



# Pillar[n]arenes-based materials for detection and separation of pesticides

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## ABSTRACT

The effective materials and methods for detection and separation of pesticides are urgently needed because most of pesticides show very harmful influence on life and environment. As a new kind of macrocyclic host compound, pillar[n]arenes show very good performance in the detection and separation of pesticides, especially for paraquat (PQ). For the pesticide detection and separation materials, their structures determine performance. Therefore, this review summarizes the recent progress of pillar[n]arenes-based materials for detection and separation of pesticides covering single/multi-pillar[n]arenes, pillar[n]arenes-based polymers, frameworks, composites, nanomaterials, etc. The structure-performance relationships of these materials have been discussed according to the cavity size, the synergistic or collaboration effect, the structure of the polymer or framework, the substrate of the composites and the size of nanomaterials and so on. Based on these, we also look forward to the future and point out the possible way for improving the pesticides detection sensitivity and separation efficiency of this kind of materials.

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## 1. Introduction

Pesticides play an important role in the development of agriculture [1–4]. For example, paraquat (PQ), quinotrione (QO) and benquitrione (BQ) are often used as herbicides [5–8]. However, environmental safety and life health are seriously threatened by the toxicity of pesticides [9–13]. So, it is of great significance to develop effective methods and materials for detecting and separating pesticides [14–21]. So far, many analytical methods for the determination of pesticides were developed based on capillary electrophoresis [22], solid phase microextraction [23], gas chromatography-mass spectrometry [24], high performance liquid chromatography [25], fluorescence sensor [26–29] and so on. However, developing simple methods and materials to sensitively detect and effectively separate pesticides is still a challenging task [30].

With the rapid development of supramolecular chemistry, macrocyclic hosts [21–44] and porous framework materials [31,32] show unique advantages in the pesticide detection and adsorption. Due to the special cavity structure, macrocyclic compounds such as cucurbituril [33], calixarene [34], cyclodextrin [35], pillar[n]arenes [36–44] show nice inclusion and complex properties for different pesticides. Among these macrocycles, pillar[n]arenes attracted more and more attentions due to their special symmetrical structure, unique rigid cavity architecture and abundant supramolecular interactions [36–44]. The pillar[n]arenes cavity can bind guest compounds through cation $\cdots\pi$ , C-H $\cdots\pi$ ,  $\pi\cdots\pi$ , hydrogen bonding, hydrophobic interactions and so on [45–47]. It worth mentioning that the electron-rich cavity of pillar[n]arenes exhibit excellent match for PQ, an electron-deficient 1,1'-methyl-4,4-bipyridinium salt. The pillar[n]arenes derivatives also show nice binding properties for other pesticides such as QO and BQ through multi supramolecular interactions. So, pillar[n]arenes provide good opportunities to develop novel and efficient materials for the detection and separation of these pesticides [48–52].

In recent years, there are lots of reviews [36,38,44,53–55] with subject on pillar[n]arenes had been published, which indicated the

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pillar[*n*]arenes attracted wide interests. Despite the pillar[*n*]arenes show various merits in pesticides detection and adsorption and lots of research articles had been published in this field, by far, there is no exclusive review article with specific subject on the application of pillar[*n*]arenes in pesticides detection and adsorption materials. Therefore, a specific review to systematically discuss the structure effect relationship of pillar[*n*]arenes-based pesticide responsive materials and describe the application of pillar[*n*]arenes in pesticide detection and adsorption is very necessary.

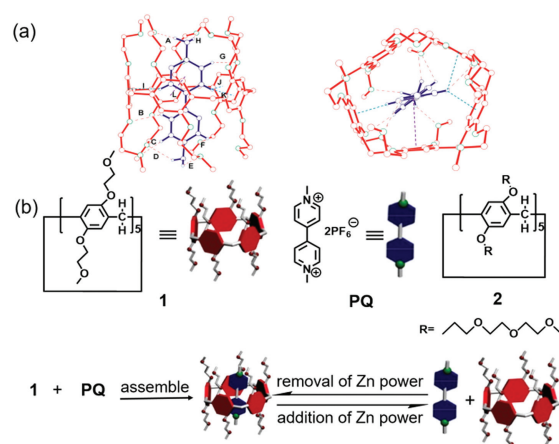
As we all know, the pesticides detection and separation features, efficiency and mechanism depend on the materials' structure [56]. Therefore, to improve the pesticides detection and separation efficiency, much efforts were put into through various designs and approaches. This review summarizes the recent efforts and progress on pillar[*n*]arenes-based materials for detection and separation of pesticides from the following aspects: single pillar[*n*]arenes, multi-pillar[*n*]arenes, pillar[*n*]arenes-polymers or frameworks, pillar[*n*]arenes-based composites, pillar[*n*]arenes-functionalized nanomaterials and so on. Meanwhile, the structure effect relationship including the influence of cavity size of different pillar[*n*]arenes, the synergistic effect between the adjacent pillar[*n*]arenes, the collaboration of the pillar[*n*]arenes with other functional groups, the structure of the pillar[*n*]arenes-based polymer or framework, the substrate of the pillar[*n*]arenes-based composites and the size of pillar[*n*]arenes-functionalized nanomaterials on the pesticides detection and separation efficiency of these materials have been discussed. Moreover, the unsolved issues and future directions of these materials are also discussed.

## 2. Single pillar[*n*]arenes

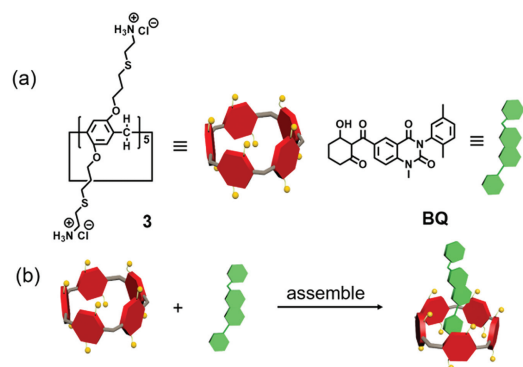
### 2.1. Host-guest interaction between pillar[5]arenes and pesticides

Pillar[*n*]arenes have been widely studied in host-guest chemistry due to their unique cavity structures [57]. Jia and Li *et al.* had selected a series of PQ derivatives to explore the host-guest interaction between pillar[5]arene and PQ [58]. The experimental results showed that PQ could enter the cavity of pillar[5]arene well. This experiment indicated that the pillar[*n*]arenes could act as nice candidate for the preparation of pesticide adsorption and separation materials. Stimulus-response plays an important role in host-guest chemistry [59–61]. Huang and co-workers synthesized [*n*]ethylene glycol-functionalized ( $n=1, 3$ ) pillar[5]arene **1** and **2** [62]. Compared with **1**, the alkyl chain of the functional part of **2** is longer. When an acetonitrile solution of pillar[5]arene **1** or **2** was mixed with equimolar PQ. The solution changed from colorless to yellow. This phenomenon could be attributed to the charge transfer between the electron-rich aromatic rings of the pillar[5]arene host and the electron-poor pyridine-groups of the PQ guest. This result can indicate the PQ entered the cavity of the pillar[5]arene. The crystal structures of **1** and **1**⊃PQ were obtained, which further proved this conclusion. This phenomenon can be used to detect PQ. In addition, the complexation constant of **1** with PQ ( $(1.79 \pm 0.38) \times 10^3$  L/mol) is higher than that of **2** with PQ ( $(3.35 \pm 0.22) \times 10^4$  L/mol) (Fig. 1), which indicated that the substituent groups on pillar[*n*]arenes-based host have a big effect on the host-guest complexation in solution. In addition, the complexation between **1** and PQ can be reversibly controlled by adding or removing Zn powder. This redox-controlled reversible complexation process provides new ideas for the design of reversible materials for the detection and separation of pesticides.

