Pillar[*n*]arene-Based Supramolecular Polymers

Supramolecular chemistry enables the manipulation of functional components on a molecular scale, facilitating a "bottom-up" approach to govern the sizes and structures of supramolecular materials. Using dynamic non-covalent interactions, supramolecular polymers can create materials with reversible and degradable characteristics and the abilities to self-heal and respond to external stimuli. Pillar[*n*]arene represents a novel class of macrocyclic hosts, emerging after cyclodextrins, crown ethers, calixarenes, and cucurbiturils. Its significance lies in its distinctive structure, comparing an electron-rich cavity and two finely adjustable rims, which has sparked considerable interest.

1. Introduction

Supramolecular chemistry, often called "chemistry beyond the molecule", centers on non-covalent interactions such as hydrogen bonding, host–guest recognition, metal coordination, π–π interaction, cation–π interaction, electrostatic binding, salt bridge, halogen bonding, and so on [1][2]. Self-assembly, a practical technique for designing and controlling materials at the nanoscale, has emerged as a powerful synthetic tool, offering control over attributes like shape, size, geometry, topology, and morphology. Developing advanced self-assembled systems through functional building blocks and "weak" intermolecular and intramolecular interactions has garnered increasing attention since 2005.

Generally, supramolecular polymers represent a fusion of supramolecular chemistry and polymer chemistry, wherein small molecules or polymers are joined through non-covalent interactions creating assemblies with defined structures or functions [3][4]. Diverse units and architectural elements can come together through supramolecular interactions to create supramolecular polymers endowed with unique functionalities. Expanding the range of new supramolecular interactions promises to enhance both the structures and the applications of these supramolecular polymers [5]. Moreover, the process of creating inclusions based on supramolecular interactions can be dynamically regulated by external stimuli, enabling the fabrication of controllable and responsive supramolecular materials with specifically desired characteristics [6]. To date, supramolecular polymer materials have found applications across a diverse range of fields.

In many supramolecular polymer structures, macrocyclic host molecules possess appealing structural attributes, encompassing a hydrophobic cavity, sites for ion binding, versatile yet precisely defined conformations, synthetic adaptability, and adjustable functionality [7][8]. Macrocyclic molecules are used in an extremely wide range of applications, including molecular recognition, analyte detection, drug release, self-healing materials, and artificial nanochannels. Chemical structures of macrocyclic supramolecular polymers can be classified into five types (Scheme 1).
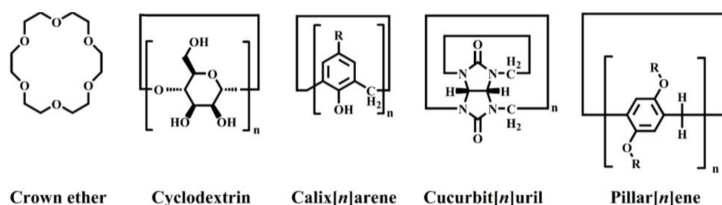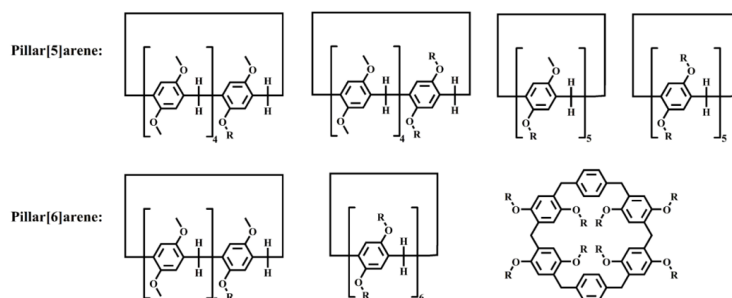

Scheme 1. Molecular structures of five different macrocyclic hosts.

Pillar[*n*]arene represents a next-generation macrocyclic molecule characterized by its robust complexation capabilities based on supramolecular interactions, which shows outstanding dynamic and modular performance attributes [9][10], especially in sensing [11][12] and catalytic activity [13][14]. Pillar[*n*]arene was first synthesized by Ogoshi in 2008. Once this unique structure had been discovered, it quickly became a research hotspot [15][16][17][18][19][20][21].

The structures and properties of pillar[*n*]arene are quite different from previously reported macrocyclic molecules: (i) Compared with crown ether and calixarene, pillar[*n*]arene has a highly symmetrical rigid structure with hydrophobic

cavities at the top and bottom edges. The adjustment of cavity size also has a higher degree of freedom, which shows stronger abilities to identify guests and incorporate catalytic units. (ii) Pillar[*n*]arene has good solubility in organic solvents, which is unique in the main macrocyclic molecules with cavities of the same size. (iii) Compared with cucurbituril, the benzene ring of pillar[*n*]arene is more easily functionalized by different substituents, which can regulate the host–guest binding characteristics more effectively. As a result, a large number of derivatives with unique properties have been obtained. (iv) Pillar[*n*]arene can be an amphiphilic molecule with hydrophobic and hydrophilic groups. A structure with such characteristics can form self-assembly structures in both water and oil phases, which has potential applications in controlled release, gene transfer, photoelectric materials, etc. (v) Pillar[*n*]arene can respond to many external stimuli, including temperature, pH, redox, enzyme, etc., especially light stimulation. These stimuli are easy to operate and can be utilized in a non-invasive and lower-cost manner. This is also one of the advantages of pillar[*n*]arene in sensing compared with other macrocyclic structures.

