

# Directing Supramolecular Collaborations in Dimeric Macrocycles

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## Abstract

Supramolecular behavior is highly dependent on many factors, including complicated microenvironments and weak interactions. Herein, we describe tuning supramolecular architectures of rigid macrocycles by synergistic effects of their geometric configurations, sizes, and guests. Two paraphenylene-based macrocycles are anchored onto different positions in a triphenylene derivative, resulting in dimeric macrocycles with different shapes and configurations. Interestingly, these dimeric macrocycles show tunable supramolecular interactions with guests. This work expands the scope of the synthesis of novel rigid bismacrocycles and provides a new strategy to construct different supramolecular systems.

**Keywords:** Supramolecular chemistry; Geometric configuration; X-ray diffraction analysis; Non-covalent interactions

## Introduction

Fullerene is one of the most extensively studied carbon nanomaterials in recent decades due to its unique chemical and electrical properties. In particular, the encapsulation of fullerenes by some specific host molecules via  $\pi$ - $\pi$  interaction has attracted much attention because of their potential applications in the separation, solubilization, and chemical modification of fullerenes. Generally, an ideal host molecule should satisfy both the structural and electronic complementarity with spherical fullerenes. Thus electron-rich macrocyclic structures, such as azacrown ethers, calixarenes, tetrathiafulvalenes-based macrocycles, pillararenes and porphyrinylene nanohoops, have long been considered as promising hosts in fullerene-containing host-guest systems [1]. Their shape complementarity greatly improves the recognition abilities and selectivities toward fullerenes. Over the past decade, carbon-rich cycloparaphenylene macrocycles and their derivatives were reported as interesting host molecules in the study of  $\pi$ - $\pi$  interactions with C60 or other fullerenes. These macrocycles usually exhibit good  $\pi$ - $\pi$  interactions with fullerenes or their derivatives in a 1 : 1 ratio. It would be intriguing if one could manipulate the supramolecular characteristics of these macrocycles to construct novel supramolecular donor-acceptor-donor (D-A-D) systems, for example, two macrocycles cooperate to bind a fullerene molecule rather than the typical one-to-one complexing.

The hosting of fullerene molecules in the cavity is mainly influenced by the ring size, geometric configuration, microenvironment, functional groups, fullerene size, and even solvent. To date, previous studies showed that only modifying a single macrocycle cannot fully achieve the abovementioned goals. Recently, the development of cycloparaphenylene bismacrocycles enriches the family of fullerene-containing supramolecular systems with a high stoichiometry ratio and tunable cavity shapes. For example, Cong and coworkers employed a cyclooctatetrathiophene unit as the linker to build a figure-of-eight bismacrocycle whose adaptive cavities enable the formation of peanut-like 1 : 2 host-guest complexes with C60 or C70. Notably, these bismacrocycles often have two macrocycles with the same sizes, shapes, and supramolecular properties because there are no other aryl groups at the linker that can affect the microenvironment of the bismacrocycle. Based on this, we envision that the geometric configurations could be finely tuned when these macrocycles are formed with different microenvironments, resulting in different and interesting supramolecular properties.

Herein, we report the design and synthesis of two novel dimeric macrocycles 1a and 1b, in which two cycloparaphenylene macrocycles with tunable sizes are anchored onto a triphenylene derivative. Interestingly, 1a exhibits a very weak host ability and can only capture one C60 or C70 molecule to form 2 : 1 host-guest complexes by cooperating with another bismacrocycle. By changing the ring size, another bismacrocycle 1b can interact with three C60 molecules to construct a 2 : 3 host-guest complex, demonstrating the first 2 : 3 host-guest complex in the supramolecular chemistry of bismacrocycles [2].

## Molecular design and synthesis

To compare the effect of microenvironments on a host-guest system, it is important to rationally select the appropriate building blocks and synthesis strategy to construct a bismacrocycle with different geometric configurations. In this work, a triphenylene derivative, 1,4-bis(4-bromophenyl)-2,3-bis(4-tert-butylphenyl)-6,11-diiodotriphenylene, is used; it is a suitable precursor since these halogen groups can provide different reactive sites for subsequent macrocycle formations, whereas the peripheral 4-tert-butylphenyl groups can influence the geometrical environment of the macrocycle to which it is connected. A prior study showed that a cyclic fragment can selectively react with the iodine groups within this precursor to form a bifunctional macrocyclic structure [3]. Inspired by this report, we can choose different curved synthones to react with this triphenylene derivative via the Suzuki coupling reaction and aromatization reaction to give target bismacrocycles with different sizes.

