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Synthesis of novel macrocycles carrying pincer-type ligands as future candidates for potential applications in size-selective, stereochemical and recyclable catalysts

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ABSTRACT

Macrocycles with ultra dense functionalities are very useful but are difficult to synthesize. In this study, we report six novel macrocycles bearing a pincer ligand alone or a combination of pincer-calixarenes, and pincer-fluorene moieties. Click chemistry was utilized to synthesize the desired macrocycles in good yields. These macrocycles were fully characterized using mass spectrometry (EI-MS, ESI-MS, and MALDI-TOF MS), and NMR spectroscopy. These macrocycles are under investigations as size-selective and recyclable catalysts for various chemical transformations.

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1. Introduction

Nature utilizes a verity of macrocycle such as hemoglobin [1], chlorophylls [2], vitamin B [3], cyclodextrins [4], cyclic peptides [5], and many cyclic natural product-based drugs [6] to fulfill life-sustainable functions. The synergistic effect of geometrical constraints and the delicate functional groups in macrocyclic enzymes facilitates both ultra-fast kinetics and high selectivity. Inspired by these naturally occurring macrocycles, intense research is underway to develop novel functional macrocycles for catalysis. For example, several classes of synthetic macrocycles including crown ethers [7,8], modified cyclodextrins [9,10], cucurbiturils [11,12], calixarenes [13,14], porphyrins [14,15], and pillararene [16,17] have been reported. However, less progress has been made in this field of macrocycle-based catalysis because of two challenges. The first of these issues involves thermodynamic control. Macrocycles are prepared by stitching together the termini of identical molecules (homocoupling) or different molecules (heterocoupling). The macrocycle formation is always accompanied by their linear analogs because a decrease in the entropy during macrocyclization occurs, and thus this process becomes thermodynamically unfavorable. The second challenge regards chemical compatibility. In the early days, C–C cross-coupling reactions such as Sonogashira and Negishi cross coupling [18], Heck reactions [19], Glaser cross coupling [20], and alkyne metathesis [21] reactions were used in the preparation of macrocycles. However, the synthetic conditions encountered during macrocycle synthesis did not readily accommodate the incorporation of ligands. [18]. As a consequence, additional protection and de-protection chemical reactions were required as well as extensive purification steps [22–24].

Because of its simplicity and friendly experimental conditions, "click" chemistry has been widely used since its discovery in 2001 [25]. "Click" chemistry, which is a azide–alkyne [2 + 3] cycloaddition reaction catalyzed by copper (CuAAC) [25], has significantly enhanced the fields of synthetic organic chemistry and materials sciences [26–30]. One of the key features of click chemistry is its tolerance for diverse functional groups necessary to synthesize macrocycles with diverse functional groups [31,32]. Also, copper-catalyzed Huisgen dipolar cycloaddition of a terminal alkyne and an azide is the most commonly version of click chemistry that yields a 1,4-disubstituted 1,2,3-triazole [32,33]. These triazole rings

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have been utilized for various applications in numerous fields, including catalysis [34–36], medicine [37–40], supramolecular chemistry [41,42], and material sciences [28,43].

Some early macrocycles prepared through click chemistry include macrocyclic polystyrene [32], crown ether-based macrocycles [44,45], secosteroids [46], and peptidomimetic [47]. Recently, click chemistry was used to prepare pyridine-based macrocycles, which bind strongly to Cu(I) and Ag(I) ions [48]. Currently, click chemistry is a commonly used strategy to efficiently prepare highly functional macrocycles [49,50].

In this study, we report the synthesis of six novel click macrocycles (Fig. 1). These macrocycles are functionalized with NNN type bisphenol based pincer ligands (macrocycles **4** and **5**), NNN type pincer-calixarenes (macrocycles **8**, **9**, and **10**), and an NNN type pincer-fluorene (macrocycle **13**). Pincer ligands are type of chelating ligands that bind via three coplanar sites to a metal. Pincers are widely used as catalysts, molecular sensors, and molecular switches [51,52]. However, the utilization of pincer macrocyclic ligands for catalysis has received very little attention and thus needs further investigation [53–55]. Meanwhile, calixarenes have

