Pillararenes Trimer for Self-Assembly

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Pillararenes trimer with particularly designed structural geometry and excellent capacity of recognizing guest molecules is a very efficient and attractive building block for the fabrication of advanced self-assembled materials. Pillararenes trimers could be prepared via both covalent and noncovalent bonds. The classic organic synthesis reactions such as click reaction, Palladium-catalyzed coupling reaction, amidation, esterification and aminolysis are employed to build covalent bonds and integrate three pieces of pillararenes subunits together into the "star-shaped" trimers and linear foldamers. Alternatively, pillararenes trimers could also be assembled in the form of host-guest inclusions and mechanically interlocked molecules via noncovalent interactions, and during those procedures, pillararenes units contribute the cavity for recognizing guest molecules and act as a "wheel" subunit, respectively. By fully utilizing the driving forces such as host-guest interactions, charge transfer, hydrophobic, hydrogen bonding, C—H···π and π—π stacking interactions, pillararenes trimers-based supramolecular self-assemblies provide a possibility in the construction of multi-dimensional materials such as vesicular and tubular aggregates, layered networks, as well as frameworks. Interestingly, those assembled materials exhibit interesting external stimuli responsiveness to *e.g.*, variable concentrations, changed pH values, different temperature, as well as the addition/removal of competition guests and ions. Thus, they could further be used for diverse applications such as detection, sorption and separation of significant multi-analytes including metal cations, anions and amino acids.

Keywords: Pillararenes trimers ; Supramolecular interactions ; Self-assembly ; Synthesis ; Applications

1. Introduction

Self-assembly has attracted much more attention in fundamental researches of material science and interesting applications to practical engineering areas [1], e.g., providing not only inspiring methodological strategy in processing, but also solid functional materials to balance morphologies and properties. Building ideal self-assembly begins from the molecular level [1], i.e., designing the structural geometry of molecules, modifying them with proper functional moieties, introducing and choosing proper inter/intramolecular interactions, as well as controlling the behavior of assembled molecules. Thus, designing appropriate building blocks from the molecular level is very significant in the construction of multi-dimensional self-assembly [1].

Macrocycles is a kind of particular cyclic oligomers with the hollow cavity for recognizing guest molecules [1], providing a possibility to introduce more functional and sensitive moieties for the fabrication of building blocks, as well as controllable self-assembly through supramolecular interactions such as host-guest interactions [1]. Pillararenes is a rising star in macrocycles [1], due to its high synthesis yield and convenient modifications. Different from other macrocycles, pillararenes composed by repeated phenol subunits possesses the electron-rich cavity and more rigid chemical structures, leading to its unique physiochemical properties such as planar chirality, as well as recognition towards neutral and electron-deficient guests. Interestingly, functionalized pillararenes monomers and dimers have been used as the building blocks to construct self-assemblies such as vesicular and polymeric architectures with small guest molecules as the template, but their morphologies are still limited [1].

2. Influence and application

To enlarge the family of assemblies with controllable multi-dimensional morphologies such as two-dimensional materials, pillararenes trimers have been designed and have attracted much more attentions recently. Different from pillararenes monomers and dimers, pillararenes trimers integrate three pieces of pillararenes units together via a "core" bridge, contribute a planar geometry as building blocks for advanced self-assemblies, and generate unique physiochemical properties such as aggregation-induced absorption [1]. We briefly summarized the recent progress about pillararenes trimers (**PT1–PT10** according to the timeline, Table 1 and Scheme 1), their synthesis method, supramolecular interactions with e.g., guest molecules (**G1–G9**, Scheme 2), driving forces for self-assembly, the fabrication of advanced self-