At present, the mainstream work of pillar[*n*]arenes is focused on prominent pillar[5]arenes and pillar[6]arenes, as shown in Scheme 2. The most commonly studied structure was pillar[5]arenes with a cavity size of approximately 4.7 Å and an average bond angle of 111.3°. The structures of pillar[*n*]arenes of other sizes have not been systematically studied. The production yields of high-level pillar[*n*]arenes (where *n* is equal to or greater than 6) typically remain below 1%, resulting in their infrequent utilization in subsequent investigations.
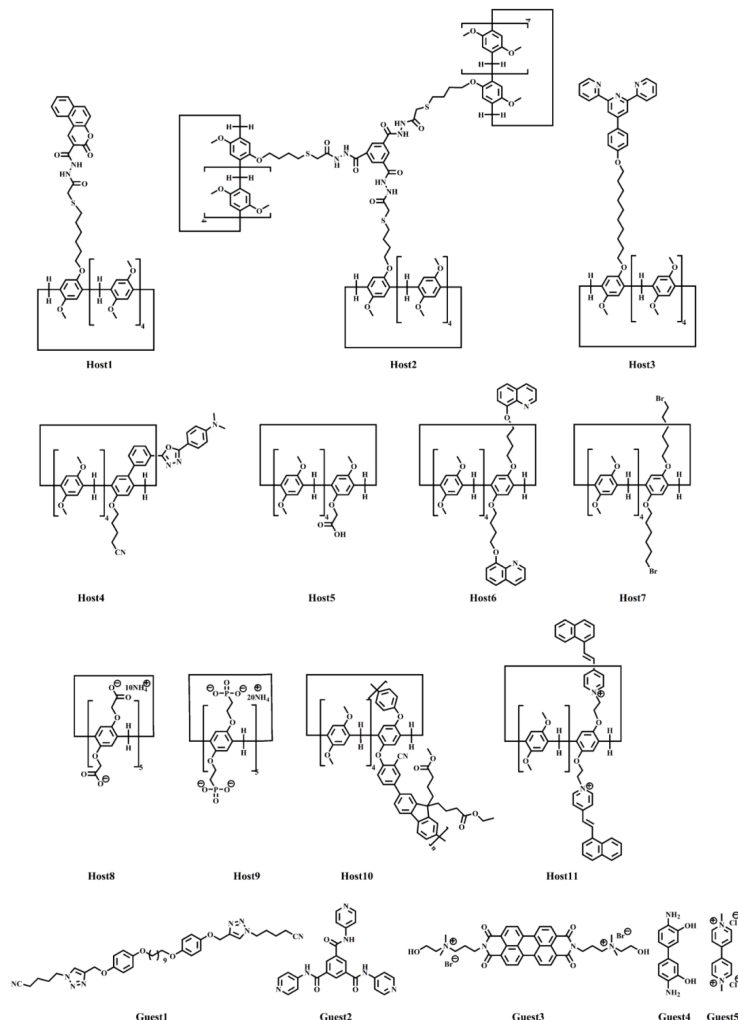

Scheme 2. Typical molecular structures of pillar[*n*]arenes. R represents different functional groups.

The electron-rich cavities of pillar[*n*]arene can form complexes with various guest molecules exhibiting neutral architectures or positive charges ascribed to supramolecular interactions. Guest molecules consisting of long carbon chains generally require cyanide, bromine, or quaternary ammonium salt as the end groups for host–guest identifications. According to the role of pillar[*n*]arenes in the construction of polymer materials, pillar[*n*]arene-based supramolecular polymers (PSPs) are mainly classified into two categories: (i) Pillar[*n*]arene firstly generates complexes with other guests, and such complexes are further assembled to form one-dimensional, two-dimensional, and three-dimensional spatial structures through the effects of non-covalent bonding such as hydrogen bonding, metal–ligand bonding, and π–π stacking [22][23][24][25]; (ii) Pillar[*n*]arene is treated as a kind of functional unit and introduced into the classical polymer substrates through covalent bonding, host–guest interactions, and other non-covalent dynamic interactions [26][27]. Based on the definition of PSPs, the PSP materials are unique in the following three points compared with the classical covalent macromolecules. Firstly, the main mechanism of supramolecular polymer formations is self-assembly. Secondly, the supramolecular polymers are able to introduce a variety of groups through host–guest recognitions or other weak interaction forces. Thirdly, pillar[*n*]arene-based molecules can self-assemble into chiral supramolecular polymers [28][29][30][31][32]. The constructed supramolecular polymers are a type of tunable material with features such as structural and mechanical integrity, good processability and recyclability, stimuli-responsiveness, self-healing, and shape memory, which holds outstanding advantages over classical covalent macromolecule polymers. In conclusion, PSPs not only inherit numerous advantages of conventional covalent polymers but also offer distinct characteristics [33].

2. Applications of PSPs

2.1. Fluorescence Sensor

As a novel sensing approach, supramolecular sensors have gained significant attention for their remarkable affinity towards a wide range of analytes. Pillararenes and their derivatives, with macrocyclic cavities, exhibit robust recognition capacities based on supramolecular interactions, particularly for ions and biomolecules, making them a focal point in this burgeoning field. Structure modifications can be achieved using various methods, including thermal responsiveness [34][35][36], electrochemical responsiveness [37][38][39], redox reactivity [40], and the incorporation of fluorescent [41][42][43][44][45][46][47][48][49] and other functional units [50][51][52][53][54][55][56][57][58]. The chemical structures of pillar[*n*]arenes and guest molecules are listed in Scheme 3.