Compared with direct irrigation of pesticides, spraying pesticides on the surface of plants helps to reduce the use of pesticides and reduce the pollution to the environment. However, most of plant leaves are superhydrophobic, so pesticide droplets are difficult to diffuse on the leaf surface [63]. BQ is a novel herbicide,



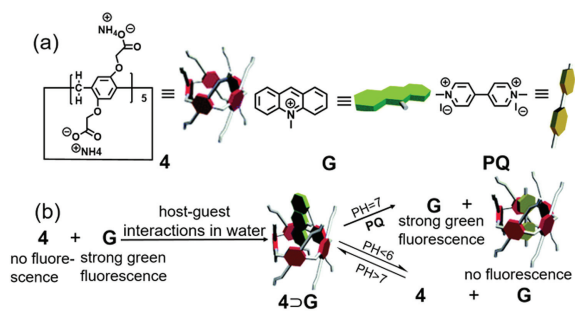
**Fig. 1.** (a) Ball-stick views of the crystal structure of **1**⊃PQ. Host **1** is red, guest PQ is blue; (b) Chemical structures of **1**, **2** and PQ and cartoon representation of redox-responsive complexation between **1** and PQ. Reproduced with permission [62]. Copyright 2013, American Chemical Society.



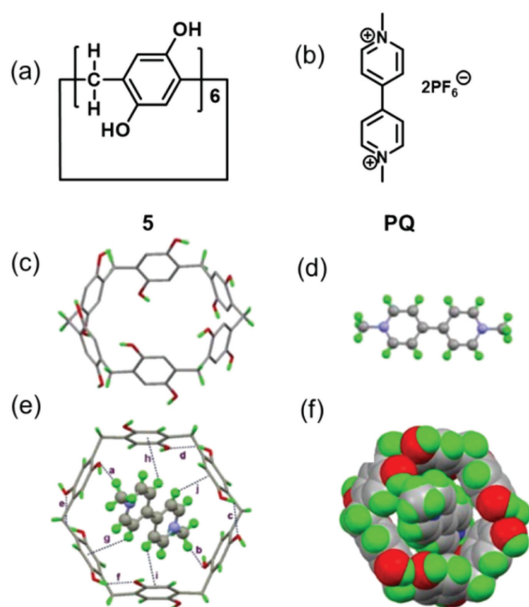
**Fig. 2.** (a) The molecular structure of **3** and BQ; (b) Reaction diagram of **3** and BQ.

it has excellent herbicidal activity against a variety of weeds. So Li and Yang *et al.* designed a water-soluble amino pillar[5]arene (**3**) [64], which can improve the spreading of BQ on plant leaves by forming effective supramolecular interaction with BQ (Fig. 2). Therefore, this supramolecular interaction plays an important role in improving the utilization of pesticides. And this also provides a new idea for the removal of pesticide BQ.

Most fluorescent probes for pesticide detection only can work in organic solvents, while most real conditions for application of pesticide are carried out in water systems. Therefore, it is necessary to construct a fluorescent probe for the effective detection of pesticides in aqueous phase. Xue and co-workers developed a single fluorescent probe based on the complexation between pillar[5]arene (**4**) and 10-methylacridinium iodide (**G**) (known as strong fluorescence), which can detect PQ in water through fluorescence signals [65]. The experiment results showed that compound **4** and **G** are complexed at a stoichiometric ratio of 1:1. When **G** was mixed with **4**, it entered the cavity of **4** quickly, forming a 1:1 inclusion complex **4**⊃**G**. While, because the complex constant of **4** and PQ ( $(1.32 \pm 0.25) \times 10^5$  L/mol) is much higher than that of **4** and **G** ( $(1.28 \pm 0.42) \times 10^2$  L/mol), when adding PQ into the **4**⊃**G** solution, the complex of **4** with **G** is dissociated, **G** came out of the cavity of **4**, and the PQ entered into the cavity of **4**. During this process, by observing the change of fluorescence, it can be judged whether PQ existed. The weak-fluorescent complex **4**⊃**G** is used as a fluorescence “turn-on” probe for the detection of PQ. Moreover, the PQ recognition process had pH-responsiveness, by changing the pH of the solution, the assembly and disassembly process between



**Fig. 3.** (a) The molecular structure of **4**, **G** and **PQ**; (b) The illustration of the fluorescence detection of **PQ**. Reproduced with permission [65]. Copyright 2014, Royal Society of Chemistry.



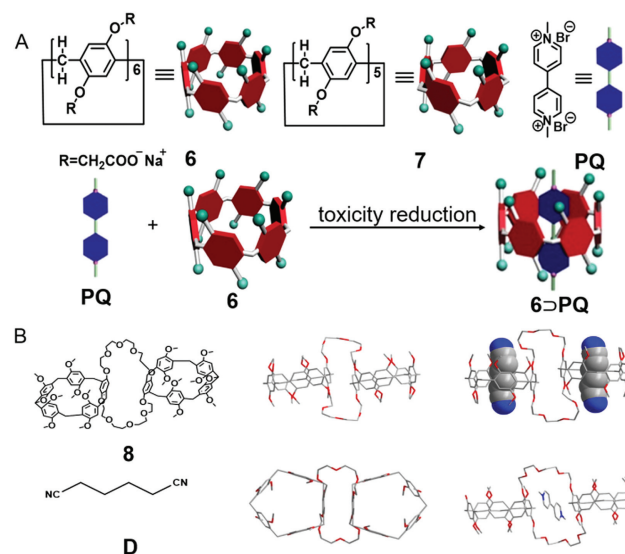
**Fig. 4.** (a) The molecular structure of **5**; (b) The molecular structure of **PQ**; (c) Crystal structure of **5**; (d) Crystal structure of **PQ**; (e) Crystal structure of **5>PQ**; (f) Space-filling model of **5>PQ** (top view). Reproduced with permission [66]. Copyright 2014, American Chemical Society.

host and guest can be reversibly controlled. This sensor provides a new idea for fluorescent detecting **PQ** in aqueous phase (Fig. 3).