assembly, and current applications in the review [1]. We will try to find the issues and concerns in the development of pillararenes trimers and their advanced self-assembly. For example, pillararenes trimer could be prepared via both covalent and noncovalent bonds[2][3][4][5][6][7][8][9][10][11][12]]. The selection of the synthesis strategy and functional precursors (Scheme 3 and Table 1) will become significant because it will further affect the molecular geometry including "star-shaped" molecules and linear foldamers, as well as driving forces for next-step self-assembly, e.g., by utilizing unoccupied pillararenes cavities via host-guest interactions or functional groups from modifications via other supramolecular interactions. In addition, the precise control over the self-assembly is always the key point during practical applications. Thus, we will analyze the sensitive supramolecular interactions of pillararenes trimers-based self-assemblies in details [1].
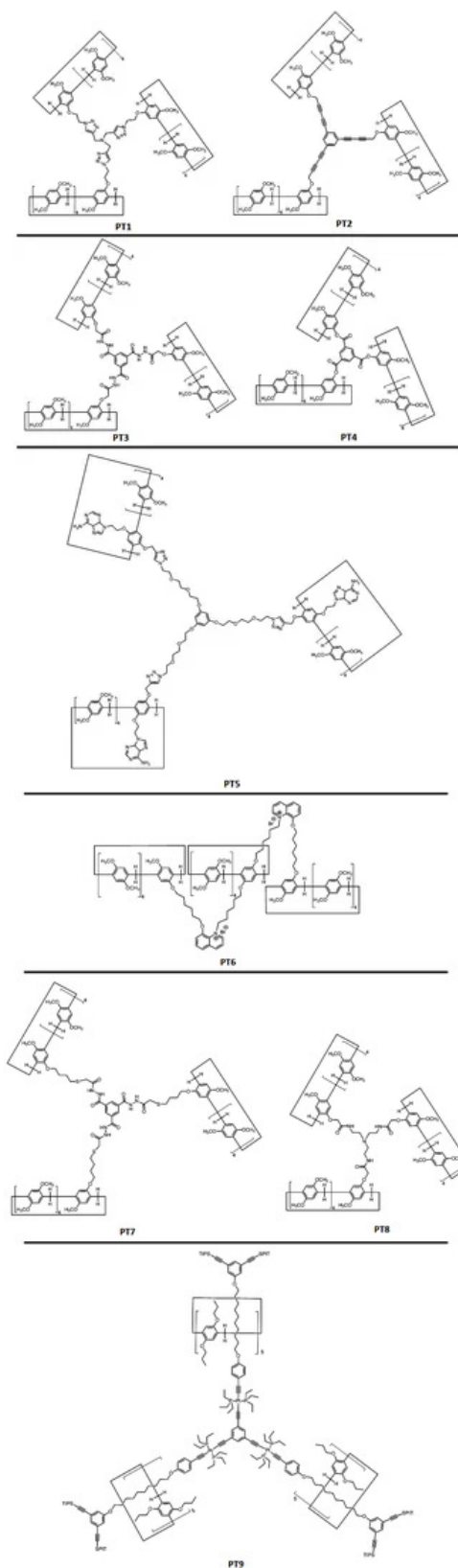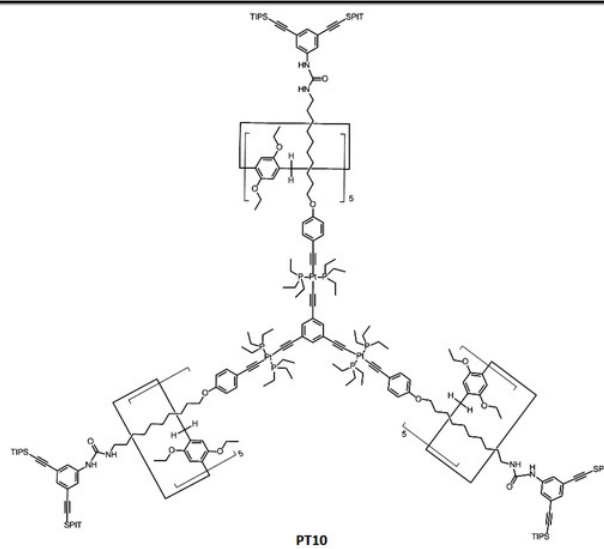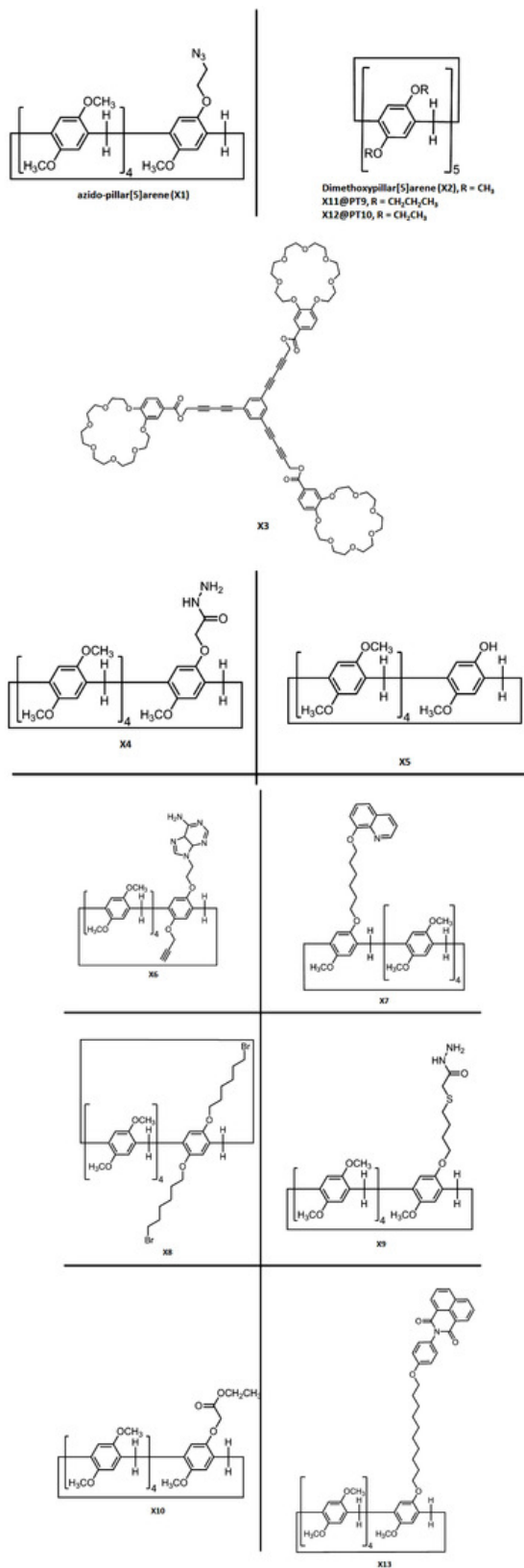
Scheme 1. Chemical structures of pillararenes trimers (**PT1**–**PT10**).
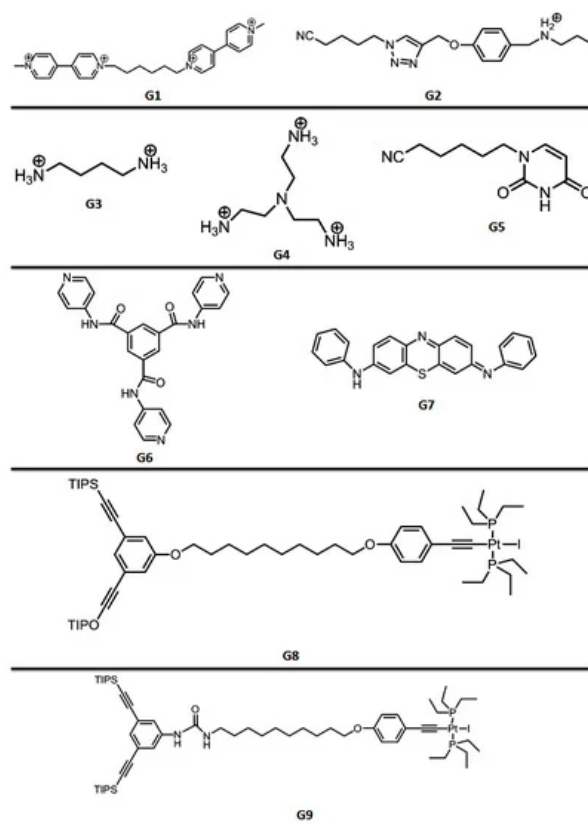
Scheme 2. Chemical structures of guest molecules (**G1**–**G9**).