Scheme 3. Molecular structures of pillar[*n*]arenes and guest molecules.

Among the numerous response mechanisms available, fluorescence-based sensors have become notable due to their simple synthesis, real-time analysis, high temporal and spatial resolution, reversibility, and exceptional selectivity and limit of detection (LOD) towards analytes [59][60][61][62][63].

PSPs can capture specific analytes, leading to observable fluorescence signals that manifest as quenching, fluorescence enhancement, or shifts in response to energy transfer, charge transfer, electron transfer, and strong coordination interactions. Functionalized pillar[*n*]arene holds promising potential for use and advancement in fluorescence sensors. These systems respond to a broad spectrum of potential analytes, encompassing metal cations, anions, drugs, pesticides, and other biomolecules.

Metal ions and amino acids are essential components within the fields of chemistry, biology, and the environment. The selective identification and testing of specific analytes and the isolation of toxicity are critical endeavors. In addressing these challenges, numerous research teams have designed and synthesized supramolecular polymers featuring diverse morphologies, including cross-linked networks and brush architectures. Detecting and separating hazardous metal ions like Fe^{3+} are crucial in environmental protection and healthcare.

In 2023, Li et al. [64] introduced a stimuli-responsive supramolecular polymer network to address this challenge. The pillar[5]arene derivative **Host1** engaged in supramolecular interactions with **Guest1**. This innovative configuration displayed impressive fluorescence characteristics attributed to the Aggregation-Induced Emission (AIE) effect and demonstrated remarkable ion-sensing capabilities in both solutions and solid states. Supramolecular polymers have the potential to undergo a transition into supramolecular gels under specific conditions. When the polymer is concentrated, it forms a polymer gel that responds to changes in temperature, mechanical force, and the competitive agent. This xerogel effectively removes Fe^{3+} from water. Additionally, a fluorescence test kit utilizing an ion-responsive film can be conveniently employed for detecting Fe^{3+}.

While it is known that AIE materials based on the supramolecular organic frameworks (SOFs) possess the ability to adjust emission, it is worth noting that there are relatively few reports on stimuli-responsive soft materials with the capacity for tunable AIE. Lin et al. [65] developed an AIE supramolecular organic framework gel (SOF-TPN-G) to detect and separate

various metal ions. This innovative material allows for recognizing multiple metal ions through the changes in fluorescent signals. **Host2** and **Guest2** join together to create supramolecular polymer networks (SPNs). TPSN serves as the π–π interactions, C−H···π interactions, and inclusion interactions. The thioacetylhydrazine moiety functions as the binding site for hydrogen bonding and coordination. The introduction of certain ions into SOF-TPN-G led to the creation of numerous metallogels exhibiting multicolor fluorescence. Leveraging these gels, an eight-unit sensor was successfully developed, with some units achieving an ultrasensitive performance. The xerogel form of SOF-TPN-G proved highly effective in adsorbing multiple metal ions. These gel materials have significant potential for applications in detection and separation processes.

Recent reports indicate that the neutral **Guest1**, featuring a cyano site and a triazole site, has proven to be an efficient guest molecule for **Host3** in supramolecular interactions. Inspired by the stable coordination compounds formed by terpyridyl groups and zinc ions, Yao et al. [66] designed a high molecular weight and fluorescent supramolecular polymer with a cross-linked network (**Figure 1**). This polymer was created through the principles of molecular recognition and metal coordination involving pillararene. Three-dimensional networks were formed through the entanglement of the supramolecular bundles, and phase transitions were achieved by alternating heating and cooling. The polymer displayed concentration-dependent fluorescence and was responsive to basic stimuli. A thin film was subsequently prepared, which is a convenient test kit for detecting OH⁻ anions.
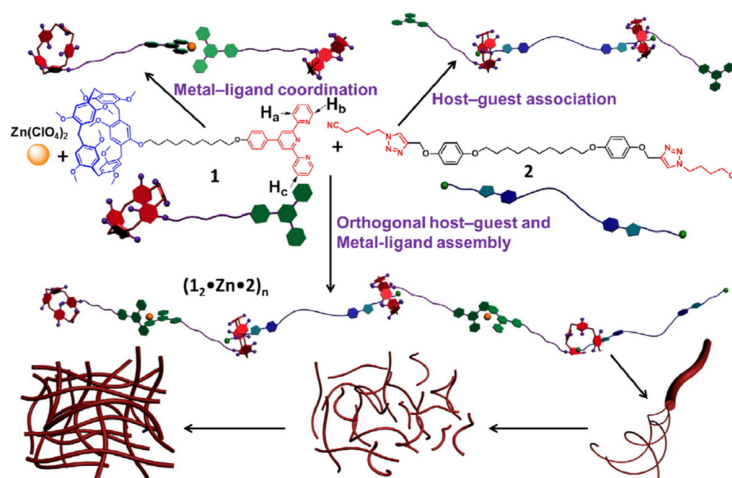

Figure 1. Representation for the formation of a fluorescent supramolecular polymer Co-P[5]Flu constructed by pillar[5]arene-based molecular recognition and zinc ion coordination.

In recent years, 1,3,4-oxadiazole (OXD) derivatives have found widespread utility in various domains owing to their exceptional photoluminescent quantum yield and chemical stability.

