

One-Step Orthogonal-Bonding Approach to the Self-Assembly of Neutral Rhenium-Based Metallacycles: Synthesis, Structures, Photophysics, and Sensing Applications

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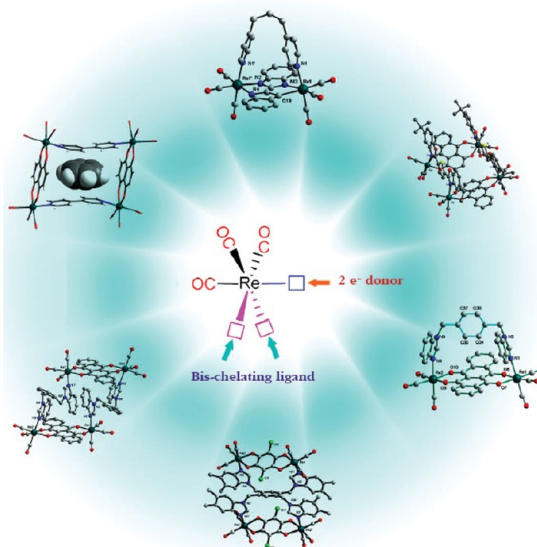
CONSPECTUS

Self-assembled metallacycles offer structural diversity and interesting properties based on their unique frameworks and host–guest chemistry. As a result, the design and synthesis of these materials has attracted significant research interest. This Account describes our comprehensive investigations of an effective orthogonal-bonding approach for the self-assembly of neutral Re-based metallacycles. We discuss the various types of assemblies that can be created based on the nuclearity of the luminophore, including bimetallic materials, rectangles, cages, and calixarenes. This approach permits the preparation of a rectangular molecule, rather than two molecular squares, in excellent yields. We extended this strategy to the high yield synthesis of a series of Re-based metallacycles with different shapes. With the rich spectroscopic and luminescence properties, Re(I) metallacycles provide an excellent platform for studies of host–guest interactions. When possible, we also present potential applications of the luminescent Re-based metallocupramolecular assemblies.

The orthogonal-bonding approach involves the simultaneous introduction of two ligands: a bis-chelating ligand to coordinate to two equatorial sites of two *fac*-(CO)₃Re cores and a monotopic or ditopic nitrogen-donor ligand to the remaining orthogonal axial site. Furthermore, by the appropriate choice of the predesigned organic ligands with various backbones and connectivity information and *fac*-Re(CO)₃ metal centers, we could also design other novel functional metallacycles including rotors, gondolas, cages, triangles, and metallacalixarenes in high yields. The incorporation of flexible ligands into the Re(I) metallacycles allows us to introduce various conformation states and novel structures. As a result, these structures acquire new functions, such as adaptive recognition properties. For example, we assembled Re(I)-based metallacyclic rotors via a one-step process. These rotors, which contain a *para*-phenylene unit that rapidly rotates within the metallacycles, are prototypes of a neutral altitudinal rotor.

Most of the metallacycles are luminescent. The ability to chemically modify the organic ligands offers opportunities to create structural diversity and to tune the photophysical properties of these Re(I) metallacycles efficiently. Several strategies for increasing emission quantum yields and excited-state lifetimes and tuning the colors in Re(I) metallacycles are available. The cyclometalated ligands in Re(I) metallacycles improve excited state lifetimes and quantum yields, and these C–H bond-activated metallacycles are considerably more emissive than their non-C–H bond-activated analogues. The introduction of crown-ether-like recognition sites into neutral gondola-shaped metallacycles that selectively recognize metal ions also enhanced emission.

Rhenium-based rectangular boxes, synthesized via a simple one-step route, contain a large and tunable hydrophobic inner cavity, which selectively recognizes benzene molecules. Such structures were the best host for benzene reported to date. In addition, we designed and synthesized novel neutral metallacalixarenes with tunable size, cavity, color, and functionality. These structures are efficient hosts for the recognition of planar aromatic guests.



1. Introduction

The design and synthesis of self-assembled metallacycles is a subject of considerable interest because of the structural diversity, characteristic properties based on their unique frameworks, and host–guest chemistry.^{1–3} These metallacyclic structures are usually constructed via the self-assembly of well-designed organic ligands in combination with transition metal ions through the formation of coordination bonds. Several general synthetic approaches to the preparation of discrete supramolecular complexes have emerged, which include directional bonding,^{4–6} symmetry interaction,⁷ and a weak-link approach.⁸ Self-assembly protocols can considerably reduce synthetic costs and frequently lead to the formation of a single thermodynamic product in high yield. By the numerous researchers who are actively engaged in this field, over the past decades, a number of metallacycles, including triangles, squares, rectangles, cages, and prisms have been explored.^{9–17} The Fujita^{5,18} and Stang¹¹ groups used a multicomponent self-assembly for designing large assemblies based on specific information encoded within the individual components. Compared with various symmetry polygons, by application the aforementioned approaches, assembling molecular rectangles by the simultaneous mixing of two rigid ligands of different lengths with *cis*-protected metal centers proved to be a more difficult task. The likely reason for this is that the strong enthalpic driving force favors the formation of two types of molecular squares instead of molecular rectangles.¹⁹ Hence, molecular rectangles represent a unique class of metallacycles because their preparation remained a challenge and a rectangular cavity would reasonably be expected to offer enhanced binding and selectivity toward aromatic guests. Hence, we developed a novel, one-step strategy, termed the orthogonal-bonding approach, which is an offshoot of the directional-bonding approach and involves the simultaneous introduction of a bis-chelating ligand to coordinate to two

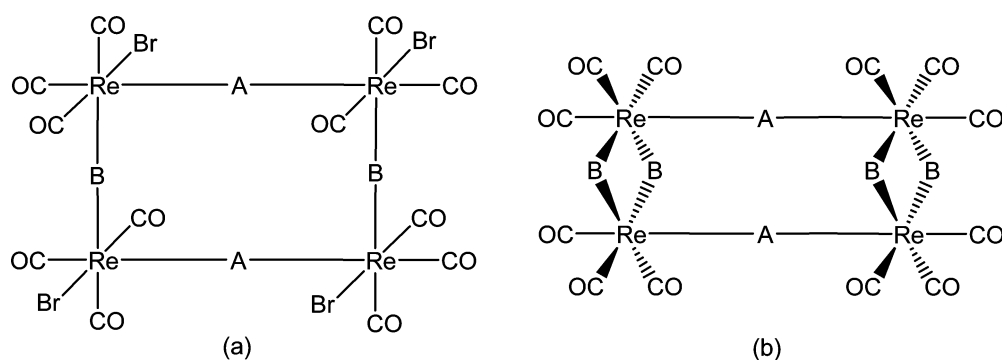
equatorial sites of two *fac*-(CO)₃Re cores and a ditopic nitrogen-donor ligand to the remaining orthogonal axial site, leading to the generation of rectangles in high yields. Furthermore, by utilizing this approach, we found that it is not only useful for the high yield preparation of rectangles but also for the vast majority of discrete neutral metallacycles, such as gondolas, rotors, triangles, cages, and boxes, with predesigned geometries. In addition, by taking advantages of the improvement in photoluminescent properties and cavity size of these host molecules to external guests, it is possible to use such systems as effective sensors. By utilizing *fac*-Re(CO)₃ cores with suitable organic linkers, Hupp and co-workers designed rhenium-based metallosupramolecules, some of which showed selectivity for different sized guest molecules.^{17,19,20} The rich and varied possibilities for creating Re(I)-based rectangles constructed in a stepwise manner or one-pot reactions were attempted by our group^{21,22} and the efficiency of their luminescence was improved by incorporating π -conjugated ligands or long alkyl chains via an aggregation process. Chart 1 shows some examples of structures of Re(I)-based metallacycles that were produced prior to 2006.

As befits an Account of this type, the discussion is entirely focused on the results obtained in our laboratory, and this Account will cover reports in the literature published from the period since 2006.

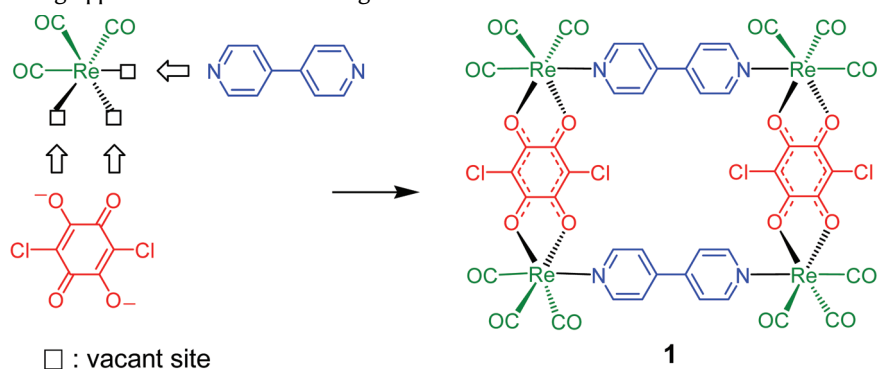
2. Molecular Rectangles

The synthesis of metal-containing rectangles from a metal precursor and two rigid ligands with different lengths was a great challenge. Two molecular squares were formed instead of a rectangle.⁴ We found that orthogonal binding sites on the metal centers can be exploited for the construction of rectangular systems containing large cavities in which a bischelating quinone moiety and pyridyl derivatives assemble through the addition of a Re precursor under solvothermal conditions.

CHART 1. Graphical Representation of Some Re(I)-Rectangles Prepared Prior to 2006^a



^a(a) A = 4,4'-bipyridine, B = pyridyl derivatives²¹ or benzimidazole;¹⁹ (b) A = 4,4'-bipyridine, B = alkyl or aromatic alcohols and thiols^{20,22,23}.