### 2.2. Host-guest interaction between pillar[6]arenes and pesticides

Compared with pillar[5]arenes, pillar[6]arenes have larger electron rich cavity. The interactions of pillar[6]arenes with pesticide molecules also have been widely studied. Hou *et al.* synthesized the per-hydroxylated pillar[6]arene (**5**), and the electron donating hydroxyl groups are arranged around the cavity of **5**, which showed that **5** is a good host for electron deficient guest, which provided conditions for the separation of **PQ**. The inclusion properties of **5** with guest was studied, the crystal structures of **5** and **5**-based host-guest complex were obtained [66]. The resultant crystal structure (Fig. 4) showed that **PQ** threaded through the cavity of **5** to form a [2]pseudorotaxane in the solid state. The complex stoichiometric ratio of **5** to **PQ** is 1:1, which is significantly different from the previously reported complex stoichiometric ratio of per-hydroxylated pillar[5]arene to **PQ** of 1:2 [58]. This may be attributed to the larger cavity of **5**. This method can be used to separate **PQ**.

It is very important to find water-soluble host with high binding ability with pesticide molecules. The complexation of **PQ** with



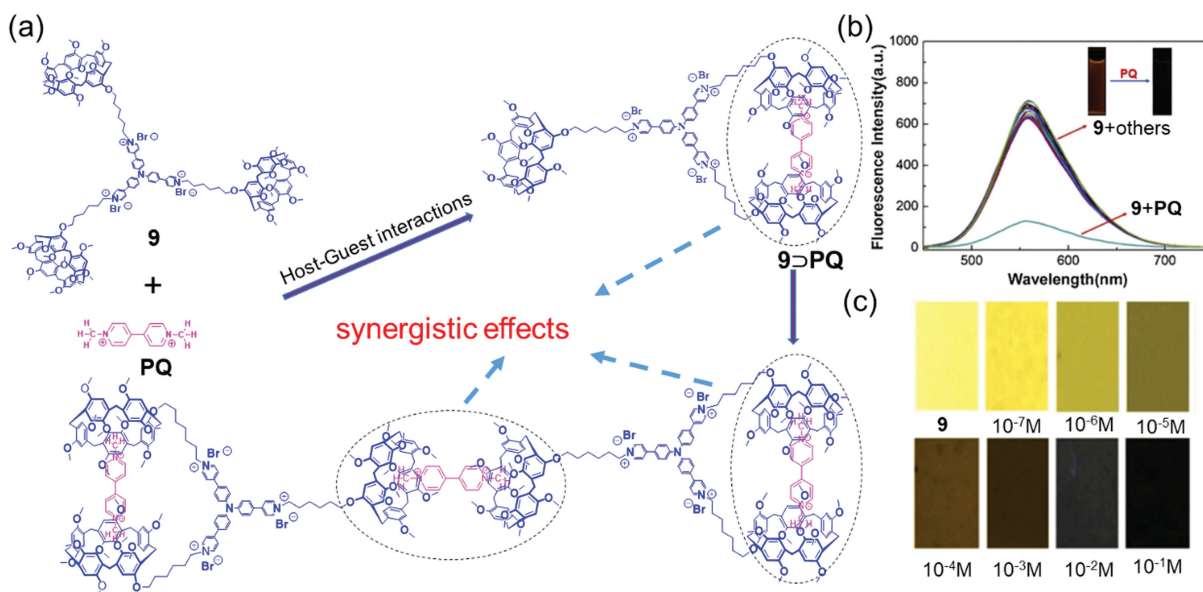
**Fig. 5.** (A) The molecular structures of **6**, **7** and **PQ** and schematic diagram of the interaction between **6** and **PQ**. Reproduced with permission [67]. Copyright 2012, American Chemical Society. (B) The molecular structures of **8** and **D**, Single crystal structure of interaction between **8** and **D**. Reproduced with permission [68]. Copyright 2015, American Chemical Society.

water-soluble pillar[6]arene (**6**) was studied by Huang and his collaborators [67]. The interactions of these two molecules are mainly driven by electrostatic, hydrophobic and  $\pi$ - $\pi$  stacking interaction, they can form stable 1:1 complexes (Fig. 5A). In addition, a water-soluble pillar[5]arene (**7**), an analogue of **6**, was synthesized and its interaction with **PQ** was studied. The result showed that the association constant of **6>PQ** ( $(1.02 \pm 0.10) \times 10^8$  L/mol) was much higher than that of **7>PQ** ( $(8.20 \pm 1.70) \times 10^4$  L/mol). Because the cavity of **6** was larger than that of **7**, the compound **6** could better match the size of **PQ** and made the interactions between **6** and **PQ** more effective. This kind of molecular recognition not only has high binding strength, but also has pH response. The complexation and dissociation of **PQ** with **6** can be controlled by adjusting the pH. When **6** and **PQ** formed a stable host-guest complex, the chance of interaction between **PQ** and intracellular reducing agent is reduced, which made the formation of free radical cation more difficult, thus effectively reducing the toxicity of **PQ**. This study is expected to be applied to the detection and removal of **PQ**.

Both the pillar[5]arenes and pillar[6]arenes could bind some pesticides such as the **PQ** and **BQ** through host-guest inclusion. Pillar[6]arenes have larger cavity size and show easier as well as more stable inclusion. While the pillar[5]arenes have the merits of easy to synthesis, and the inclusion ability for **PQ** and **BQ** is also considerable. The binding and sensing ability of pillar[*n*]arenes host can be tuned by the functionalization of the pillar[*n*]arenes moiety.

### 3. Multi-pillar[*n*]arenes

For pesticides detection and separation, high detection sensitivity and separation efficiency are very important and urgently needed. In order to improve the detection sensitivity and separation efficiency, lots of efforts have been devoted to enhancing the host-guest binding properties. Among of various approaches, improving the binding ability of pillar[*n*]arenes to pesticide molecules through the synergistic effect between pillar[*n*]arenes and other functional groups is an important way. Generally, the synergistic effect is carried out through the collaboration of adjacent pillar[*n*]arenes groups in the rational designed materials which based on bis-pillar[*n*]arenes, tri-pillar[*n*]arenes and multi-pillar[*n*]arenes.



**Fig. 6.** (a) The mechanism of “synergistic effect” in tripodal tri-pillar[5]arene (**9**). (b) Fluorescence color changes of **9** and **9** in the presence of PQ under UV lamp. (c) The fluorescence changes of **9**-based test papers after addition different concentration of PQ.