In collaboration with Zhang and his research team, Han [67] developed a supramolecular brush polymer named Poly(P5-OXD) through the self-assembly of **Host4**, featuring a 1,3,4-oxadiazole unit and a cyanobutoxy group. This polymer exhibited responsiveness to Cu^{2+} ions, resulting in an ON-OFF fluorescent switch. Upon adding Cu^{2+}, the supramolecular brush polymers displayed altered structural characteristics, as evidenced by fluorescence quenching, suggesting the potential transformation into cross-linked supramolecular networks.

Over the past decade, AIE has grown significantly across numerous domains. The collaboration between supramolecular materials and coordination chemistry holds immense potential to enhance the rapid advancement of multifunctional materials further. Creating fluorescent coordination polymers incorporating supramolecular macrocyclic rings is a novel and complex research area. In this context, pillarenes are regarded as organic linkers due to their inherent porous properties. In 2018, Wu and Yang [68] developed a fluorescent coordination polymer named CP5-PCP. This polymer featured dicarboxylic acid-containing copillar[5]arene (**Host5**) as the organic linker and Cr^{3+} as the nodes. This sophisticated fluorescent material found applications in detecting Fe^{3+}, acetone, and nitrophenols. The creation of this synthetic material has significantly contributed to the advancement of both supramolecular materials and coordination chemistry.

Recently, there has been a growing focus on ultrasensitive response materials because of their remarkable sensitivity to target substances. Furthermore, the ability to detect exceedingly low concentrations of targeting analytes in environmental or biological systems holds significant importance. Fe^{3+} is the most prevalent and extensively used metal ion in living organisms, ranking among the most critical transition metal ions. Nonetheless, a deficiency and an excess of Fe^{3+} can lead to severe biological disorders and disruptions in normal bodily functions, resulting in diseases. Fluoride ions (F⁻)

naturally occur in the environment and are present in the human body. However, excessive fluoride levels lead to environmental contamination and pose health risks, including kidney problems, acute stomach issues, and conditions like dental and skeletal fluorosis. Hence, there is a pressing need to devise novel and straightforward ultrasensitive methods for detecting Fe^{3+} and F^- ions. Zhang et al. [69] significantly addressed this challenge by successfully developing a supramolecular organic framework gel PQPA. They achieved this by utilizing bilateral 8-hydroxyquinoline-modified pillar[5]arene (**Host6**) and bilateral bromohexyl-functionalized pillar[5]arene (**Host7**) through supramolecular interaction binding. The LOD achieved by PQPA for Fe^{3+} was an impressive 0.102 nM, highlighting this gel's selective and ultrasensitive properties. Notably, PQPA proved effective for the detection of Fe^{3+} in real-life samples. Simultaneously, by introducing Fe^{3+} into PQPA gel, a non-fluorescent Fe^{3+} coordination metal gel, PQPA-Fe, can be created. This gel exhibited a "turn-on" fluorescent response to F^- due to competitive coordination. The LOD for F^- achieved by PQPA-Fe was 9.79 nM. Furthermore, the PQPA xerogel demonstrated the ability to efficiently remove Fe^{3+} at lower concentrations with a high adsorption rate.

Organic solvents are undesirable for ion detection in biological and environmental systems. Consequently, there is significant importance in developing water-soluble derivatives that exhibit exceptional detection capabilities in aqueous solutions.

The sensitivity of perylene diimide derivatives was constrained due to their inherent aggregation-induced quenching (ACQ) properties in aqueous environments. In 2017, Yin et al. [70] introduced a supramolecular interaction system that relied on **Host8** and a quaternized perylene diimide **Guest3** designed for use in aqueous media. In this process, the hydrophobic effects and electrostatic interactions played pivotal roles. In an aqueous solution, **Guest3** formed strong fluorescent aggregates. However, when **Host8** was introduced into the **Guest3** aqueous solution, a change in morphology occurred, leading to a fluorescence "turn-off" phenomenon due to the photoinduced electron transfer (PET) process. The addition of Fe^{3+} reversed this supramolecular PET process, resulting in a "turn-on" fluorescent response. The detection of Fe^{3+} exhibited specific, ratiometric, and reversible behavior, with an LOD of 2.13×10^{-7} M.

Inclusion compound probes that are built using macrocyclic compounds have garnered significant research interest and can detect various metal cations sensitively. Yang et al. [71] introduced a highly sensitive and selective fluorescence sensor capable of quantitatively analyzing Au^{3+} ions in aqueous systems. This sensor achieved an LOD as low as 6.9×10^{-8} M. The sensor relies on the supramolecular interactions between **Guest4** and **Host9**, forming an inclusion complex prepared using the saturated solution method. Including **Guest4** by **Host9** significantly increased the water solubility of **Guest4**, boosting it by 177-fold. The inclusion complex IC exhibited a larger Stokes shift in aqueous conditions alone. The stoichiometric ratio between **Host9** and **Guest4** was determined to be 1:1, and the binding constant was calculated to be $(4.62 \pm 0.15) \times 10^4$ M^{-1}. Notably, the IC displayed robust resistance to interference and demonstrated excellent adaptability over a wide range of pH values.

The PSPs find extensive applications in drug detection. Investigations were also focused on studying another typical pesticide, namely paraquat (PQ). PQ is a non-selective and fast-acting herbicide that, if accidentally ingested, can severely damage human lungs, liver, kidneys, and other vital organs. Given the significant clinical and environmental implications of PQ, there is a pressing need to design new methods for its high-sensitivity and accurate detection. PQ can interact not only with electron-rich molecules but also form supramolecular interaction complexes and columnar structures with macrocyclic molecules like calixarenes, cucurbiturils, and others.