SCHEME 1. Orthogonal-Bonding Approach to Molecular Rectangular Box **1**

This orthogonal-bonding approach can completely switch the direction of the reaction, permitting the formation of molecular rectangles without producing any squares. This approach is a breakthrough for the development of molecular rectangles.

The simultaneous introduction of a bis(chelating) dianion to coordinate to two equatorial sites of two *fac*-(CO)₃Re cores and a ditopic nitrogen-donor ligand to the remaining orthogonal axial site led to the formation of high yields of rectangles [{(CO)₃Re(μ-L)Re(CO)₃ }₂(μ-L')₂] (**1**, L = chloranilic acid (H₂CA), L' = 4,4'-bipyridine (bpy); **2**, L = chloranilic acid (H₂CA), L' = *trans*-1,2-bis(4-pyridyl)ethylene (bpe); **3**, L = 5,8-dihydroxy-1,4-naphthoquinone (H₂dhnq), L' = bpy; **4**, L = H₂dhnq, L' = bpe) under solvothermal conditions (Scheme 1, eq 1).²⁴ This orthogonal-bonding approach was found to be an ideal method for the synthesis of rectangles in high yields by a one-step process, with no squares being produced. The Re metal center obeys the 18 electron rule in rectangles, whereas the unstable squares would contain either 17 or 19 electrons, which would lead to the formation of rectangles in high yields.

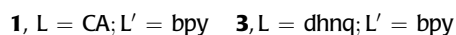
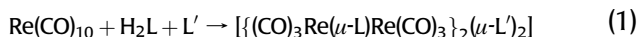


Figure 1 depicts the solid-state structure of **3**, which has a rectangular structure with dimensions of 11.4 × 8.5 × 6.5 Å³. The two bpy units in **3** are bowed slightly inward, thereby reducing the width of the cavity from 8.5 to 7.1 Å and increasing the π–π interactions with the benzene guest (3.5 Å).

The electronic absorption spectrum of **1** in THF at 298 K 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 metal–ligand charge

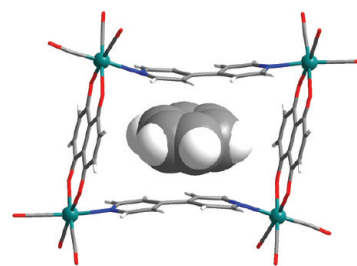
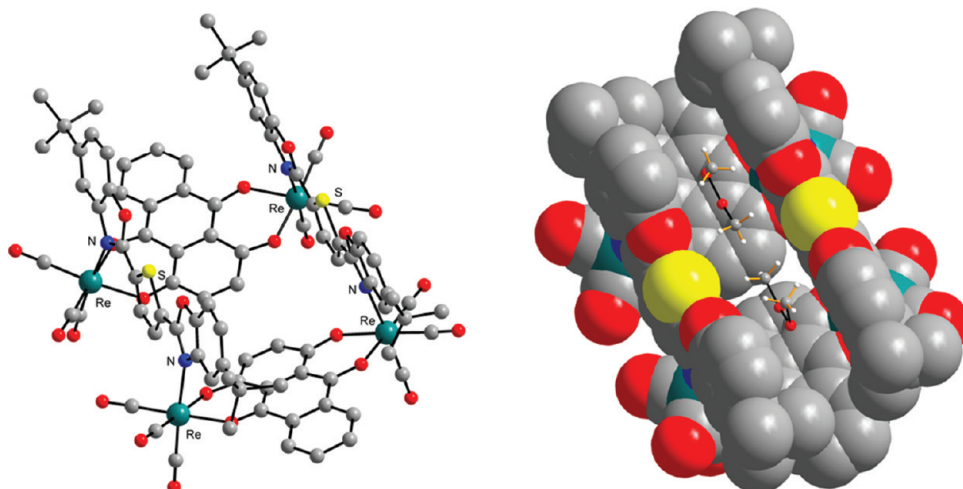
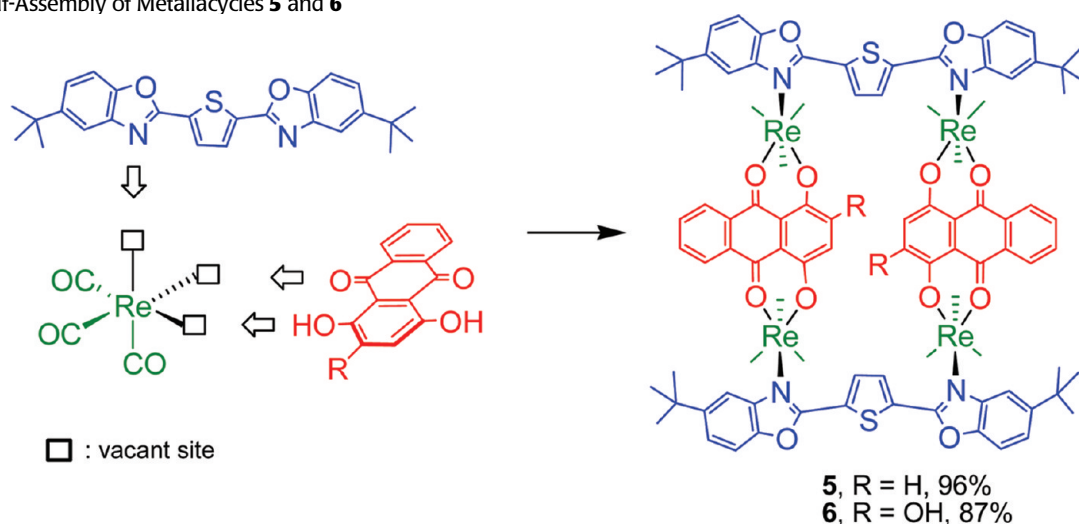


FIGURE 1. Crystal structure of the molecular rectangle **3**, showing the recognition of a benzene molecule.

transfer (MLCT) and intraligand transitions of the quinone unit, respectively.

Reliable evidence for the host–guest properties of **1** toward benzene derivatives was obtained from UV–vis spectroscopic data, which showed hydrocarbons encounter **1–4** in a 1:1 molar ratio based on the Benesi–Hildebrand relationship.²⁵ Of particular interest is that benzene exhibits a strong affinity ($K = 1.7 \times 10^5 \text{ M}^{-1}$ for **1** and $K = 5.0 \times 10^4 \text{ M}^{-1}$ for **2**) compared with mesitylene ($K = 4.2 \times 10^4 \text{ M}^{-1}$ for **1** and $K = 4.0 \times 10^3 \text{ M}^{-1}$ for **2**). Not only the presence of π–π interaction between benzene and the bpy units of **1** but also the compact cavity size of **1** toward benzene might be responsible for the high value of K compared with the bpe units of **2**. The cyclic systems reported by others^{26–28} also recognize benzene but show binding constants on the order of 10^2 – 10^3 M^{-1} . Hence, the rectangular box **1** is the best host for a benzene molecule that has been reported to date.

The versatility of this orthogonal-bonding approach can also be demonstrated by the preparation of gondola-shaped metallacycles **5** and **6**, which are produced by the reaction of equimolar amounts of Re₂(CO)₁₀, 2,5-bis(5-*tert*-butyl-2-benzoxazolyl)-thiophene (tpbb), and 1,4-dihydroxy-9,10-anthraquinone (H₂dhaq) or 1,2,4-trishydroxy-9,10-anthraquinone (H₂thaq) in refluxing mesitylene in excellent yields (Scheme 2).²⁹ The metallacycles are remarkable in terms of

SCHEME 2. Self-Assembly of Metallacycles **5** and **6**FIGURE 2. Crystal structure and space-filling representation of **5**.

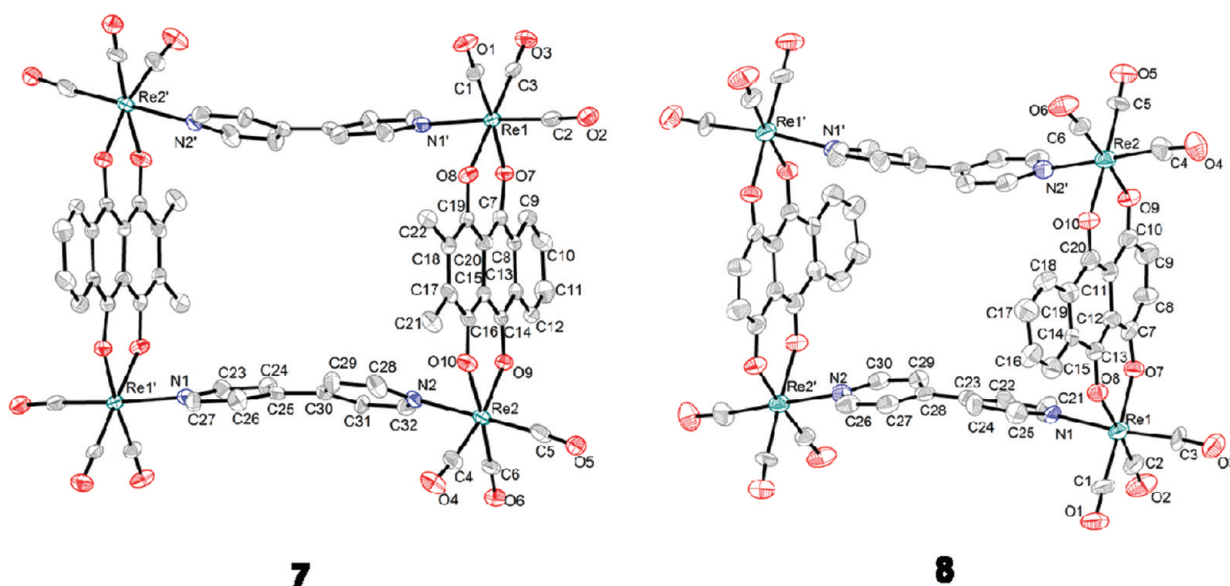
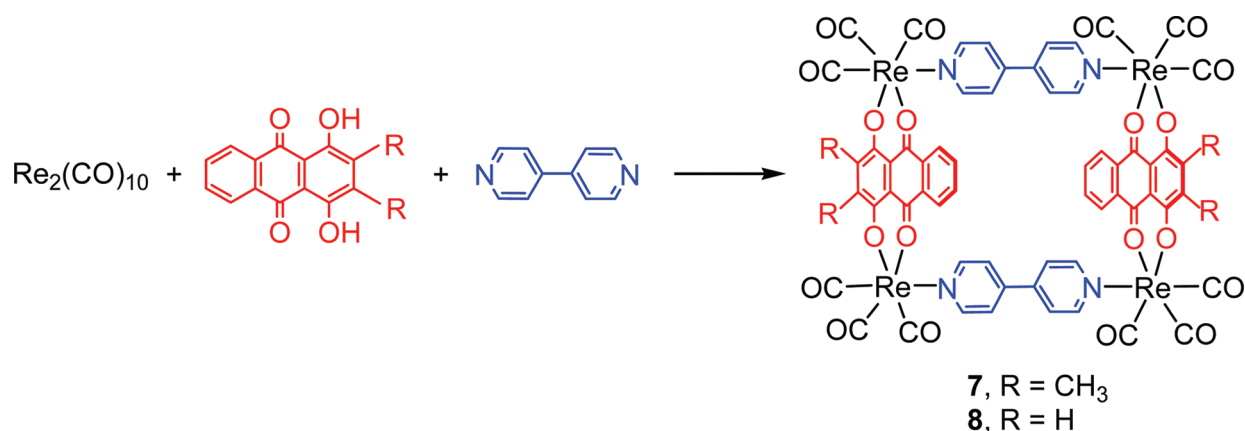
their structure, blue-light-emitting property, multiple functional sites, and selective binding ability toward mercury cations and anthracene molecules.