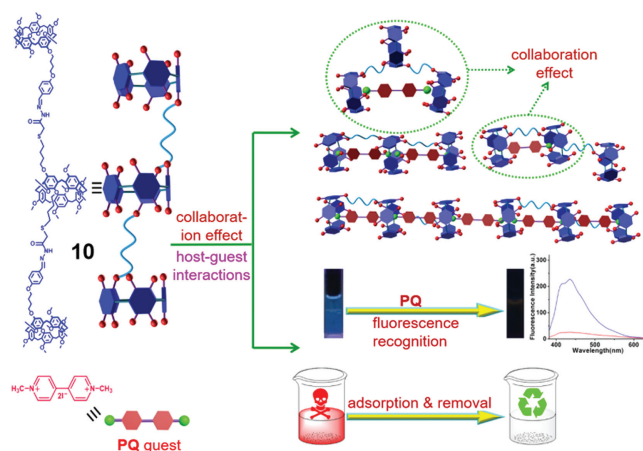
### 3.1. Bis-pillar[*n*]arenes

Wen *et al.* synthesized a novel tricyclic host molecule (**8**) that consists of two pillar[5]arene units and a crown ether ring [68]. The two pillar[5]arene subunits in **8** could selectively form a double-threaded complex (**2D**⊂**8**) with 1,4-dicyanobutane (**D**), while PQ could enter the crown ether ring in **8** to form a stable complex (PQ⊂**8**) (Fig. 5B). In addition, the tricyclic host **8** could simultaneously bind two **D** and one PQ, and form a four-component supramolecular complex **2D**⊂**8**⊃PQ. Due to the influence of the shape and size of macrocyclic host and foreign guest, PQ entered the crown ether cavity rather than the pillar[5]arene cavity. This process can be used to separate PQ from the solution.

### 3.2. Tri-pillar[*n*]arenes

In order to improve the detection sensitivity and separation efficiency of pillar[5]arenes-based materials for PQ, our group designed and synthesized a novel tripodal tri-pillar[5]arene (**9**) by connecting three pillar[5]arenes with tripyridyl triphenylamine [69]. The tripodal tri-pillar[5]arene structure had a synergistic effect to increase the interaction between **9** and PQ (Fig. 6). Therefore, the **9** showed better detection and removal efficiency for PQ. The adsorption efficiency of **9** for pesticide PQ was up to 90.10% and remove capacity was 99.11 mg/g, which higher than single pillar[5]arenes based sorbent and active carbon (Table 1) [69–80]. In this process, synergistic effect plays a key role. So, **9** has a good application prospect in the detection and separation of pesticide PQ.

For the purpose of investigating the structure-function relationships of the tri-pillar[5]arenes based materials for detection and separation of PQ, a new linear three pillar[5]arene based PQ receptor (**10**) was designed and synthesized [73]. The linear three pillar[5]arene receptor not only detect PQ by fluorescence phenomenon, but also can effectively separate PQ. Compared with activated carbon, single pillar[5]arenes receptor and other adsorbents (Table 1), the adsorption rate of PQ by linear tri-pillar[5]arene receptor is higher, which is due to the synergistic effect of two adjacent pillar[5]arene groups in linear three pillar[5]arene receptor. Based on this concept, the adsorption rate of PQ on pillar[5]arene



**Fig. 7.** The possible host-guest interaction mechanism of host (**10**) and guest (PQ); Schematic diagram of fluorescence recognition and adsorption for PQ.

adsorption material is successfully increased. The process of PQ recognition by **10** is shown in the Fig. 7.

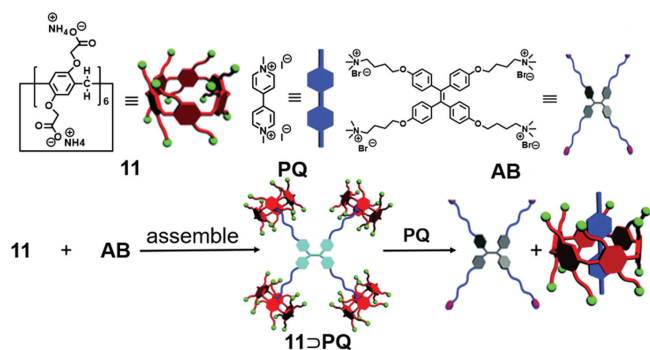
### 3.3. Tetra-pillar[*n*]arenes

To improve the PQ detecting sensitivity, tetra-pillar[*n*]arenes-based system also has been investigated. Huang *et al.* synthesized pillar[6]arene (**11**) [81] and compound **AB** [82], which is a derivative of tetraphenylethylene. After adding **AB** into **11**, the intramolecular rotation of benzene ring in **AB** is hindered. So the complex **11**⊃**AB** emitted strong fluorescence in dilute solution [83]. When PQ was added to this complex, compound **AB** slipped out of the cavity of **11** and **11** combined with PQ and fluorescence quenching (Fig. 8). This host-guest complex can be used as a novel material for highly sensitive detection of PQ.

Through the synergy between pillar[*n*]arenes and other functional groups, the host-guest binding and recognition signal output could be enhanced. It's a feasible way to improve the detection sensitivity and separation efficiency of pillar[*n*]arenes-based pesticides sensor and adsorbents.

