

Metallotweezers | Hot Paper |

 Discrete Supramolecular Stacks Based on Multinuclear Tweezer-Type Rhodium ComplexesBei-Bei Guo,^[a] Mohammad Azam,^[b] Saud I. AlResayes,^[b] Yue-Jian Lin,^[a] and Guo-Xin Jin^{*,[a]}*Dedicated to Professor Kazuyuki Tatsumi on the occasion of his 70th birthday*

Abstract: By taking advantage of self-complementary π - π stacking and CH- π interactions, a series of discrete quadruple stacks were constructed through the self-aggregation of U-shaped dirhodium metallotweezer complexes featuring various planar polyaromatic ligands. By altering the conjugate stacking strength and bridging ligands, assemblies with

a range of topologies were obtained, including a binuclear D-shaped macrocycle, tetranuclear open-ended cagelike frameworks, and duplex metallotweezer stacking structures. Furthermore, a rare stacking interaction resulting in selective C-H activation was observed during the self-assembly process of these elaborate architectures.

Introduction

Noncovalent intra- and intermolecular interactions occur frequently in programmed biological and chemical processes,^[1-4] such as protein folding, (bio)catalysis, and molecular recognition, and are a major research focus in the field of artificial supramolecular chemistry. These interactions are always weak but specific, and play significant roles in product assembly by controlling the ordered combination of building blocks. Based on this principle, numerous examples of this type of precise control over product assembly have been reported over the past few decades,^[5-7] such as the construction of molecular knots, links, shuttles, and stacked aromatics, and this has greatly extended the available libraries of programmed topological structures. In addition, important processes such as recognition, chemical transport, and catalysis have also been expressed in these structures. Therefore, the ability to utilize and modulate noncovalent interactions in a rational manner has been a significant goal in the design of supramolecular architectures.

In an effort to mimic complex biological processes, the synthesis of molecular machines with specific functionalities has attracted wide attention. Therein, molecular tweezers play a key role due to their interesting recognition properties, in

which their open cavities allow guest binding through a variety of noncovalent interactions, such as π - π stacking, hydrogen bonding, and electrostatic effects. The term "molecular tweezers" was introduced in 1978 by Whitlock and Chen, and such species are characterized by two identical flat arms in a *syn* conformation linked by a significantly rigid tether.^[4] The average separation between two arms of about 7 Å facilitates complexation with aromatic substrates through π - π interactions and endows the tweezers with diverse properties.


In addition to specific noncovalent interactions, metal-ligand coordination has also played a leading role in the programmed design of metallasupramolecules. These dynamic bonds provide the possibility of predefining a product assembly due to the often predictable coordination geometries of the applied metal units. However, whereas the majority of the reported tweezers feature purely organic structures,^[8,9] metallotweezer structures are limited.^[10,11] Nevertheless, metal-based tweezers have gradually attracted attention throughout the last two decades, mainly due to their mild and concise synthesis relative to traditional organic receptors.

Half-sandwich [Cp*M] (M = Ir, Rh)^[12,13] units have proven to be excellent building blocks for the construction of supramolecules. Although a variety of topological structures based on these units have been assembled by following well-established design principles, the preparation of molecular tweezers based on [Cp*M] fragments remains a gap in this research field. Furthermore, although we and others have demonstrated that products formed by C-H activation are usually unique assemblies and structurally stable due to the robust M-C bonds formed,^[14] the self-assembly of metallasupramolecules involving C-H activation has in general been ignored, has thus far resulted in structures with relatively conventional topologies, and hence is in need of expansion.

Herein, by taking advantage of controllable, selective C-H activation of conjugate proligands, a series of discrete quadruple

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