Compound **5** exhibits an unusual gondola-shaped structure (Figure 2) with a hydrophobic internal cavity ($5.6 \text{ \AA} \times 7.0 \text{ \AA} \times 17.8 \text{ \AA}$), which is sufficiently large to accommodate four MeOH guest molecules.

The absorption spectrum of **5** in CH_2Cl_2 showed intense absorption bands in the 230–395 nm range, which are attributed to $\pi-\pi^*$ transitions of the dhaq and tpbb ligands, and the weak shoulder at 420 nm is assigned to a $\text{Re} \rightarrow \text{tpbb}$ (MLCT) transition. The weak absorption bands at 585 and 632 nm are attributable to an intraligand transition of the dhaq unit. Compound **5** emits a structured band centered at 438 nm with a short lifetime of 1.4 ns, revealing the $\pi-\pi^*$ excited state of tpbb ligand.

A study of the host–guest chemistry of **5**, using its absorption and luminescent features, reveals that noticeable changes are not observed when metal ions such as Li(I), Sr(II), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), and Ag(I) are added. However, upon the gradual addition of Hg(II) ions, the absorption maxima of **5** at 357 and 378 nm decreased and a new absorption peak at 425 nm gradually appeared while the emission maximum of **5** at 438 nm was quenched and the emission intensity at 490 nm gradually increased. The binding constant was found to be $1.3 \times 10^3 \text{ M}^{-1}$ with a 1:1 ratio. The emission enhancement of **5** may be attributed to the chelation of metal ions thereby leading to the formation of more rigid complexes, which reduces the nonradiative decay process.

Analogously, the self-assembly of molecular rectangles [$\{(\text{CO})_3\text{Re}(\mu\text{-QL})\text{Re}(\text{CO})_3\}_2(\mu\text{-bpy})_2$] (**7**, QL = 6,7-dimethyl

SCHEME 3. The Preparation of Rectangles **7** and **8**FIGURE 3. ORTEP diagrams of compounds **7** and **8**.

1,4-dioxido-9,10-anthraquinone (QL₁); **8**, QL = 1,4-dioxido-9,10-anthraquinone (QL₂)) was achieved as shown in Scheme 3.³⁰

The X-ray analysis of **7** and **8** show that the Re center is coordinated with dianionic QL²⁻ ligand through its four oxygen atoms and pyridyl ligands, with dimensions of 11.41 × 8.57 and 11.45 × 8.58 Å², respectively (Figure 3). The 4,4'-bipyridine ligands are bowed inward, such that the cavity widths of **7** and **8** are reduced slightly to 7.20 and 7.60 Å, respectively.

UV–vis–NIR spectroelectrochemical studies indicate that the first reduction of **7** and **8** to the 1– state reduced the MLCT and LMLCT band intensities followed by the appearance of absorption bands at 524 and above 840 nm, which are characteristic of the radical anion of 4,4'-bipyridine. The second reduction to the 2– state caused the regeneration of

a new LMLCT band. Further reduction to **7**³⁻ or **8**³⁻ causes a slight increase in the LMLCT state, in which the electron is transferred to the quinone moiety. Complex **8** exhibited multiple emissions from the ³IL, ³MLCT and ³LLCT levels and showed biexponential decay, whereas in complex **7**, the ³IL emission was absent and only a single-exponential decay was observed.

In our continuing efforts to synthesize rectangles, an unprecedented partial reduction of 2,2'-bipyrimidine (bpym) occurred during the self-assembly of Re(I)-based molecular rectangles [₂{(CO)₃Re(*μ*-H₆bpym)Re(CO)₃}]₂(*μ*-L)₂ (**9**, L = pyrazine; **10**, L = 4,4'-bipyridine) under solvothermal conditions (Scheme 4).³¹ The bimetallic complex **11**, as a precursor for the preparation of **9** and **10**, was also synthesized. Solution ¹H NMR data for **9**–**11** reveal the partially reducing characteristics of the aromatic region.

The solid-state structures of **9** and **10** and bimetallic complex **11** revealed the reduced bpym ligand within the

SCHEME 4. The Self-Assembly of Re(I)-Based Rectangles **9**, **10** and Bimetallic Complex **11**

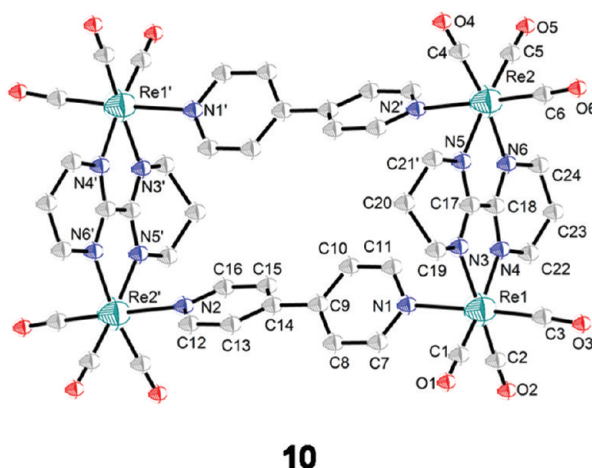
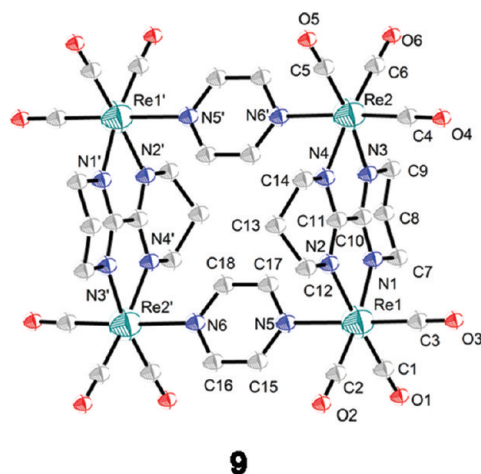
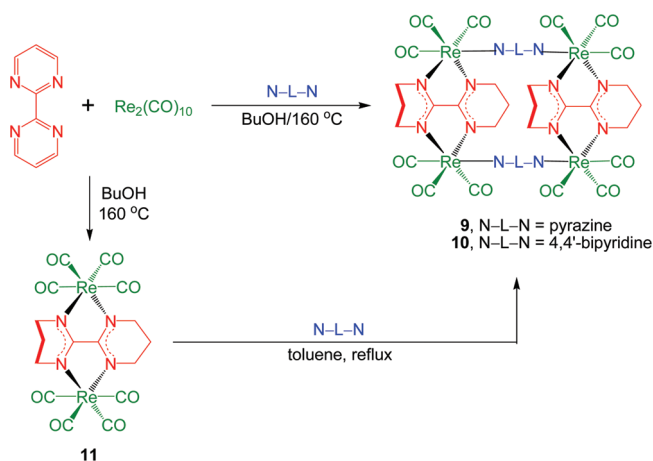


FIGURE 4. ORTEP diagrams of **9** and **10**.

architecture, consistent with the solution ^1H NMR data. The structure of **9** (Figure 4) is rectangular with a cavity dimension of $5.79 \times 7.31 \text{ \AA}^2$, in which two $(\text{CO})_3\text{Re}-(\text{pz})-\text{Re}(\text{CO})_3$ edges are bridged by two reduced bpym moieties with C–C single bond lengths ranging from 1.485(10) to 1.514(11) Å and an sp^3 configuration. The bond lengths for Re–N are shorter ($\sim 0.19 \text{ \AA}$) than those of Re–N(pz), suggesting a

