** and 444 nm for **2a** can be attributed to the presence of an arene group capable of inducing further stabilization of the π*-orbital of the ligand. In addition, the weak bands at 497–677 nm for **2a** can be attributed to intraligand transitions of the quinone moiety.[9]

Intrigued by the X-ray structures of $(\text{arene})_n \subset \mathbf{1}$, we set out to study the host–guest properties of **1a** toward benzene derivatives in solution using UV-Vis spectroscopy. The absorption maxima of the aromatic guest increases upon the addition of host **1a**, suggesting binding of the guest inside the host cavity. The binding constant (*K*) for these host–guest interactions can be evaluated on the basis of the Benesi–Hildebrand relationship[10] which shows a much higher affinity for benzene ($K = 1.7 \times 10^5$ M^{-1}) than mesitylene ($K = 4.2 \times 10^4$ M^{-1}). The high *K* of **1a** towards benzene is likely due to the compact cavity size of **1a** for benzene, which is stacked firmly by two bpy units. To our knowledge, rectangular box **1a** is by far the best host for a benzene molecule. Among the other notable cyclic systems for benzene recognition,[11] cucurbit[6]uril gave a high *K* value (8.9×10^3 M^{-1}) which is still two orders lower than that of **1a**. Metallacycle **1b** also shows a higher affinity towards benzene ($K = 5.0 \times 10^4$ M^{-1}) than mesitylene ($K = 4.0 \times 10^3$ M^{-1}). The higher *K* for **1a** than those of **1b** indicates that the π–π interaction of benzene with the bpy units of **1a** is more effective than that of the bpe units of **1b**, respectively. These results suggest that the complementary size and shape of the host and guest are critical for the binding of benzene.

Our present work demonstrates a new method for the generation of Re-based rectangular boxes with large, tunable inner cavities *via* an orthogonal-bonding approach. The rectangular box shows size and shape selectivity towards aromatic guest molecules, and benzene in particular. The effective one-step preparation, high stability, tunable nanoscale cavity dimension, and recognition capability make these Re-based rectangular boxes intriguing and potentially useful supramolecules.

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Notes and references

‡ *Crystal data* for **1a**·mesitylene. $C_{53}H_{28}Cl_4N_4O_{20}Re_4$, M = 1927.39, monoclinic, space group $P2_1/n$, a = 11.0200(2), b = 18.4422(5), c = 14.9444(4) Å, β = 104.0179(11)°, U = 2946.75(1) Å^3, T = 150(1) K, Z = 2, μ(Mo-Kα) = 8.448 mm^{-1}, 18829 reflections measured, 6751 unique (R_{int} = 0.0909) which were used in all calculations. The final $wR(F_2)$ was 0.1654 (all data). CCDC reference number 678660.

§ *Crystal data* for **2a**·2benzene. $C_{64}H_{36}N_4O_{20}Re_4$, M = 1925.77, orthorhombic, space group *Cmca*, a = 12.277(3), b = 19.785(4), c = 26.044(5) Å, U = 6326(2) Å^3, T = 153(2) K, Z = 4, μ(Mo-Kα) = 7.707 mm^{-1}, 25 744 reflections measured, 2944 unique (R_{int} = 0.0777) which were used in all calculations. The final $wR(F_2)$ was 0.0973 (all data). CCDC 678661.

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