Fluorene possesses a planar and rigid biphenyl structure with a high fluorescence quantum yield. To enhance the solubility of the material, chemical modifications were performed on fluorene derivatives by introducing functional side chains at the C9 position of the fluorene molecule. Covalent-bonded conjugated polymers exhibited a molecular wire effect that enhances the response signal in fluorescence sensing applications.

Building on the principles mentioned earlier, Li, along with Xiao and their team [72], synthesized a novel conjugated polymer named (Co-P[5])Flu. This polymer was obtained through the copolymerization of a difunctionalized pillar[5]arene (**Host10**) and a fluorene derivative monomer. The intramolecular rotations of the pillar[5]arene unit were constrained in Co-P[5]Flu, resulting in an AIE enhancement (AIEE) effect. Pesticide PQ (paraquat, **Guest5**) could enter the pillar[5]arene cavity within Co-P[5]Flu. In EtOH/H2O, Co-P[5]Flu exhibited fluorescence quenching in response to PQ, attributed to the synergistic effects of polypseudorotaxane formation and PET. Co-P[5]Flu demonstrated exceptional selectivity and sensitivity in detecting PQ, with a low LOD of 1.69×10^{-8} M and a determined Stern–Volmer constant (K_{sv}) of 2.11×10^4 M^{-1}. This polymer chemosensor proved to be valuable for the practical detection of PQ.

Researchers are actively designing and synthesizing materials with improved performance for PQ detection to enhance the sensitivity of detection. The combination of two different macrocyclic compounds in such efforts holds significant promise and is an intriguing avenue of exploration. Indeed, there has been limited research on the potential applications of such materials thus far.

However, a new category of supramolecular polymers involving two distinct macrocyclic host molecules, namely pillar[n]arene NTP5 (**Host11**) and Q[10], was successfully synthesized by Xiao et al. [73]. Representation for the formation of a fluorescent supramolecular polymer was shown in **Figure 2**. The inclusion of the macrocyclic Q[10] significantly positively impacted the fluorescence properties of NTP5 by constraining its intramolecular rotation. Specifically, the 4-[2-(1-naphthalenyl)ethenyl]pyridine moiety of NTP5 was encapsulated by Q[10], leading to the formation of a supramolecular interaction complex. The introduction of Q[10] caused a transformation in the morphology of NTP5, changing it from a spherical structure to a porous one, resulting in enhanced fluorescence. Interestingly, the fluorescence of Q[10]-NTP5 could be quenched by adding PQ, making it suitable for molecular recognition and bioimaging applications.
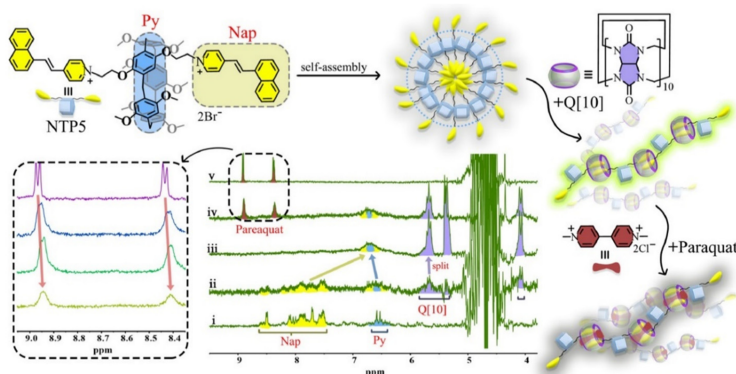

Figure 2. Schematic representation of a novel pillar[5]arene-cucurbit[10]uril−based complex and its application for the detection of paraquat. Illustration (top) of the interactions of NTP5, Q[10]-NTP5, Q[10]-NTP5-PQ, and the 1H NMR spectrum (bottom) (inset: Q[10]-NTP5 at different concentrations of PQ).