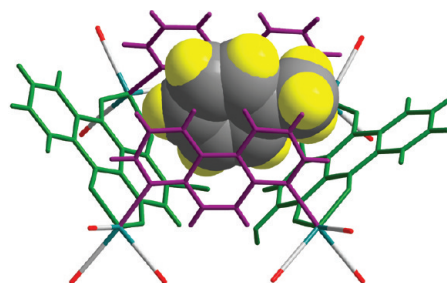
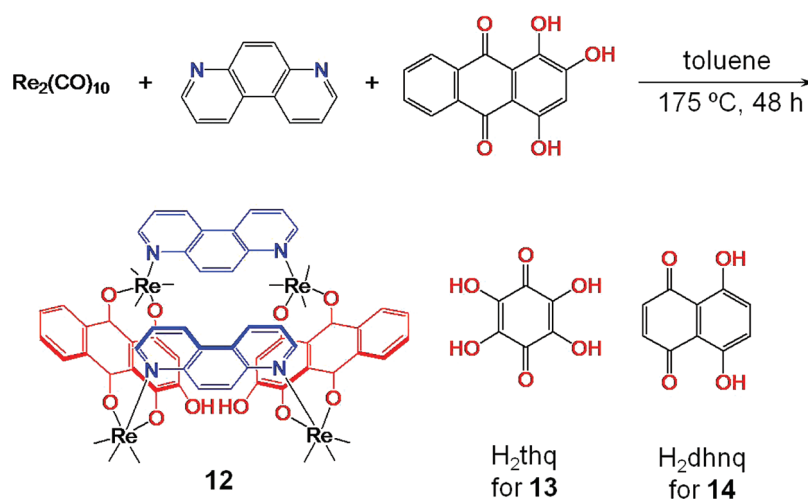
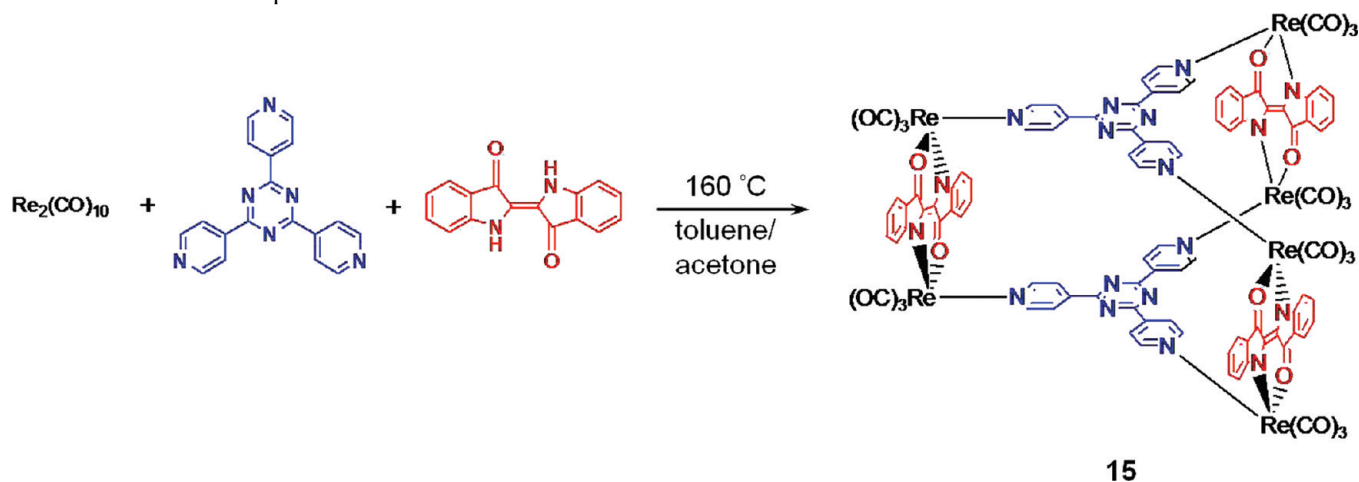


FIGURE 5. Molecular structure of **12**- C_7H_8 .

SCHEME 5. Synthetic Route for the Preparation of **12–14**



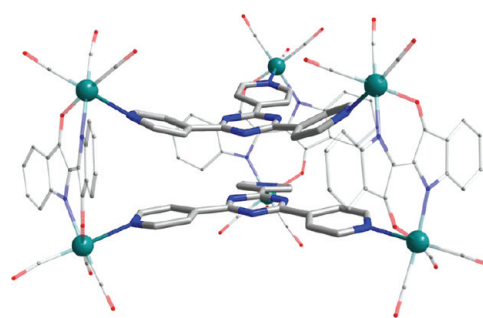
SCHEME 6. Route for the Preparation of Prism **15**

negative charge on the N atoms of H_6bpym^{2-} . From the analysis, it would be expected that BuOH would participate in the redox reaction, supplying electrons and protons followed by the transformation of the $Re_2(bpym^{2-})$ intermediate to the observed product **9** in high yield.

The electronic absorption spectra of **9** and **10** in CH_2Cl_2 display a ligand-centered (LC) transition at 230–351 nm and $d\pi(Re) \rightarrow \pi^*(pz \text{ for } \mathbf{9}, \text{ bpy for } \mathbf{10})$ transition at 563 and 466 nm for **9** and **10**, respectively. Complexes **9** and **10** show a broad and structureless MLCT at 685 and 605 nm, respectively. The cyclic voltammometric behavior of **9** and **10** shows that the H_6bpym^{2-} species is not reduced because of the presence of two additional electronegative nitrogen atoms.

As far as we are aware, the metallacalixarenes with $-OH$ functionalization are rare examples of a calix[4]arene analogue.³² Neutral metallacalixarenes [$\{(CO)_3Re\}_4(L)_2(4,7\text{-phen})_2\} \cdot 2C_7H_8$ (**12**, $L = 1,2,4\text{-trishydroxy-9,10-anthraquinone}$ (thaq); **13**, $L = \text{tetrahydroxy-1,4-quinone}$ (thq); **14**, $L = 5,8\text{-dihydroxy-1,4-naphthaquinone}$ (dhnq); 4,7-phen = 4,7-phenanthroline) with tunable size, cavity, color, and functionality, using the orthogonal-bonding approach, were achieved by the solvothermal reaction of $Re_2(CO)_{10}$, 4,7-phen, and the corresponding quinone ligands (Scheme 5).³³ The interesting structural features of **12**–**14** are (i) a one-step synthetic route with high yields, (ii) neutral species, (iii) single and rigid conformation, (iv) the presence of large hydrophobic and hydrophilic groups, (v) tunable size, cavity, color, and functionality, and (vi) efficient host for recognizing planar aromatic guests.

A single-crystal X-ray diffraction analysis shows that the 4,7-phen and quinone ligands in **12**–**14** are bent, giving the

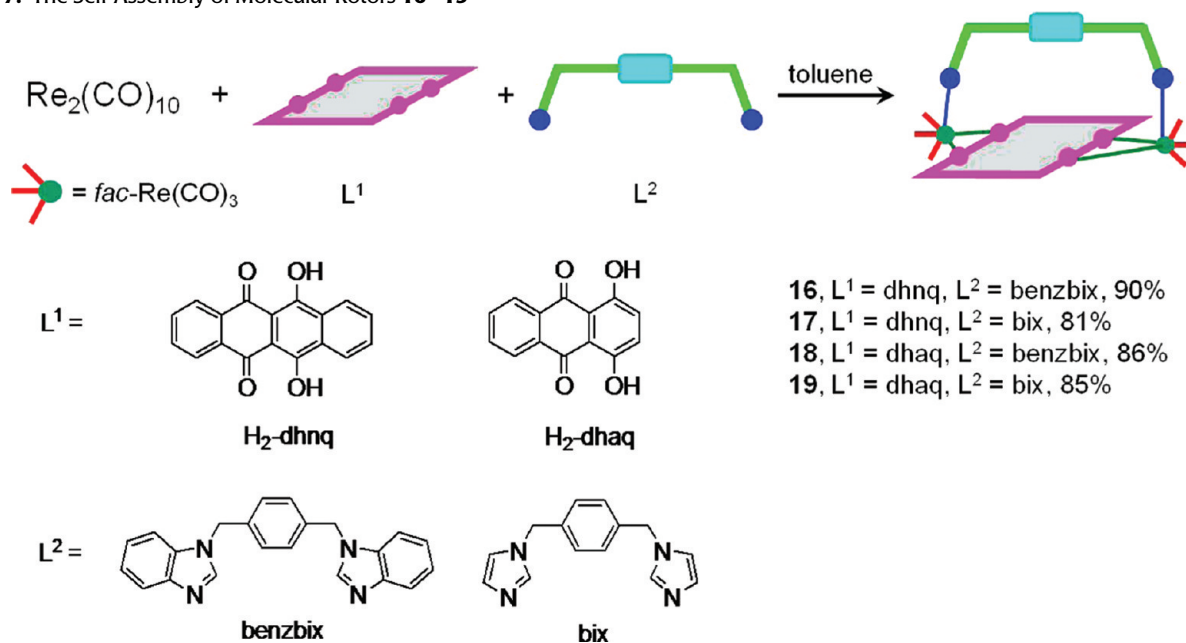
FIGURE 6. The molecular structure of **15**.

assembly a bowl shape, which can be described as metal calix[4]arenes, in which the Re corners and the two thaq ligands are analogous to methylene linkers and 1,3-arranged phenol moieties, respectively, and the 4,7-phen ligands mimic the 2,4-arranged arene blocks. A strong $\pi \cdots \pi$ stacking interaction between 4,7-phen and toluene is observed when one toluene guest molecule lies within the bowl (Figure 5).

The fluorescence quenching interaction between **13** and various planar aromatic guests such as naphthalene, anthracene, phenanthrene, and pyrene with 1:1 stoichiometry was evaluated, and the binding constant was determined to be 8.0×10^4 , 1.7×10^4 , 6.7×10^4 , and $8.4 \times 10^4 \text{ M}^{-1}$, respectively. In addition, a 1H NMR study also supported the host–guest interaction. Hence, it is believed that the complexation is accompanied by the presence of both $\pi-\pi$ and $CH \cdots \pi$ interactions between the host **13** and guests.