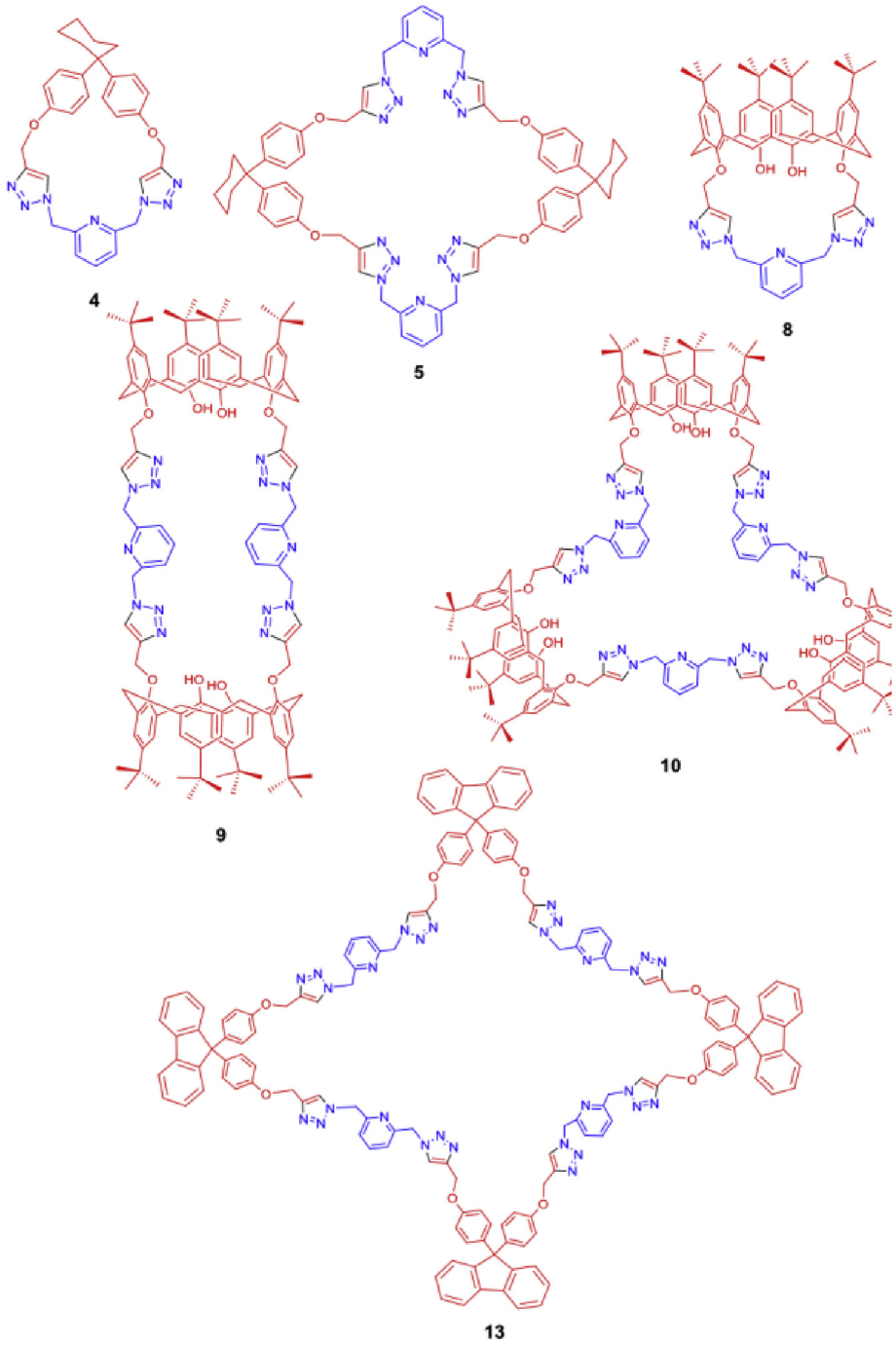

Fig. 1. The chemical structures of the macrocycles synthesized in this report using click chemistry. The red coloured shows part of the macrocycles derived from the alkyne precursors while the blue part in each macrocycle originated from the azide precursors. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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