**Table 1**  
Performance of some adsorbents and pillar[5]arenes-based materials.

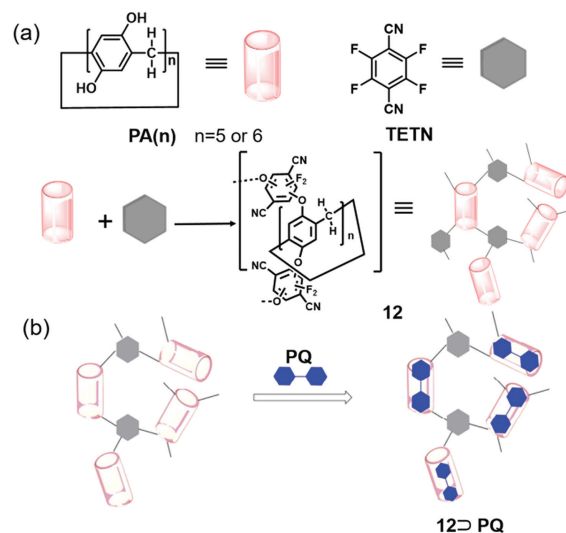
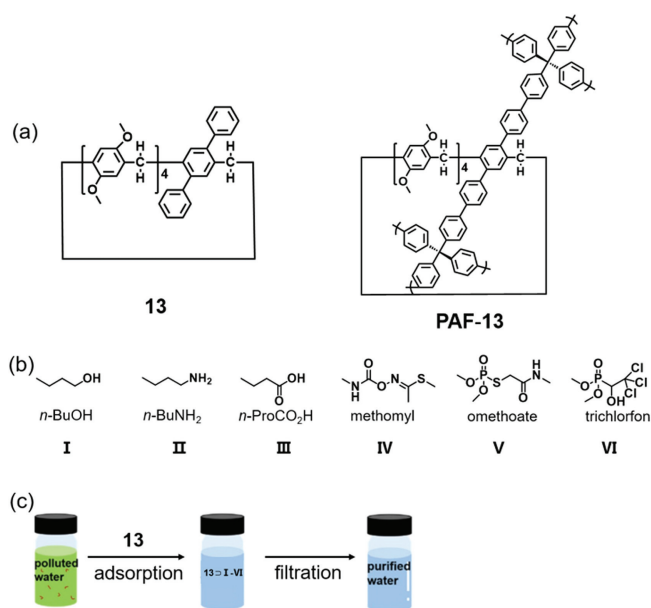
Adsorbent	Pesticides	Detection limit (mol/L)	Uptake (%)	$q_e$ (mg/g)	Refs.
Active carbon	PQ	/	62.87	69.19	[69]
Single-pillar( <i>n</i> )arene	PQ	/	12.10	26.62	[69]
Mesoporous silica	PQ	/	/	13.6	[70]
TEMPO-oxidized cellulose nanofibers	PQ	/	/	110.0	[71]
Methacrylic acid-modified rice husk	PQ	/	/	144.6	[72]
<b>9</b>	PQ	$2.23 \times 10^{-7}$	90.10	99.11	[69]
<b>10</b>	PQ	$1.95 \times 10^{-6}$	90	198.0	[73]
<b>12</b>	PQ	/	/	209	[74]
<b>14</b> @graphene	PQ	$6.0 \times 10^{-8}$	/	/	[75]
<b>15</b> -rGO	PQ	$3.5 \times 10^{-9}$	/	/	[76]
<b>16</b> -G	PQ	$1.04 \times 10^{-3}$	/	/	[77]
<b>18</b> -Si	PQ	/	/	64.11	[78]
<b>19</b> -Si	PQ	/	/	157.63	[78]
<b>23</b> -PC-AuE	QO	$1.0 \times 10^{-8}$	/	/	[79]
<b>24</b> @Ag@COF	PQ	$1.4 \times 10^{-8}$	/	/	[80]

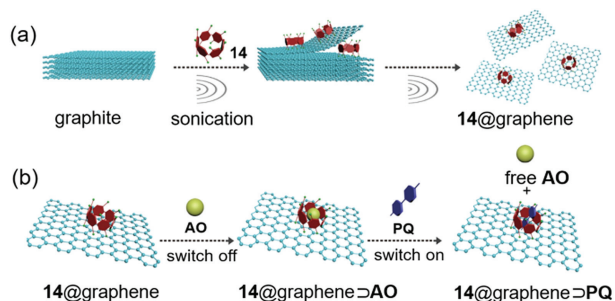
**Fig. 8.** Compounds used in this study and the cartoon representation of the formation of the luminescent supramolecular inclusion complex and its application in the detection of PQ. Reproduced with permission [83]. Copyright 2014, Royal Society of Chemistry.

#### 4. Pillar[*n*]arenes-based polymer and framework

For pesticide adsorption materials, stability is as important as efficiency. In order to improve the stability and adsorption efficiency, polymer and framework structures are designed and applied to pesticide adsorption materials based on pillar[*n*]arenes. For example, a pillar[*n*]arene-based porous polymers (**12**) was synthesized by Ma research group [74]. This polymer could be used as adsorbents to remove PQ from water through host-guest interactions (Fig. 9). The adsorption was especially efficient for PQ with a very fast uptake kinetics (at least 5 times faster than any existing adsorbent for PQ) and a high removal capacity. This excellent PQ uptake ability is based on the unique rigid  $\pi$ -rich cavities possessing nice affinity for electron deficient PQ. While, the stable polymer structure makes these polymers promising adsorbents for waste-water treatment.

Due to the porous characteristics, the framework structures show good properties in adsorption and separation. Wen *et al.* constructed a highly branched porous aromatic framework (**PAF-13**) based on tetraphenylmethane- and phenyl-functionalized-pillar[5]arene (**13**) moiety [84]. The **13** and tetraphenylmethane scaffold were integrated into the porous aromatic frameworks to produce a three-dimensional structure. Under the synergistic action of the cavity of **13** and porous three-dimensional structure, the adsorption capacity and selectivity would be enhanced. Then the adsorption capacity of **PAF-13** to different organic pollutants in aqueous solution was studied [85–90]. The results showed that **PAF-13** could adsorb short chain alkyl derivatives **I–III** and pesticides **IV–VI** with high sensitivity and could be reused (Fig. 10). The adsorption of **PAF-13** to **I–VI** was driven by the host guest interac-

**Fig. 9.** (a) The molecular structures of PA(*n*), TETN and the synthesis of **12**; (b) Schematic diagram of the role of **12** and PQ. Reproduced with permission [74]. Copyright 2017, Royal Society of Chemistry.**Fig. 10.** (a) The structures of **13** and **PAF-13**; (b) The structure of hosts **I–VI**; (c) Adsorption of the short-chain alkyl compounds (**I–III**) and pesticides (**IV–VI**) by **13**. Reproduced with permission [84]. Copyright 2021, American Chemical Society.



**Fig. 11.** (a) Schematic illustrating the **14** assisted exfoliation and stabilization of graphene; (b) competitive host-guest recognition for PQ sensing using **14**@graphene as receptor and AO as signal probe. Reproduced with permission [75]. Copyright 2019, Elsevier.

tion between **13** and pollutants. The described work offers a new perspective for the separation of pesticides in wastewater.

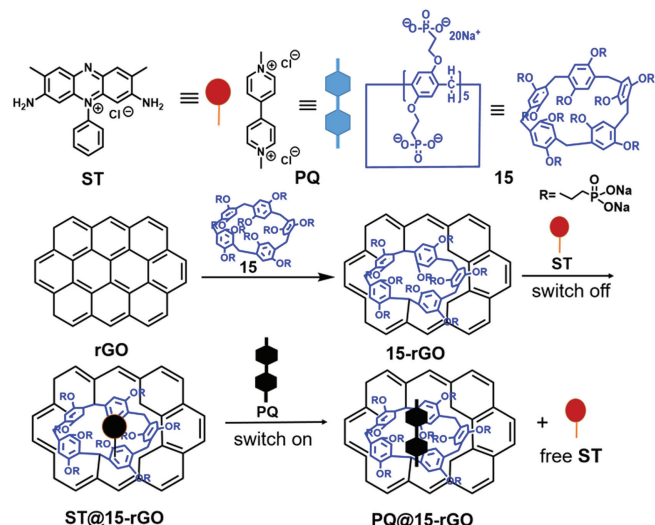
Through the formation of polymer and framework structure, the stability and efficiency of the pillar[*n*]arenes-based pesticide adsorbents could be improved. Porous frameworks structure can effectively promote the interaction between pillar[*n*]arenes cavity and pesticide molecules, and greatly improve the adsorption efficiency of pesticides.