3. Molecular Cages

The design of triangular prismatic cages requires six building blocks, two angular tritopic subunits, and three linear

SCHEME 7. The Self-Assembly of Molecular Rotors **16**–**19**

connecting units. A number of cages based on Pd(II), Re(I), Ru(II), Ir(I), and Rh(I) metal centers with a tridentate ligand, $\text{tpt} = 2,4,6\text{-tri-}4\text{-pyridyl-}1,3,5\text{-triazine}$, and simple $\text{N,N}'$ - or O , O' -donors have been reported.^{34–37} In these $\text{M}_3(\text{tpt})$ -based triangular metalloprisms, π - π interaction of tpt is enhanced; in particular, its geometry is altered.

The orthogonal-bonding approach can be extended as an effective strategy for the construction of the neutral molecular cage $[\{(\text{CO})_3\text{Re}(\mu\text{-ind})\text{Re}(\text{CO})_3\}_3(\mu_3\text{-tpt})_2]$ (**15**) by reacting $\text{Re}_2(\text{CO})_{10}$ with tpt and indigo at 160 °C (Scheme 6).³⁸

An X-ray crystallographic study established that the six rhenium atoms define a triangular metalloprism with 11.56–13.56 Å trigonal edges and 6.38–6.48 Å cage heights (Figure 6). Interestingly, the two central face-to-face triazine rings from the two distinct tpt ligands are separated by a distance of 3.52 Å and exhibits a low C_1 symmetry, which is different from the high symmetry of D_{3h} or apparent D_{3h} in other tpt -based triangular metalloprisms.^{34–37}

UV–vis absorption spectra of **15** show a ligand-centered π - π^* transition in the high-energy region. The absorption bands at 335 and 410 nm can be attributed to $\text{Re} \rightarrow \text{indigo}$ and $\text{Re} \rightarrow \text{tpt}$ MLCT transitions, respectively. An emission from **15** was observed at 392 nm and is assigned to a π - π^* excited state of the indigo moiety with a quantum yield of 0.01 and a lifetime of 5.5 ns. The static fluorescence quenching of **15** was studied using nitroaromatics and the quenching constants ranged from 8.0×10^{10} to $3.2 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ with red shift from 392 to 397 nm. Significant differences in

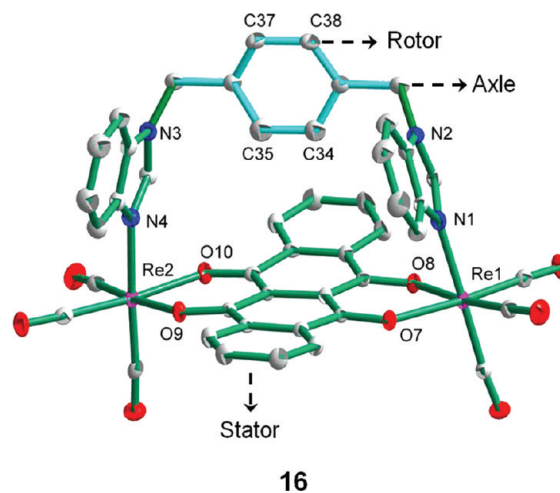


FIGURE 7. An ORTEP plot of molecular rotor **16**.

K_a values (2.0×10^2 to $4.2 \times 10^3 \text{ M}^{-1}$) were observed for nitrobenzene derivatives with a 1:1 binding stoichiometry.

4. Other Metallacycles

A binuclear metallacycle requires metal ions and ligands with convergent coordination sites and donor atoms, respectively, and is, therefore, the simplest oligometallic assembly. Their role in the assembly and structural and functional properties are briefly discussed below.

(a). Molecular Rotors. In an attempt to mimic the functions of biological molecular machines, one of the most challenging components is molecular rotors or swimmers

that can perform work and collectively induce controlled motion in much larger objects.³⁹ By introduction of an imidazole derivative into a bimetallic edge of the quinone motif and a Re precursor, using a one-pot orthogonal-bonding approach, neutral metallacyclic rotors **16**–**19** were synthesized in high yields (Scheme 7).⁴⁰ It is noteworthy that compounds **16**–**19** are remarkable examples, since the rotational motion is realized by the rotation of the *para*-phenylene rotor in the Re(I) metallacycle in solution with respect to the stator. Hence, these compounds can be considered as a prototype of altitudinal rotors.

Metallacycle **16** exhibits a dinuclear chair-shaped structure (Figure 7), as evidenced by a single-crystal X-ray diffraction analysis, and can be regarded as a molecular rotor, in which the dianionic dhnq unit is related to the stator, the *para*-xylene unit is related to the axle, and the *para*-phenylene group is related to the rotor.

A variable-temperature ¹H NMR study of **16** in acetone-*d*₆ revealed that, at low temperature, complete decoalescence of *para*-phenylene rotation was not observed. The proton signals of the benzimidazole units were shifted upon cooling or heating the sample, revealing that the benzimidazolyl units are flexible with a *syn/anti* conformational exchange/equilibrium process. However, at low temperature, the imidazolyl proton was shifted more downfield compared with the fused arene of the benzimidazolyl unit, since this proton is moving away from the shielding zone. Furthermore, swinging of the benzimidazole rope around the dhnq seems unlikely because of steric hindrance. Hence, metallacycle **16** is best depicted as a rotor.

(b). Flexible Metallacycles. The incorporation of flexible units into metallacycles offers several potential advantages, such as adaptive recognition properties and breathing ability in the solid state. However, flexible ligands with a limited number of conformations (Schemes 8 and 9) for constructing metallacycles are still scarce.

The selection and use of 1,4-bis(4-pyridyl)piperazine (bpp) not only as a flexible ligand but also as a semi-rigid moiety that can exist as a chair and twist-boat forms for constructing unusual metallacycles is rare. Under solvothermal conditions, metallacycles **20** and **21** were assembled by

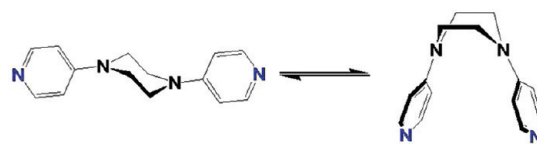
treating Re₂(CO)₁₀ with bpp and H₂dhnq or 2,2'-bis(benzimidazole) (H₂bbim), respectively (Scheme 10).⁴¹ Solution ¹H NMR spectrum of **20** revealed a boat or twist-boat conformation of the piperazine moiety.

X-ray crystallographic studies showed that complexes **20** and **21** adopt a dinuclear architecture, in which the bpp ligand bridges two Re(I) centers in a boat or twist-boat form, respectively (Figure 8), consistent with the NMR data. Because of the presence of shorter Re···Re distance (5.73 Å) in **21**, the bpp ligand adopts a bent conformation with strong π – π stacking interactions (3.23–4.67 Å) between the pyridyl moieties. The angles of N2–Re1–Re2 and N3–Re2–Re1 in **20** are 59.6° and 65.1°, respectively, giving rise to the formation of a regular triangle whereas the N1–Re1–Re2 and N2–Re2–Re1 angles in **21** are 75.0° and 76.2°, respectively, producing an isosceles triangle.

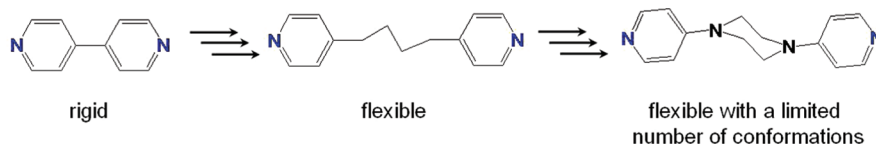
The rigidity-modulated conformation control of a flexible building unit by a rigid motif in the self-assembly of metallacycles is reported. Following a similar strategy as demonstrated in Scheme 10, compounds **22** and **23** were prepared by the reaction of a mixture of Re₂(CO)₁₀, α,α' -bis(benzimidazol-1-yl)-*o*-xylene (XyBim) and 2,2'-bisbenzimidazolyl (H₂-Bim) or 6,11-dihydroxy-5,12-naphthacenedione (H₂-dhnq) in toluene under solvothermal conditions.⁴²