## Physical characterizations

Supramolecular chemistry is a branch of chemistry that focuses on the study of non-covalent interactions between molecules and the formation of highly organized and functional structures. Dimeric macrocycles, which consist of two cyclic molecules joined together through non-covalent interactions, have attracted significant attention

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due to their unique properties and potential applications in various fields, including materials science, catalysis, and drug delivery. Physical characterization techniques play a crucial role in understanding and elucidating the nature of supramolecular interactions in dimeric macrocycles [4].

- **Nuclear magnetic resonance spectroscopy (NMR):** NMR spectroscopy is a powerful technique for investigating supramolecular interactions in dimeric macrocycles. Through NMR experiments, one can obtain information about the molecular structure, conformation, and dynamics of the dimeric macrocycles.

- **X-ray crystallography:** X-ray crystallography is a widely used technique for determining the three-dimensional structures of supramolecular complexes. By growing single crystals of the dimeric macrocycles and their complexes, and subjecting them to X-ray diffraction analysis, it is possible to obtain precise information about the arrangement and orientation of the molecules within the crystal lattice[5].

- **Mass spectrometry:** Mass spectrometry is a versatile technique that can provide valuable insights into the supramolecular interactions of dimeric macrocycles. Electrospray ionization mass spectrometry (ESI-MS) and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) are commonly used methods for analyzing the non-covalent complexes formed by dimeric macrocycles.

- **Circular dichroism spectroscopy (CD):** CD spectroscopy is a sensitive technique that can probe the chiral properties of dimeric macrocycles and their complexes. By measuring the differential absorption of left- and right-circularly polarized light, CD spectroscopy can provide information about the secondary structure and chirality of the macrocycles, as well as changes in their conformation upon binding to a partner molecule .

- **Isothermal titration calorimetry (ITC):** ITC is a thermodynamic technique that measures the heat released or absorbed during a binding event. By titrating a solution of dimeric macrocycles with their binding partners while monitoring the heat changes, one can determine the binding affinity, stoichiometry, and thermodynamic parameters of the interaction.

- **Scanning probe microscopy (SPM):** SPM techniques, such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM), can be employed to visualize and characterize the supramolecular assemblies formed by dimeric macrocycles.

Photophysical properties play a crucial role in understanding the behavior and applications of dimeric macrocycles in various fields such as optoelectronics, sensing, and light-harvesting systems [6]. These properties describe how the dimeric macrocycles interact with light and include absorption, emission, fluorescence quantum yield, lifetime, and energy transfer. In this discussion, we will explore some of the key photophysical properties exhibited by dimeric macrocycles [7-10].

- **Absorption:** The absorption spectrum of dimeric macrocycles provides information about the wavelengths of light that can be absorbed by the molecules . By measuring the absorption spectrum, one can determine the maximum absorption wavelength ( $\lambda_{max}$ ) and the molar absorption coefficient, which indicates the efficiency of light absorption.

- **Fluorescence:** Fluorescence is the emission of light by a

molecule after absorbing photons. Dimeric macrocycles can exhibit fluorescence when excited by light of appropriate wavelengths. The emission spectrum provides information about the wavelengths of light emitted by the macrocycles .

- **Fluorescence quantum yield:** The fluorescence quantum yield ( $\Phi_f$ ) is a measure of the efficiency of fluorescence emission. A high  $\Phi_f$  indicates a high efficiency of fluorescence emission. The quantum yield can be influenced by various factors, including the macrocycle's structural features, solvent polarity, and molecular interactions.

- **Lifetime:** The fluorescence lifetime is the average time that a molecule spends in the excited state before returning to the ground state. It is a valuable parameter for studying the photophysical behavior of dimeric macrocycles.

- **Energy transfer:** Dimeric macrocycles can undergo energy transfer processes, including Förster resonance energy transfer (FRET) and Dexter energy transfer, which involve the transfer of energy from an excited donor molecule to an acceptor molecule.

- **Photostability:** It is an important characteristic for applications that involve continuous or intense light exposure. Understanding the photostability of dimeric macrocycles is crucial for their use in optoelectronic devices and other light-driven technologies.

## Conclusion

Dimeric macrocycles are fascinating molecular systems that exhibit unique supramolecular interactions and photophysical properties. The design and synthesis of these macrocycles have opened up new avenues for applications in various fields such as optoelectronics, sensing, and light-harvesting systems. Overall, dimeric macrocycles represent a rich field of research with great potential for advancements in various disciplines. Continued exploration of their physical characterization and photophysical properties will undoubtedly contribute to the development of innovative materials and technologies with wide-ranging applications in the future.

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