2.2. Substance Adsorption and Separation

Pillar[n]arene offers a diverse range of supramolecular interactions, making it a highly sought-after building block for SPs (supramolecular polymers) with multifunctionality [74][75]. Additionally, the structure of the polymers can create novel voids within the networks and spaces [76], complementing inherent pillar[n]arene cavities, which functions as new binding sites for guest molecules [77][78]. Achieving the environmentally friendly and efficient removal of various pollutants is a crucial challenge in environmental science and industrial applications. This issue directly impacts human health and the health of aquatic ecosystems [79][80][81][82][83][84][85]. Pillararene materials serve as protective containers, accurately capturing and safely storing harmful molecules [86][87][88]. The properties and applications of polymers are influenced by factors such as the size of the macrocyclic pore, connectivity, and the chemical environment within the hosts. Self-assembly aggregates contribute to the removal effect. This concept provides a novel approach to adsorbing and separating ions and organic substances. Meanwhile, the chemical structures of pillar[n]arenes and guest molecules are listed in Scheme 4.
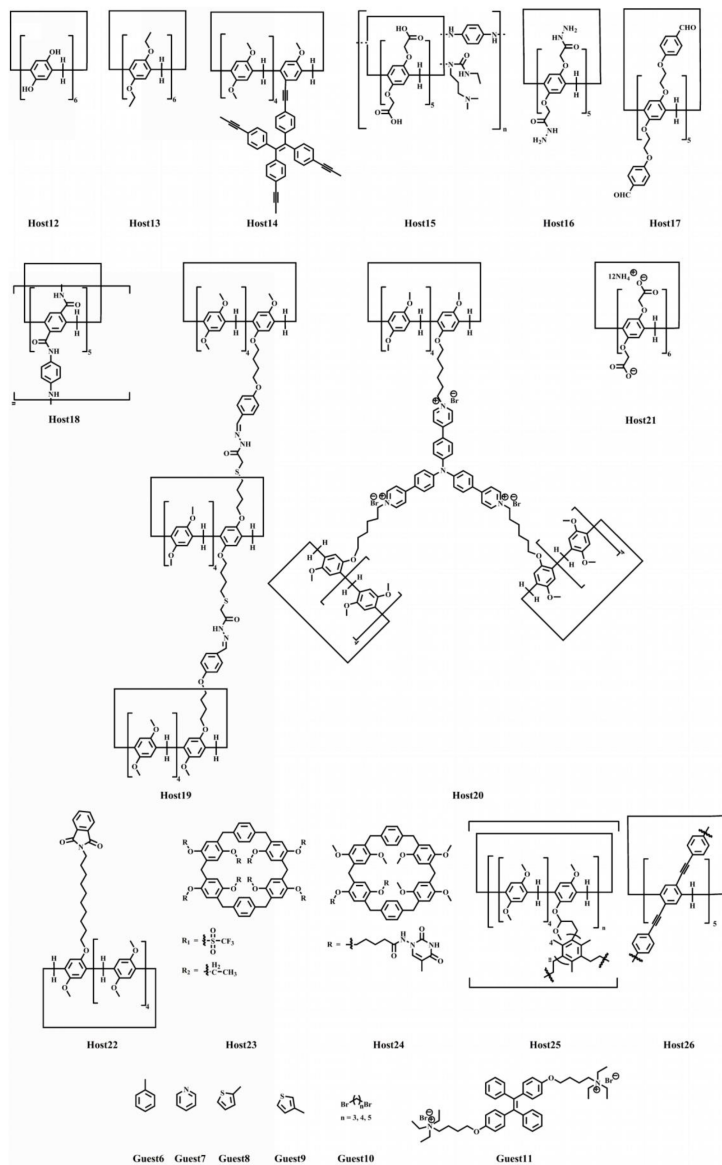
Scheme 4. Molecular structures of pillar[*n*]arenes and guest molecules.

Materials featuring micropores are highly suitable for gas storage and separation applications. A growing focus has recently been on discrete organic molecules instead of 1D-3D networked materials. This shift is driven by the advantages of solubility, flexibility, and the feasibility of obtaining these materials through organic synthesis. Ogoshi et al. [89] found that the aromatic molecule within the pillar[6]arene (**Host12**) forms a highly ordered 1D channel with a diameter of 6.7 Å. This supramolecular assembly channel can capture various gases, including water vapor-saturated hydrocarbons. The organic gas and vapor adsorption capacity of pillar[6]arene in a solid state presents a promising avenue for further exploration.

In industrial processes, toluene is primarily derived from coal and petroleum sources through catalytic reforming, pyrolysis of hydrocarbons, and coking. However, these processes often leave trace amounts of heterocyclic compounds behind, which can significantly impact the properties of toluene. Therefore, efficiently removing these heterocyclic compounds is crucial for obtaining high-purity toluene.

Zhu et al. [90] introduced a separation strategy for mixtures of toluene and heterocyclic compounds using non-porous adaptive guest-loaded crystals of perethylated **Host13**. The approach successfully enhanced the purity of toluene, increasing it from 96.78% to 99%. The stability difference strongly influenced the selectivity of this material in the EtP6 crystal structure after incorporating various guest molecules (**Guest6, 7, 8,** and **9**). Upon removing the guest molecules, the structure of EtP6 reverted to its original state.

Tetraphenylethylene (TPE), which stands for AIE properties, was linked to P[5] using a Sonogashira–Hagihara cross-coupling reaction, resulting in the formation of P[5]-TPE (**Host14**). In their study, Yang et al. [91] introduced a macrocyclic cross-linked reticular polymer, P[5]-TPE-CMP, which demonstrated remarkable properties, including resistance to photobleaching, insolubility, recyclability, and selective sensing capabilities for Fe^{3+} ions and 4-amino azobenzene (**Figure 3**). P[5]-TPE-CMP also functionalized as a two-photon fluorescence sensor, detecting wavelengths in the 300–400 nm

and 650–800 nm ranges. In solution, it exhibited a range of microstructures, including various sizes of spherical and/or rodlike structures. Both P[5]-TPE-CMP materials displayed remarkable thermal stability, remaining stable up to 300 °C in air. The material demonstrated sensitivity and selectivity in the detection process, making it a promising candidate for removing harmful safety-related substances.
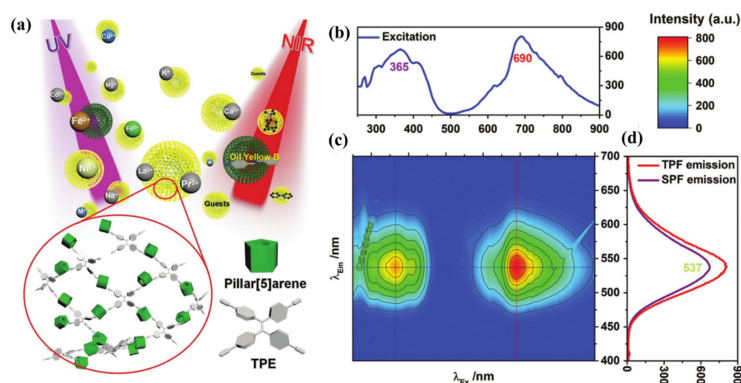

Figure 3. (**a**) Schematic representation of a conjugated macrocycle polymer (P[5]-TPE-CMP) based on pillar[5]arene and TPE and its two-photon sensing for metal ions and organic molecules. (**b**) Excitation spectrum (blue). (**c**) The 3D fluorescence contour spectroscopy of P[5]-TPE-CMP. (**d**) Single-photon fluorescent emission spectrum (purple) and two-photon fluorescent (TPF) emission spectrum (red).