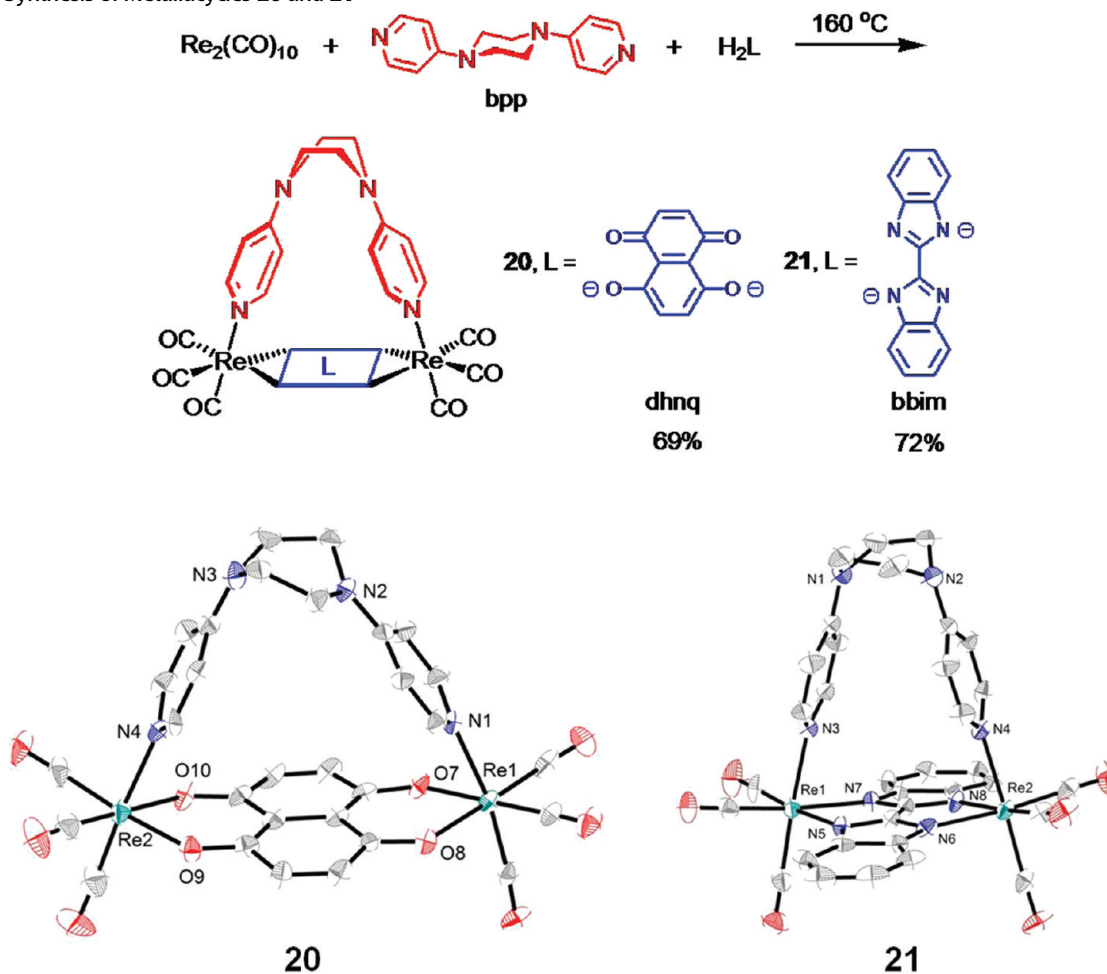
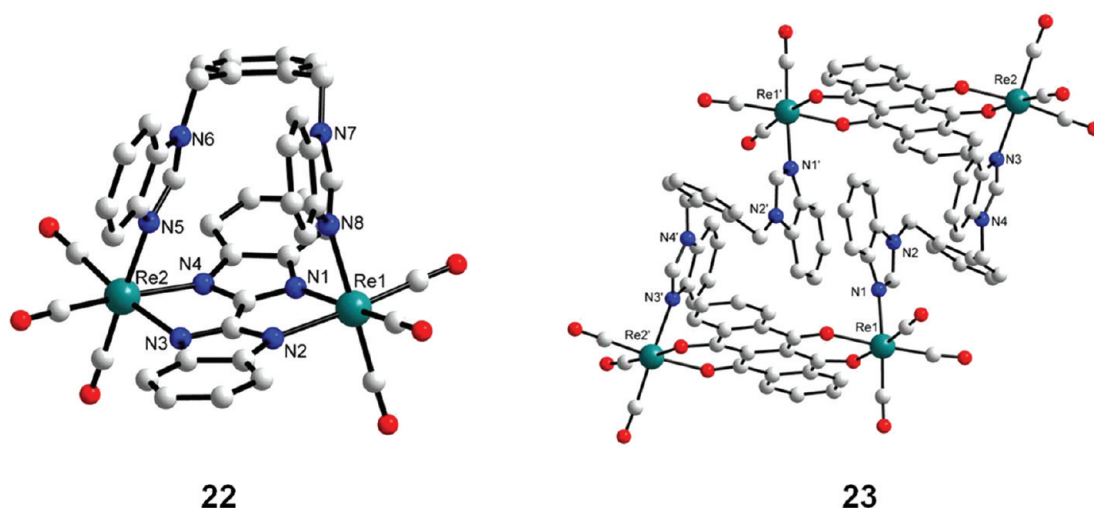
An X-ray analysis revealed that the coordination geometry around the Re centers is a distorted octahedral structure with a C₃N₃-donor or C₃NO₂-donor environment with Re–Re distances of 5.7 Å and 8.6 Å in **22** and **23**, respectively (Figure 9). The XyBim ligand in **22** possesses a *syn*-conformation mode, while both benzimidazole arms are on the same side, thereby leading to weak π – π stacking interactions (3.57–4.71 Å) through two face-to-face parallel benzimidazole rings. The XyBim ligand in **23** adopts an *anti*-conformation mode; two benzimidazole arms are located on two sides

SCHEME 9. Chair–Boat Form Transformation of the bpp Ligand



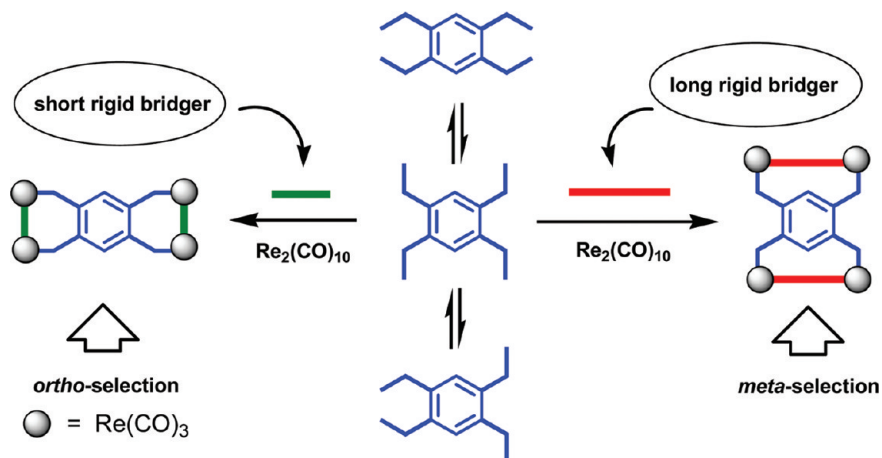
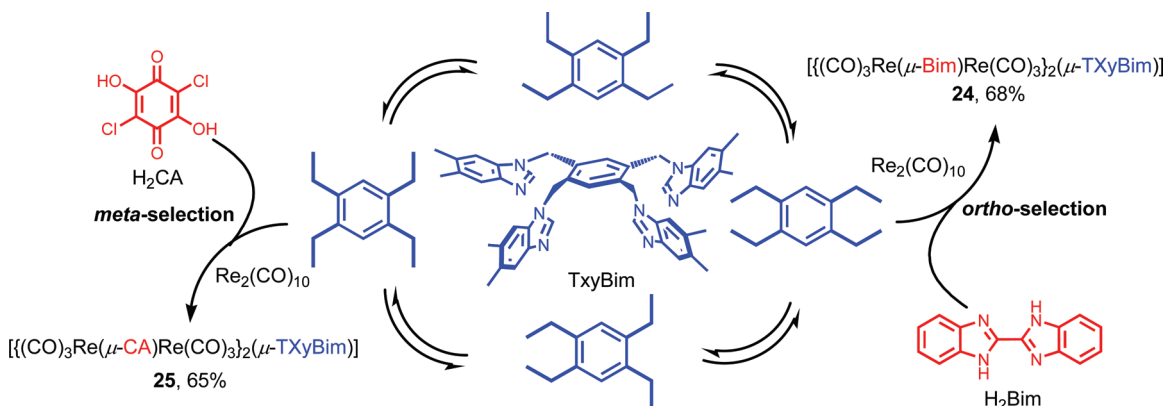
SCHEME 8. Development of a Flexible Pyridine-Based Ligand with a Limited Number of Conformations



SCHEME 10. Synthesis of Metallacycles **20** and **21**FIGURE 8. ORTEP diagrams of **20** and **21**.FIGURE 9. Ball and stick representation of the crystal structures of **22** and **23**.

and serve as a “Z-type” bridging unit, utilizing the benzimidazole-N atoms to bridge the bis-chelated dirhenium unit.

This structure is stabilized by extensive interligand $\pi-\pi$ stacking interactions.

SCHEME 11. Conformational Control of the Flexible Motif with Simultaneous Use of a Short or Long Rigid Bis(chelator), Tetratopic Flexible N-Donor, and *fac*-Re(CO)₃ Cores**SCHEME 12.** Self-Assembly of Metallacycles **24** and **25**

In another contribution from our laboratory, we reported that the rigid anionic linker responsible for determination of $M \cdots M$ separation allows for conformational control of the flexible motif with the simultaneous use of a short or long rigid bis(chelator), tetratopic flexible N-donors (1,2,4,5-tetrakis(5,6-dimethylbenzimidazol-1-ylmethyl)benzene, TxyBim), and *fac*-Re(CO)₃ cores during self-assembly (Scheme 11). Compounds **24** and **25** were assembled by reacting a mixture of Re₂(CO)₁₀, TxyBim, and H₂Bim or H₂CA in toluene under solvothermal conditions in a one-step process (Scheme 12).⁴³

The coordination geometry around the Re centers in **24** and **25** is described as a distorted octahedral shape with a C₃N₃⁻ and C₃NO₂⁻ donor environment, respectively, as evidenced by solid-state structures (Figure 10). The Re \cdots Re distance in **25** is 8.141 Å, representing ~ 2.9 Å longer than that found in **24**. The TxyBim ligand in **24** adopts a *syn,anti, syn,anti* conformation mode, with both *o*-benzimidazole

arms on the same side, but it acts as an *anti, syn, anti, syn* conformation mode with both *meta*-benzimidazole arms in **25** serving as two molecular clips. The phenylene of TxyBim in **24** is sandwiched within the cleft of two benzimidazolyls of Bim at distances ranging from 3.81 to 4.76 Å, suggesting weak π - π stacking interactions. The *m*-benzimidazolyls in **25** are orientated in a *head-to-head syn* conformation.