Scheme 3. Chemical structures of precursors for the synthesis of pillararenes trimer, as well as other significant building blocks for the construction of assemblies (**X1**–**X13**).

Table 1. Comparison of various pillararenes trimer (**PT1**–**PT10**), guest molecules (**G1**–**G9**), precursors, and other significant building blocks (**X1**–**X13**) for self-assembly and external stimuli responsiveness.

Pillararenes Trimer	Guest	Precursor	Interactions	Assembly	External Stimuli	Applications	Ref
PT1	G1	X1	Host-guest interactions	Hollow spherical, tubular and layered assemblies	Concentration-dependent	Morphological control in comparison with X2	[2]
PT2	G2	-	Host-guest interactions	Supramolecular hyperbranched alternating polymers	K^+ (crown ether X3)	-	[3]

Pillararenes Trimer	Guest	Precursor	Interactions	Assembly	External Stimuli	Applications	Ref
PT3	-	X4	Hydrogen bonding, van der Waals forces, C–H⋯π and π–π stacking interactions	Supramolecular polymer	Cations	Fluorescence detection and separation of Hg^{2+}	[4]
PT4	G3/G4	X5	Host-guest interactions	Supramolecular polymer	-	-	[5]
PT5	G5	X6	Hydrogen bonding, π–π stacking and host-guest interactions	Hyperbranched supramolecular polymer	Heat and acid/base	-	[6]
PT6	-	X7/X8	π–π stacking interactions	(Metal ions coordinated) supramolecular organic frameworks	Fe^{3+}/Hg^{2+}/Cr^{3+} and CN^-/$H_2PO_4^-$	Fluorescence ultrasensitive detection	[7]
PT7	G6	X9	Hydrogen bonding, C–H⋯π and π–π stacking interactions	Supramolecular polymer network/supramolecular polymer framework	Metal cations/anions/amino acid	Fluorescence detection/adsorption capacity for cations	[8]
PT8	G7	X10	-	-	Competitive complexation with Anions	Fluorescence detection of F^-/AcO^-/$H_2PO_4^-$	[9]
PT9	G8	X11	Mechanical interlocked molecule	Dendrimer	-	-	[10]
PT10	G9	X12	Mechanical interlocked molecule	Dendrimer	Dimethylsulfoxide and acetate anion	-	[11]
X13⊃G6	G6	X13	Hydrogen bonding, π–π stacking and host-guest interactions	Supramolecular polymer networks/gel	Heat/cooling, pH, competitive guests and mechanical	Dye sorption, ultrasensitive detection and separation of Fe^{3+}	[12]

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