## 5. Composites based on pillar[*n*]arenes

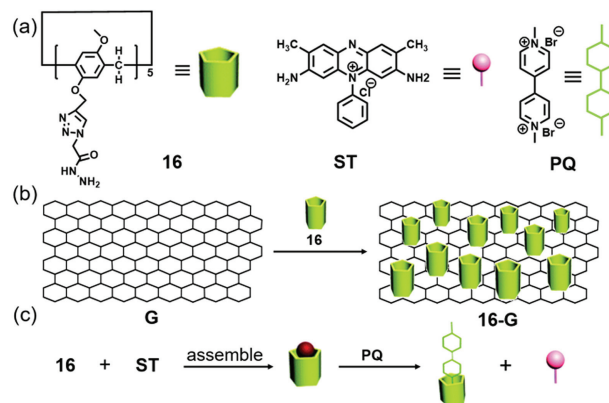
For sensor and separation materials, composites have been widely studied because of their excellent chemical stability, easy to functionalization and so on. Graphene is widely used in the sensor materials because of its unique two-dimensional single-layer structure. It has the characteristics of small volume, large surface area, and good biocompatibility, which can improve the performance of the sensors. This provides a new platform for the design of pesticide sensing and adsorption materials based on pillar[*n*]arenes.

Graphene has been widely used in the preparation of nano-fluorescent sensors [91,92]. For instance, Yang *et al.* reported a novel approach for the synthesis of 2D graphene nanosheet in water phase exfoliated by the water-soluble phosphate pillar[6]arene (**14**) [75]. This method was environmentally friendly and the obtained graphene nanosheets were stable. The obtained **14**@graphene maintained the integrity of graphene crystal and improved the dispersion of graphene in water. Acridine orange (AO) is a fluorescent pigment with strong fluorescence. Upon the addition of **14**@graphene into AO solution, with the increasing of **14**@graphene concentration, the fluorescence intensity of AO decreased, which indicated that AO molecules entered the cavity of **14**@graphene. Then PQ was gradually added to this system, and with the continuous addition of PQ, the fluorescence of AO gradually recovered and the fluorescence intensity was related to the concentration of PQ. In this process, AO first entered the cavity of **14** to form **14** ⊃ AO complex, and then PQ entered the cavity due to the competitive relationship, meanwhile, the AO was released from the cavity (Fig. 11), which induced a fluorescence "on-off-on" response. This competitive host-guest recognition provides a method to detect PQ with low detection limit.

The host-guest recognition ability of phosphorylated pillar[5]arenes is very excellent, which supplied a way for pillar[5]arenes-based materials improving the selectivity and sensitivity for PQ [93,94]. Tan and co-workers described a competitive fluorescence sensing platform based on water-soluble phosphate pillar[5]arene (**15**), which could be used to determine PQ [76]. The introduction of phosphoric acid group into pillar[5]arene could increase the water solubility of pillar[5]arene and improve the sensitivity of PQ detection. The receptor (**15**-rGO) was obtained by



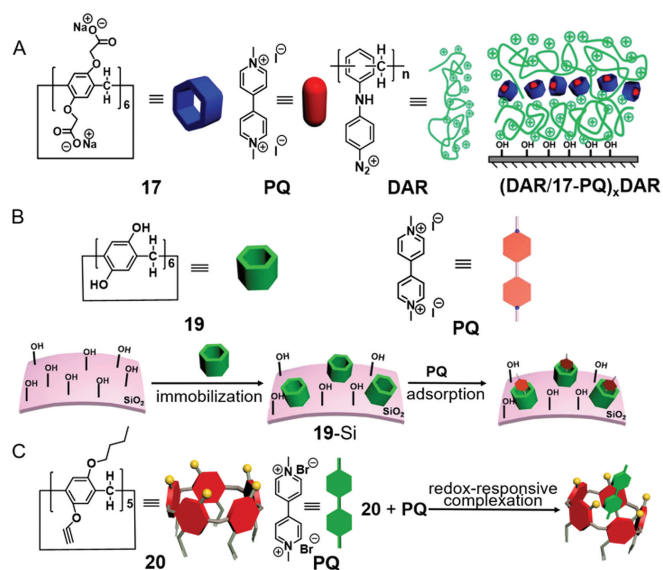
**Fig. 12.** (a) The molecular structure and cartoon representation of ST, PQ and **15**; (b) The illustration of **15**-rGO nanohybrids-based fluorescent sensing method towards PQ.



**Fig. 13.** (a) The molecular structure of **16**, ST and PQ; (b) Schematic diagram of loading **16** onto graphene; (c) Cartoon representation of interaction between **16** and PQ. Reproduced with permission [77]. Copyright 2016, Royal Society of Chemistry.

connecting **15** to the surface of reduced graphene (rGO) by  $\pi$ - $\pi$  stacking. The indicator dye safranin T (ST) (strong fluorescence) first bound to the receptor **15**-rGO and forming ST@-15-rGO, in this process, ST entered the cavity of **15** and fluorescence quenched (turn-off). Then the competitive PQ was added to the sensing ensemble. Due to the competitive relationship between the objects, ST came out of the cavity of **15** and PQ entered, in the meantime, ST fluorescence turn-on. Therefore, PQ was successfully determined by a competitive fluorescence method based on host and guest competitive recognition (Fig. 12). The sensor system has great application space in detecting PQ in tap water and lake water samples.

Graphene can be used as an "turn on" fluorescent probe to detect biomolecules in cells [95,96]. Li research group synthesized hydrazino-pillar[5]arene (**16**) [97] functionalized graphene (**16**-G), which could be used as a fluorescent sensor to detect PQ in living cells [77]. The hydrazine group could be used as a fixing unit. After adding safranin T (ST) to **16**, **16** could bind ST and ST fluorescence quenching (Fig. 13). After addition of PQ, ST was released and PQ combined with **16**. It indicates that **16** has a better affinity for PQ. In this process, ST fluorescence on. This process accompanied with a phenomenon of fluorescence "off" to "on". This can be used to fluorescent "turn on" detection PQ. Graphene based materials can