The electronic characteristics of the radical-anionic and dianionic states of quinonoid ligands in the forms of free and Re(I)-complexes have been described.⁴⁴ As depicted in Scheme 13, the dirhenium(I) metallacycles [Re(CO)₃]₂(μ -L)(μ -L')] (**26**, L = dhnq²⁻; **27**, L = dhaq²⁻; L' = 1,4-bis(5,6-dimethylbenzimidazol-1-ylmethyl)-naphthalene, *p*-NBimM) via the orthogonal-bonding approach were assembled.

An X-ray crystallographic analysis shows that the *p*-NBimM moiety in **26** and **27** is chelated as a molecular clip to bind the two *fac*-Re(CO)₃ cores in a *syn* conformation (Figure 11). Since the dihedral angle between the two

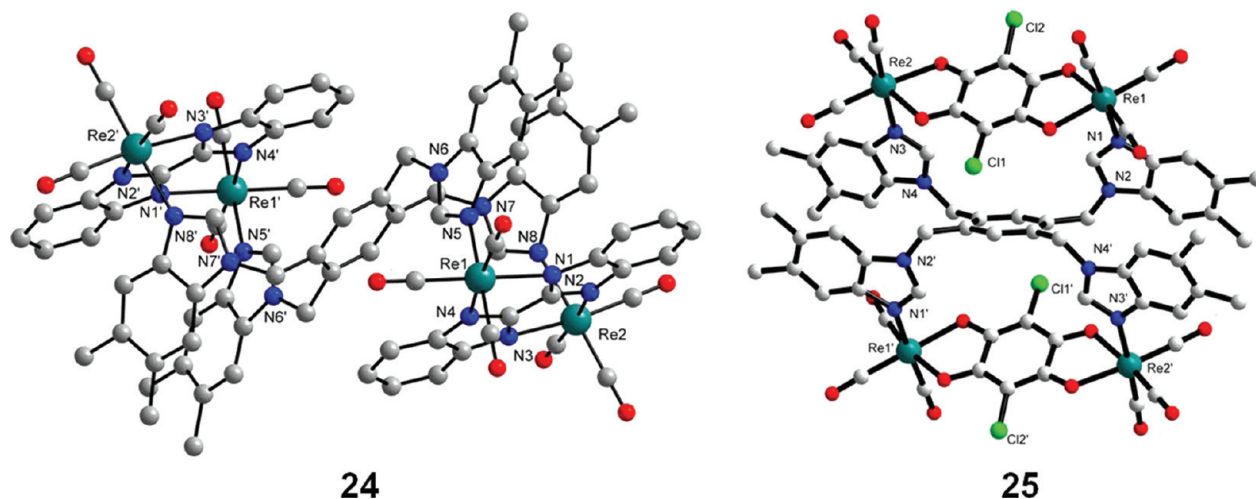
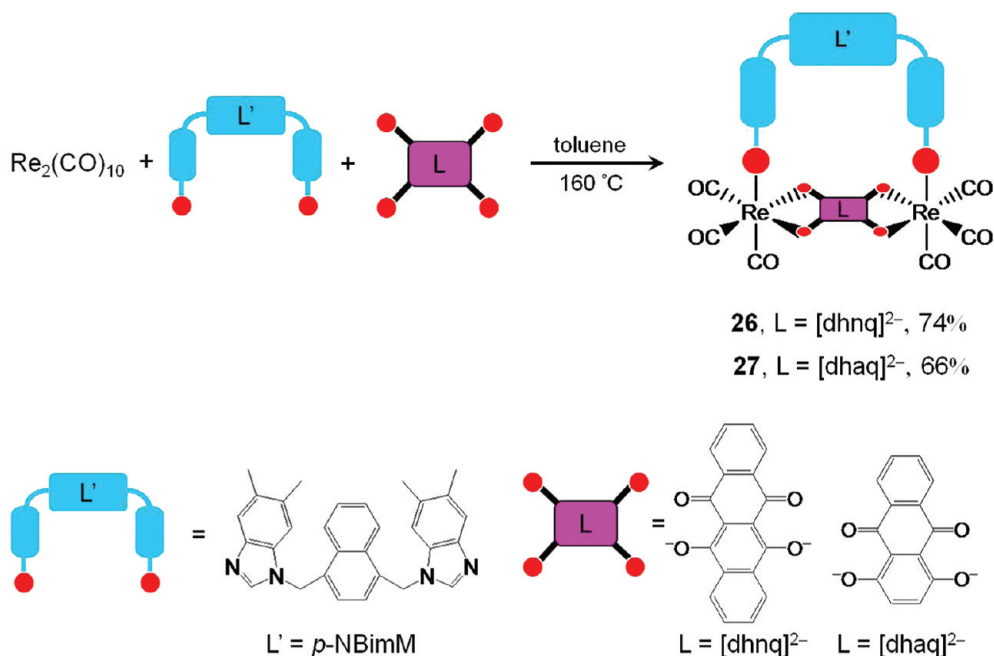


FIGURE 10. Ball and stick representation of the crystal structures of **24** and **25**.

SCHEME 13. Preparation of Metallacycles **26** and **27**



benzimidazole groups of the *p*-NBimM ligand in **26** is smaller than that of **27**, compound **26** appeared as a “closed” chair-like structure whereas **27** is an “opened up” metallacycle.

Electrochemical studies showed the large thermodynamic stability for **26**^{•-} and **27**^{•-}. UV–vis–NIR spectroelectrochemical study revealed a large blue-shift from the NIR to the visible range, indicating the subsequent addition of an electron followed by an increase in the π^* MO energy of the quinone ring upon the double reduction in **26** and **27**.

(c). Cyclometalated Metallacycles. Cyclometalation is a highly attractive and versatile synthetic process for generating organometallic complexes with wide potential applications.^{45,46}

Though the design of new compounds using ruthenium, osmium, rhodium, iridium, palladium and platinum have received the most attention, only a few reports have emerged regarding cyclometalated rhenium(I) complexes in which a carbon atom acts as the σ -donor atom.⁴⁷

When 2-(2-pyridyl)benzimidazole (HBim-C₅H₃N, PB) is incorporated as a new dianionic cyclometalating ligand and a flexible N–N bidentate ligands such as α' -bis(benzimidazol-1-yl)-*o*-xylene (*o*-XyBim), 1,3-bis(benzimidazole-1-ylmethyl)-2,4,6-trimethylbenzene (*m*-TXyBim), 2-bis(4-pyridyl)ethane (bpea), and 1,3-bis(4-pyridyl)propane (bppa) with rhenium precursor, a facile one-pot synthesis of

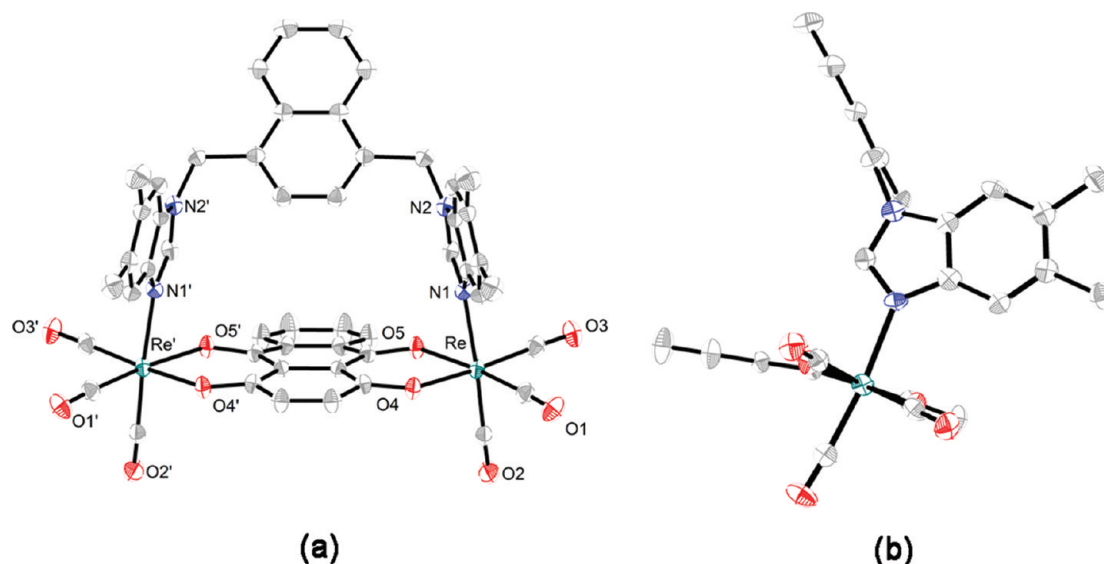
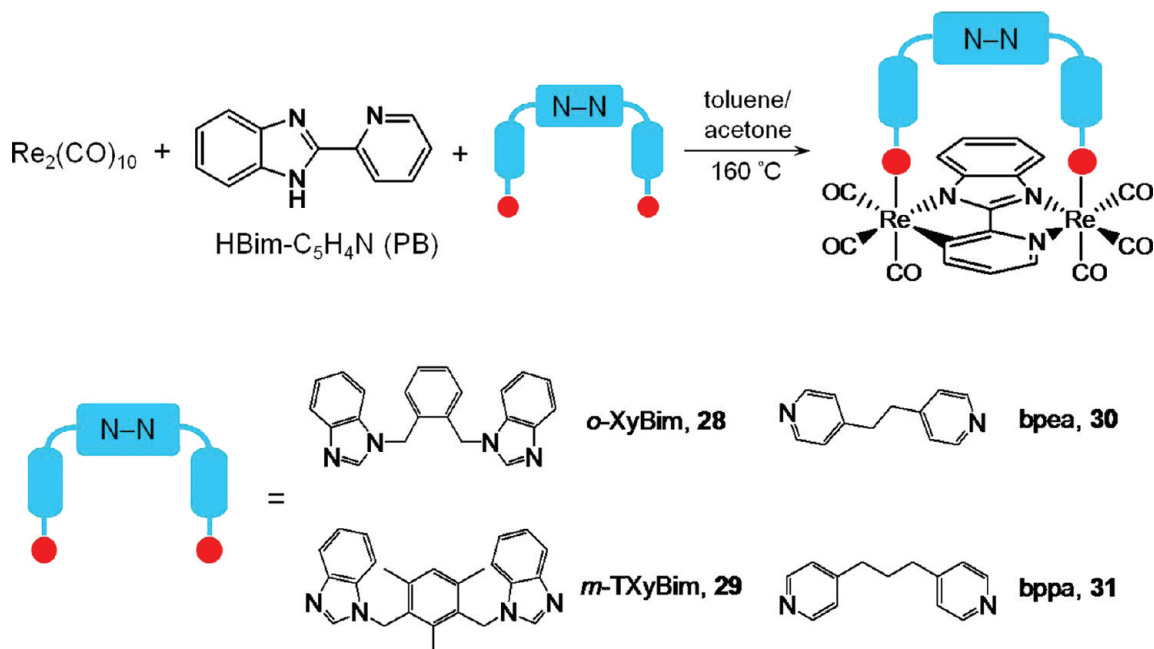