Organic micropollutants, including drugs, hormones, pesticides, and industrial chemicals in water systems, threaten human health and aquatic ecosystems. Consequently, creating rapid, efficient, and cost-effective chemical and physical water treatment methods is a pressing challenge for material chemists. The design and synthesis of sustainable adsorbent materials that offer fast adsorption and high absorption capacity remain significant challenges in addressing the removal of organic micropollutants from water.

In 2017, Shi et al. [92] developed a 3D network polymer known as P5-P (**Host15**), which was cross-linked using carboxyl-derived pillar[5]arene and *p*-phenylenediamine. This polymer exhibited excellent capabilities for adsorbing and removing organic micropollutants from water. Furthermore, this polymer demonstrated recyclable adsorption performance, particularly for fluorescein sodium and methyl orange. The 3D network polymer exhibited the potential for rapid waste-water treatment. Two years later, they applied hydrazide-functionalized pillar[5]arene (**Host16**) and 4-aldehydephenyl-functionalized pillar[5]arene (**Host17**) to obtain another intelligent hydrogel [93]. The hydrogel exhibited a remarkable removal efficiency of 91.5% for organic micropollutants in water. The primary driving force behind its action was the supramolecular interactions between the macrocycle and pollutant molecules. The hydrogel material could be regenerated at least five times by disrupting the supramolecular interaction complex.

The most prevalent sources of water pollution stem from industrial waste discharges and municipal sewage, which release a combination of chemicals and microorganisms. Recognizing the severity of this issue, Wen et al. [94] developed a conjugated polymer based on pillar[5]arene (**Host18**), which is an acid-derivatized poly-*p*-phenylene pillar[4]arene[1]terephthamide (P[5]-PPTA). In P[5]-PPTA, the pillar[5]arene rings engage in supramolecular interactions with short-chain alkyl derivatives. The polymer exhibited a unique absorption capability for low-molecular-weight alkylamines, alcohols, and carboxylic acids in water, and it maintained its performance across five successive cycles of reuse without degradation. Furthermore, P[5]-PPTA could be thermally reactivated, enhancing its versatility for water treatment applications.

In the studies of separation materials, Wang et al. [95] designed an adsorbent material for PQ by harnessing the combined effect of linear tri-pillar[5]arene-based compounds (**Host19**). This design linked three pillar[5]arene groups within a single acceptor molecule. This material demonstrated several advantages, including a faster adsorption rate for PQ compared to activated carbon and single-pillar[5]arene-based materials. Additionally, its removal efficiency met expectations, with a remarkable 98% adsorption rate for commercial pesticide PQ in water. A year later, Zhang et al. [96] introduced a highly effective tripodal molecule based on tri-pillar[5]arene (**Host20**), which exhibited a "synergistic effect" for the efficient detection and removal of the pesticide PQ through supramolecular interactions. Each molecule featured two adjacent pillar[5]arene groups capable of binding one PQ molecule through multi-non-covalent interactions. The LOD was impressively low, reaching 2.23×10^{-7} M. The testing paper utilizing **Host20** could be a detection kit for PQ in water across a wide concentration range (10^{-6}–10^{-1} M). Moreover, it demonstrated exceptional adsorption capabilities in water, with an impressive adsorption efficiency of 98.40% for commercial PQ and a removal capacity of 108.24 mg/g. Yang et al. [97] designed and successfully prepared a controllable supramolecular coordination polymer Zn^{2+}@WP5 (**Host21**) in a

related development. The polymer displayed outstanding adsorption and removal capabilities for PQ, owing to its negative charge, high surface area, and recognition capacity based on supramolecular interactions. The maximum adsorption capacity for PQ reached approximately 203.60 mg/g. The polymer was successfully employed in real sample applications and could be regenerated by exchanging the guest structure.

Anions are crucial in maintaining human health, biological systems, and environmental stability. The precise detection and separation of these ions are of paramount importance. Consequently, the ultrasensitive detection and separation of various environmental ions are gaining significance. Lin et al. [98] developed a smart blue-white AIE gel material (PMDP-G), which was constructed using functionalized **Host17** and **Host22**, utilizing "exo-wall" π–π and supramolecular interactions. PMDP-G demonstrated remarkable sensitivity in detecting and separating multiple analytes, achieved through the interplay between "exo-wall" π–π and cation–π interactions. The low LOD underlined its high sensitivity. PMDP-G exhibited the capacity to adsorb and separate multiple metal ions from aqueous solutions, including Fe^{3+}, Hg^{2+}, and Ag^+, with adsorption rates ranging from 90.12 to 99.95%.

Water contamination from heavy metal ions poses a grave threat to humans and animals globally. The development of a comprehensive approach for real-time sensing and the swift removal of mercury(II) ions holds immense significance in materials chemistry, chemical engineering, and environmental science. In recent years, there has been a growing emphasis on designing and synthesizing cost-effective and efficient materials for the adsorption and removal of Hg^{2+} ions. Developing novel technologies for detecting Hg^{2+} in the atmosphere and industrial waste water is essential to enhance environmental protection and safeguard life on our planet.