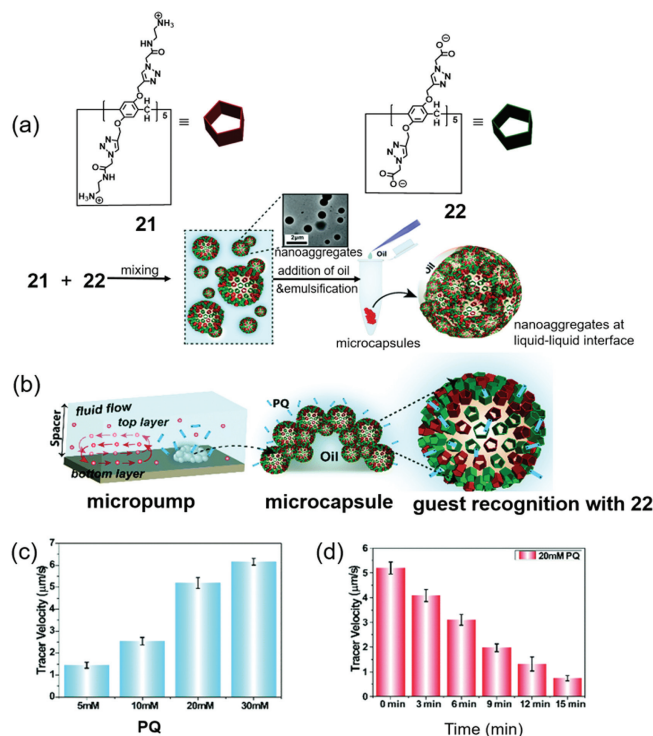
**Fig. 14.** (A) Schematic representation of  $(\text{DAR}/17\text{-PQ})_x\text{DAR}$  multilayer films and the structures of the building blocks for the layer-by-layer assembly. Reproduced with permission [103]. Copyright 2016, American Chemical Society. (B) Schematic illustration of the immobilization of **19** onto silica surfaces and the adsorption of PQ by the hybrid materials in an aqueous solution. Reproduced with permission [78]. Copyright 2015, American Chemical Society. (C) The molecular structure of **20** and PQ and cartoon representation of redox-responsive complexation between **20** and PQ.

be effectively transported to living cells, which has a good application prospect in the detection of PQ in living cells, and provides a novel idea for the detection in living cells [98].

For composites, silica and silica gel are good substrates. Layer by layer (LBL) assembly has been widely used to construct multilayers composites [99–102]. Zhang *et al.* synthesized pillar[6]arene (**17**)-containing multilayer films  $(\text{DAR}/17\text{-PQ})_x\text{DAR}$  [103]. Among them, the part providing negative charge is specially treated silica. Then, multilayer films with artificial binding sites were prepared by removing PQ. The host molecule **17** acted as a very stable binding site in the polymer layer environment with its rigid structure. The films showed good molecular absorption and release properties and selectivity to PQ molecules (Fig. 14A). In addition, the conditions could be controlled so that the absorption and release of PQ by the multilayer film were reversible. It can be reused when PQ was removed. Therefore, this film has a potential application prospect in the separation of PQ.

Yang *et al.* immobilized hydroxyl functionalized pillar[5]arene and pillar[6]arene (**18** and **19**) onto the chlorinated surface of silica supports, to form organic-inorganic hybrid materials **18**-Si and **19**-Si (Fig. 14B). Pillar[*n*]arenes without additional modification usually have poor solubility [78]. Loading it on the silicon surface could increase its solubility. Due to host-guest interaction, this material had specific adsorption capacity for PQ. Moreover, due to the influence of cavity size, the adsorption effect of **19**-Si was more obvious than that of **18**-Si. So, pillar[*n*]arenes-silica hybrid materials has potential application in separating PQ and other harmful substances from aqueous phase.

Li *et al.* created tiltable pillar[5]arene (**20**)-modified silicon surface, the alkynyl group at the lower end of **20** can be connected to the silicon surface and this silicon surface can simulate the surface of leaves [104–106]. Through the interaction between the host **20** and guest PQ, the PQ droplets selectively and dynamically self-assembled to the silicon surface (Fig. 14C) [107]. This work can effectively reduce the use of PQ and is expected to quickly detect PQ in environmental monitoring.



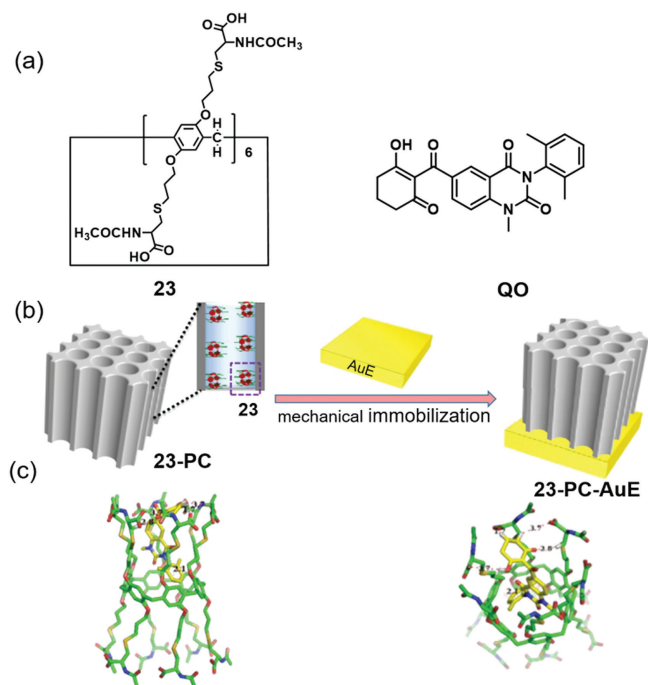
**Fig. 15.** (a) Schematic illustration for the formation of pillar[5]arene microcapsules; (b) Graphical representation of “host-guest” micropump; nanoaggregate stabilized MCs inside the chamber turn on fluid flow in presence of PQ; (c) Tracer velocity increases with increasing “guest” concentration; (d) Temporal velocity of tracer particles in presence of 20 mmol/L PQ. Reproduced with permission [111]. Copyright 2020, Royal Society of Chemistry.

Developing pillar[*n*]arenes-based composites is an efficient way to enhancing the stability, increasing the adsorption efficiency and raising detection sensitivity of pesticides detection and separation materials. Due to the high stability, this kind of materials show good reusability. They have a good application prospect in the removal of pesticides.

## 6. Nanomaterials containing pillar[*n*]arenes

Nanomaterials have the characteristics of large specific surface area, many active sites and stable structure. These characteristics provide opportunities for the detection and removal of pesticides. Self-powered microengine mimicking the biological machineries [108] are new type of intelligent device with wide application prospects in sensing [109] and drug delivery [110]. Patra and Joseph *et al.* reported the fabrication of cationic and anionic pillar[5]arenes (**21**, **22**) stabilized microcapsules *via* self-assembly and crosslinking of cationic **21** and anionic **22** nanoaggregates at liquid-liquid interface [111]. Due to “host-guest” molecular recognition, these microcapsules microengines turned on fluid flow in the presence of PQ (Fig. 15). The fluid velocity was increased with increasing PQ concentration. It will open up a new avenue for the development of next generation microcapsules for application like capture and release of micropollutants and other hazardous species such as PQ.