FIGURE 11. (a) Front view and (b) side view of the molecular structure of **27**.

SCHEME 14. Self-Assembly of the C–H Bond-Activated Metallacycles **28–31**



rhenium(I)-cyclometalated complexes $[\{\text{Re}(\text{CO})_3\}_2(\mu\text{-Bim-C}_5\text{H}_3\text{N})(\mu\text{-N-N})]$ (**28–31**) via an orthogonal-bonding approach was achieved in high yield (Scheme 14).⁴⁸ For a purpose of comparison, a non-C–H bond-activated analogue, **32**, was also synthesized using a bisbenzimidazole (H_2BiBzIm) instead of a PB ligand with *bppa* and a rhenium precursor.

Single-crystal X-ray diffraction analyses show that the rhenium(I) centers in **28–31** and **32** are organized in pairs by a $\text{Bim-C}_5\text{H}_3\text{N}$ ligand with CN_3 tetradentate and BiBzIm

ligands with N_4 tetradentate doubly chelating sites, respectively (Figure 12).

UV–vis absorption spectra of **28–31** in DMF show an intense absorption band at ~ 305 nm and a structureless band at 360–400 nm corresponding to $\pi\text{-}\pi^*$ and intraligand charge-transfer transitions of $\text{Bim-C}_5\text{H}_3\text{N}$ and $\mu\text{-N-N}$, and a spin-allowed MLCT ($\text{Re} \rightarrow \text{Bim-C}_5\text{H}_3\text{N}$) mixed with a LLCT ($\text{Bim-C}_5\text{H}_3\text{N} \rightarrow \mu\text{-N-N}$ ligand), respectively. Time-dependent density functional theory (TDDFT) approach also confirmed these assignments.

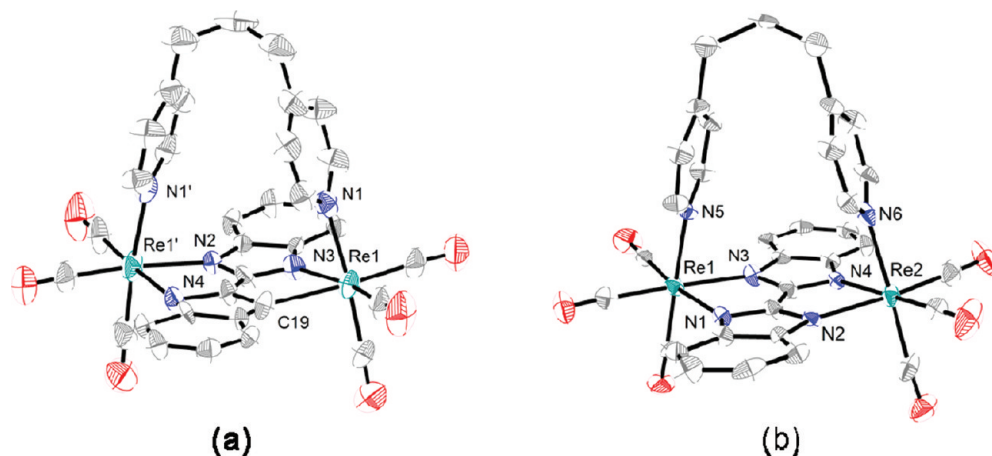
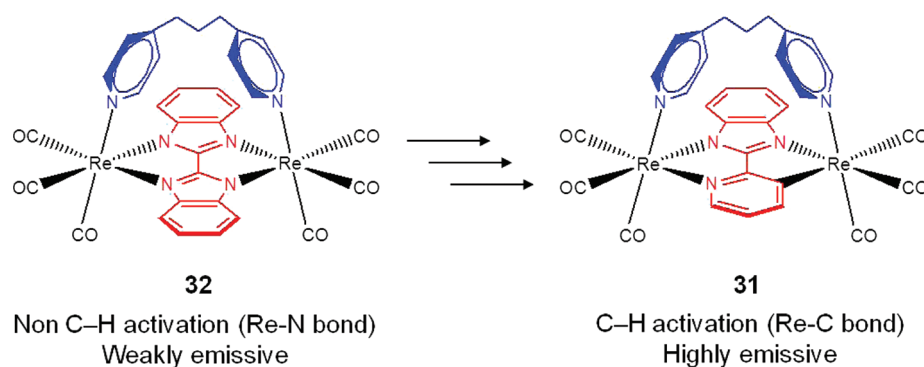


FIGURE 12. ORTEP plot of the (a) cyclometalated rhenium(I) complex **31** and (b) noncyclometalated complex **32**.

SCHEME 15. C–H Activation toward the Design of Highly Emissive Compound **31**



Metallacycles **28–31** exhibit an intense luminescence (Φ_{em} between 0.4 and 0.5) with a peak wavelength in the range of 523–527 nm and a lifetime of 4–8 μ s, indicating an admixture of 3 MLCT and 3 LLCT. Compound **32** showed a relatively weak ($\Phi_{em} = 0.01$), blue-shifted emission at 480 nm, for which the lifetime was determined to be $\tau_{obs} = 183$ ns, revealing ligand $\pi^*(\mu-N-N)$ to BiBzIm delocalized π transition. The computational results indicate that the contribution of 3 MLCT is appreciable, being $\sim 30\%$ and 3.7% for **31** and **32**, respectively. The relatively weaker σ -donor strength for the noncyclometalated compound **32** compared with **28–31** should reduce the MLCT characteristics as well as decrease the $d\pi-d\sigma^*$ gap thereby increasing the nonradiative decay rate and giving a short emission characteristics (Scheme 15).

5. Concluding Remarks

We developed a novel strategy that involves a one-step process, termed the orthogonal-bonding approach, to the production of neutral rectangles in high yields. This approach can completely switch the direction of the reaction

to form molecular rectangles without the formation of any squares and is a breakthrough in the development of molecular rectangles. Furthermore, by utilizing this approach, we found that it is not only useful for the preparation of rectangles but also for a wide variety of discrete neutral metallacycles, such as gondolas, rotors, triangles, cages, and boxes, with predesigned geometries in high yields. Most of them are luminescent in nature. The structures and excited state energies of the self-assembled supramolecular materials can be tuned by the judicious choice of ligands, such as flexible, conjugated, and cyclometalated ligands. We also emphasize that our self-assembled materials are capable of selectively binding neutral guests and metal ions. Depending on the size of the cavities, these structures can act as hosts for various guest molecules. This approach additionally may offer interesting possibilities for producing switchable systems, host–guest based sensors, light-harvesting assemblies, and molecular machines.

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BIOGRAPHICAL INFORMATION

Pounraj Thanasekaran received his Ph.D. in 1998 from Madurai Kamaraj University, India. In 1999–2001, he received a Research Associateship from Council of Scientific and Industrial Research, India. He worked as a Postdoctoral Fellow at the Institute of Chemistry, Academia Sinica, Taiwan, in Prof. Kuang-Lieh Lu's group (2001–2006) then in Prof. David M. Stanbury's group, Auburn University, AL, USA (2006–2007). He served as a Lecturer in the School of Chemistry, Madurai Kamaraj University (2007–2008) before moving to Prof. Lan-Chang Liang's laboratory, National Sun-Yat Sen University, Taiwan as a Postdoctoral Fellow in 2008–2009. Since 2009, he has again been working as a Postdoctoral Fellow with Prof. Kuang-Lieh Lu. His research interests include design and synthesis of supramolecular materials, photophysics, and host–guest chemistry.

Chung-Chou Lee received his Ph.D. degree in chemistry from National Taiwan University in 2005. Then he joined Prof. Kuang-Lieh Lu's group at the Institute of Chemistry, Academia Sinica, as a Postdoctoral Fellow. Currently, he is a Researcher at Industrial Technology Research Institute, Taiwan, where he focuses on high-throughput synthesis and analysis.

Kuang-Lieh Lu obtained his Ph.D. in 1989 from National Taiwan University. He is currently a Research Fellow in the Institute of Chemistry at Academia Sinica and Adjunct Professor at National Taiwan Normal University and National Central University. Current research interests include metallacycles, metal–organic materials, supramolecular chemistry and green chemistry. In the past few years, his research effort has been devoted primarily to the design of very efficient synthetic self-assembly strategies and to the understanding of the simplicity-to-complexity processes that occur in supramolecular systems.

FOOTNOTES

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