As reported by Yang in 2018, leaning tower[6]arenes (LT6, **Host23**) exhibit a distinctive leaning tower conformation with minimal substituents, which sets them apart from the traditional pillar[6]arenes structures. These molecules have shown excellent performance in supramolecular interaction systems and macrocyclic chemistry. Yang's group developed a set of four novel CMPs (CMP-*n*, *n* = 1–4) using per-triflate-functionalized and [2]biphenyl-extended pillar[6]arene (**Figure 4**) [99]. CMP-4 exhibited an exceptional affinity for I_2, with a vapor uptake capacity of 208 wt % and a remarkable removal efficiency of 94 %. These properties were attributed to the well-suited cavity size of the tower[6]arene and numerous aromatic rings within the framework. CMP-2 displayed no capacity to adsorb N_2, making it highly selective for CO_2 capture.
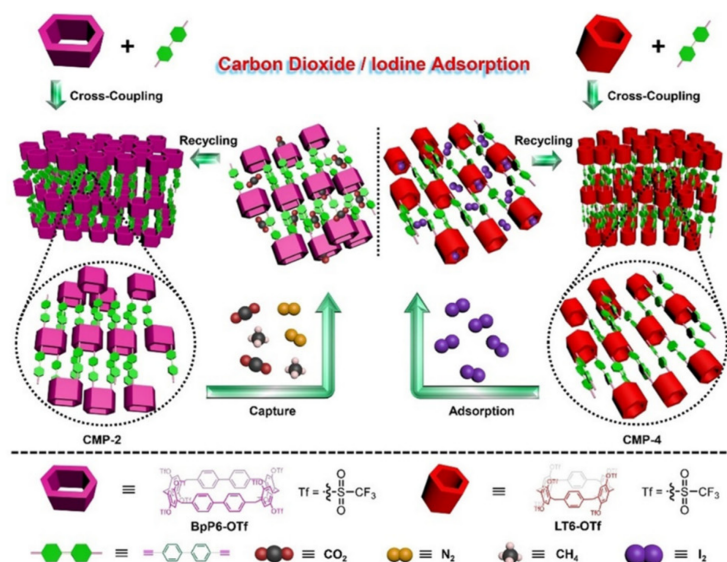

Figure 4. Illustration of the construction of four CMPs (CMP-*n*, *n* = 1–4), selective capture of CO_2, and efficient adsorption of I_2.

In 2019, Wu et al. [100] introduced a straightforward separation method utilizing a novel type of non-porous adaptive crystals built upon inclined pillar[6]arene (**Host23**). These deoxidized perethyl-inclined pillar[6]arene crystals (EtLP6) displayed non-porous characteristics, exhibiting a preference for 1-bromoalkane isomers over 2-bromoalkane isomers in the separation process. EtLP6 demonstrated the ability to separate 1-bromopropane, 1-bromobutane, and 1-bromopentane from their 1/2 isomer mixtures at a 1:1 (*v/v*) ratio in a single adsorption cycle. The obtained purities ranged from 89.6% to 96.3%. This selectivity is due to the distinct supramolecular interaction binding modes and varying stability of EtLP6 crystals loaded with one-site and two-site isomers.

In 2019, Dai et al. [101] introduced a fluorescent supramolecular polymer. This polymer was created using a [2]biphenyl-extended **Host24** with two thymine sites as arms, along with a tetraphenylethylene-bridged bis(quaternary ammonium) **Guest11**. Spherical nanoparticles were generated upon adding Hg^{2+}, increasing the emission intensity. This approach was suitable for the real-time detection and removal of Hg^{2+}. It demonstrated a rapid response, high selectivity, and fast adsorption rates. Additionally, the material could be recycled by treatment with Na_2S.

Arunachalam et al. [102] made significant contributions to the removal of iodine vapor by successfully synthesizing a recyclable 3D cross-linked microporous polymer based on pillar[5]arene **Host25**, which demonstrated an iodine vapor capture capability of 3.84 g/g at 80 °C. The polymer adsorbent efficiently removed over 83% of iodine within 15 min of shaking in an aqueous solution. Pillar[*n*]arene holds significant potential for applications in environmental remediation. Additionally, their versatility allows for various possibilities for further functionalization, enhancing their utility in environmental improvement.

To address the issue of water stability in separation systems, Talapaneni et al. [103] introduced an efficient conjugated microporous polymer based on pillar[5]arenes (P5-CMPs, **Host26**). These P5-CMPs were created by attaching triflate-functionalized P5 to 1,4-diethynylbenzene and 4,4′-diethynyl-1,1′-biphenyl linkers. The P5-CMPs exhibited an impressive surface area of up to 400 $m^2 \cdot g^{-1}$. In earlier studies, porous materials displayed isosteric heats of adsorption (Q_{st}) for propane at zero coverage in the range of 32.9–36.9 kJ/mol. The Q_{st} value increased as the propane loading increased, indicating stronger intermolecular interactions between propane molecules. The Q_{st} value reached a maximum of 53 kJ/mol at zero coverage and then gradually decreased to approximately 35 kJ/mol as the loading of propone increased. This phenomenon was attributed to the formation of a robust supramolecular complex between propane and pillar[5]arenes, facilitated by multiple C–H···π interactions. This method introduced a thermodynamic selective separation of saturated hydrocarbons with low polarizability. The strong affinity of P5-CMPs for propane allowed for efficient breakthrough encapsulation and separation from natural gas mixtures under simulated conditions at 298 K.

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