In recent years, nanoporous sensors have become a research hotspot due to their excellent selective recognition ability and amazing sensitivity to analytes [112–114]. Li and Sun *et al.* synthesized *N*-acetylcysteine-decorated pillar[6]arene (**23**) and it was modified on the surface of nanoporous polycarbonate (PC) film (**23**-PC) [79]. Finally, **23**-PC was pressed on the surface of gold electrode to prepare two kinds of nanopore sensors (**23**-PC-AuE) with

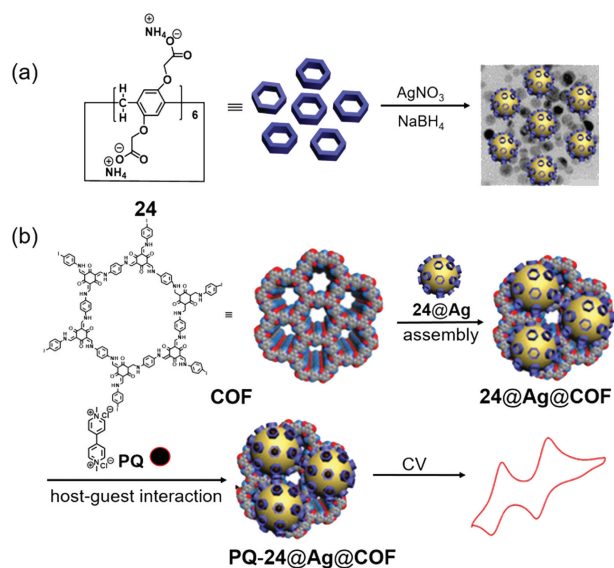


**Fig. 16.** (a) The molecular structures of **23** and QO. (b) Schematic diagram of nanoporous electrode based on **23**. (c) Calculated geometries for the interaction between **23** and guest molecules. Reproduced with permission [79]. Copyright 2021, American Chemical Society.

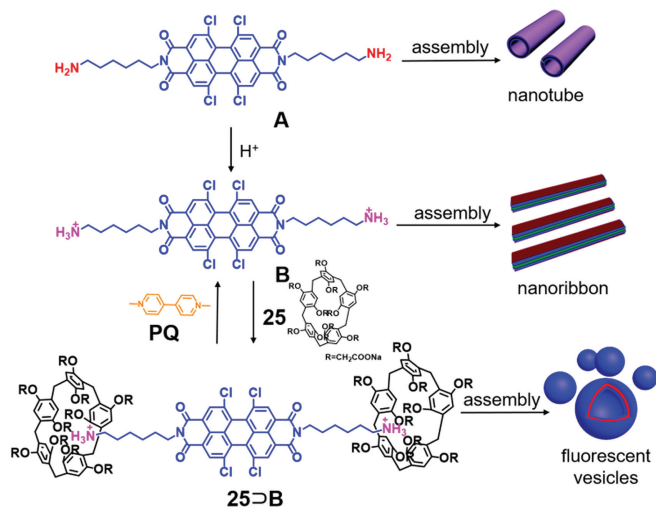
different pore diameters (200 nm, 400 nm). This sensor could selectively detect the pesticide QO (Fig. 16). Moreover, the nanopore sensor with smaller pore diameter had higher sensitivity to detect QO. That was because the synergetic effects of the increased double layer overlap in smaller nanopores, creating enrichment of the nanopores' interior. This nanoporous sensor has potential applications in detecting trace amounts of QO.

Metal functionalized covalent organic framework (COF) is a hot topic in recent years. It can be used as an effective heterogeneous material and has a wide range of applications in catalysis and energy storage [115–117]. Zhao and Tan *et al.* reported a novel pillar[6]arene (**24**)-modified Ag nanoparticle (**24@Ag**)-functionalized two-dimensional (2D) COF hybrid material (**24@Ag@COF**), which had high recognition capability for electrochemical detection of PQ, as shown in Fig. 17 [80]. It had been successfully applied to the detection of PQ, and had high sensitivity (the lowest detection limit is  $1.4 \times 10^{-8}$  mol/L) and selectivity. The formed COF structure had good porosity and high surface area, which was a key factor to improve the sensitivity of PQ identification. This is the first report of a heterogeneous-functional composite material between COF pillar[*n*]arenes and Ag nanoparticles. This functional material has broad application prospects in the detection of PQ.

Amphiphilic molecules have attracted extensive attention because they can self-assemble into dynamic soft materials in water [118]. Perylene bisimide is widely used in materials because of its excellent properties. Yao and Sun *et al.* synthesized a hexamethylenediamine functionalized tetrachloropyrene bisimide (**A**), which can self-assemble to form nanotubes in aqueous solution. The addition of  $H^+$  to a protonated the amino group to form compound **B**, which can be self-assembled into single-layer nanoribbons (weak fluorescence). Then, water-soluble pillar[5]arene (**25**) were added to **B**, due to the interaction between host and guest, **B** complexed with **25** to form a fluorescent vesicle **25**⊃**B** (strong fluorescence) [119]. After adding PQ into **25**⊃**B** system, the vesicle structure was destroyed and the fluorescence was quenched



**Fig. 17.** (a) The synthetic route of COF and assembly of **24**-modified Ag nanoparticles on the surface of COF; (b) Its application for electrochemical sensing of PQ. Reproduced with permission [80]. Copyright 2019, American Chemical Society.



**Fig. 18.** Chemical structures and cartoon representations of hexamethylenediamine functionalized tetrachloropyrene bisimides **A**, **B**, PQ, and **25**. Reproduced with permission [119]. Copyright 2017, Royal Society of Chemistry.

(Fig. 18). This is because the complexation constant between **25** and PQ is greater than that between **25** and ammonium group in water [120]. This process can be applied to the ultrasensitive detection of PQ in water.

Pillar[*n*]arenes-based nanomaterials show special merits on water solubility and high sensitivity. It supplies a good opportunity to developing feasible materials for ultrasensitive detection pesticides in water and biosystems.

## 7. Conclusions and outlook

In brief, this review summarizes the recent progress on application of pillar[*n*]arenes to developing novel materials for the detection and separation of highly toxic pesticides such as PQ. Due to its electron rich cavity structure and abundant intermolecular interactions, pillar[*n*]arenes show nice binding ability for some pesticide molecules. This review summarize and discuss the structure-activity relationship of pillar[*n*]arenes-based materials for detection and separation pesticides through pillar[5]arene,

pillar[6]arene, mutli-pillar[n]arenes, pillar[n]arenes-based polymers, frameworks, composites and nanomaterials. The application property of pillar[n]arenes-based materials can be tuned by using different pillar[n]arenes with different cavity size, employing synergistic effect through mutli-pillar[n]arenes or by constructing different materials such as frameworks, composites and nanomaterials. Through corresponding methods, the detection selectivity and sensitivity as well as adsorption efficiency of these pillar[n]arenes-based materials could be improved. However, there are still many challenges in this field.

- (1) How to develop high-order pillar[n]arenes for the detection and separation of some large pesticide molecules is an interesting challenge.
- (2) Developing pillar[n]arenes-based pesticide antidote is an important and urgent task.
- (3) How to increase the detection sensitivity and the separation efficiency for pesticide through the synergy between pillar[n]arenes and other functional groups remains a lot of research space.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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