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Mini Accounts

# Self-Assemblies Based on Perylene Bisimides and Macrocyclic Hosts

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**Abstract** Perylene bisimides (PBIs) and its derivatives, a robust class of *n*-type organic materials, have attracted intense interest because of their intriguing π···π stacking and outstanding optoelectronic properties. The construction of well-defined nanoscopic supramolecular architectures through combining macrocyclic hosts and PBIs is a fascinating topic of interdisciplinary researches on chemistry, materials science, and nanotechnology, which is expected to gain new nano-materials with unique electronic and photonic properties. In this mini review, we mainly summarize our recent progresses in directing the formation of the desirable PBI superstructures through introducing macrocyclic hosts into PBI systems by covalent or non-covalent methods. The combination of macrocyclic hosts and PBIs may not only modulate photophysical behaviors of PBIs but also endow corresponding assemblies with novel physicochemical properties, which show a wide range of intriguing applications in sensory materials and optoelectronic devices. Thus, these researches extend the construction of desired functional supramolecular architectures from PBI building blocks. It is hopeful that this review can provide a sophisticated pathway for further designing fascinating PBI-macrocyclic systems.

**Key words** self-assembly; supramolecular architectures; perylene bisimides; macrocyclic hosts; non-covalent force; π···π stacking

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## 1 Introduction

In recent years, fabricating well-defined nanoscopic supramolecular architectures from extended aromatic building blocks has been one fascinating topic of interdisciplinary researches including chemistry, life science, material science, and nanotechnology, which is expected to gain new self-assembled materials with unique electronic and photonic properties benefiting from the excitonic interactions between adjacent aromatic units[1—4]. Among such building blocks, perylene bisimides (PBIs) and its derivatives, a robust class of *n*-type organic materials, have attracted intense interest because of their strong π…π stacking and outstanding optoelectronic properties[5—7]. Therefore, various PBI derivatives have been employed to construct nanoscopic supramolecular architectures, which have shown a wide range of intriguing applications, including liquid crystals, organogels, artificial light harvesting systems, organic electronic devices, vapor sensing materials, and so on[8,9]. To direct the formation of the desirable superstructures, several non-covalent forces have been developed, such as π…π stacking, hydrogen bonding, coordinative bonding and ionic interactions[5,10—13]. Besides these conventional forces, another specific assembling strategy, introducing macrocyclic hosts into PBI systems, has also been explored by covalent or non-covalent methods[14—36].

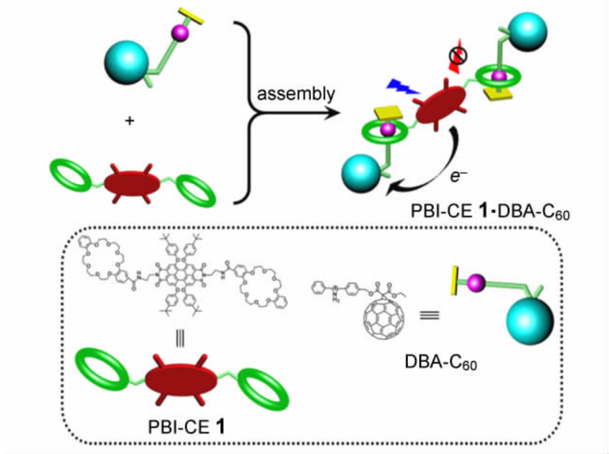
Macrocyclic chemistry has expanded phenomenally since the synthesis of crown ethers (CEs) and the discovery of their complexing properties toward alkali metal cations in 1967[37]. The award of the 1987 Nobel Prize in Chemistry to Pedersen, Lehn, and Cram is a testimony to the importance of this rapidly expanding field. Along with the development of macrocyclic chemistry, a variety of macrocyclic hosts have been devised, which have been extensively used in the recognition and self-assembly[38,39]. Especially, the conventional macrocyclic hosts, such as CEs[40—43], cyclodextrins (CDs)[44—47], calixarenes (CAs)[48—51], and cucurbit[*n*]uril (CB[*n*])[52,53], have been successfully employed as building blocks to construct various functional supramolecular architectures, because of their unique cavity-shaped architectures and preorganized binding sites. Therefore, it is valuable to attempt the combination of PBIs and macrocyclic hosts to fabricate various PBI supramolecular architectures, which may not only modulate photophysical behaviors of PBIs but also endow corresponding assemblies with novel physicochemical properties.

Along this line, our laboratory, as well as others, have been engaged for several years in the design and construction of novel functional PBI supramolecular architectures based on PBI-macrocyclic systems. This mini review mainly addresses our recent progresses in exploring PBI-macrocyclic systems, however, in order to comprehensively describe this field, a quantity of correlative works reported by others are also contained. And it is described in four principal sections: (1) self-assemblies and properties of PBI-CE systems; (2) self-assemblies and properties of PBI-CD systems; (3) self-assemblies and properties of PBI-CA systems; (4) self-assemblies and properties of PBI-CB systems. It is hopeful that this review can simultaneously provide valuable and inspiring guidelines for further designing fascinating PBI-macrocycle systems in the future.

## 2 PBI-CE systems

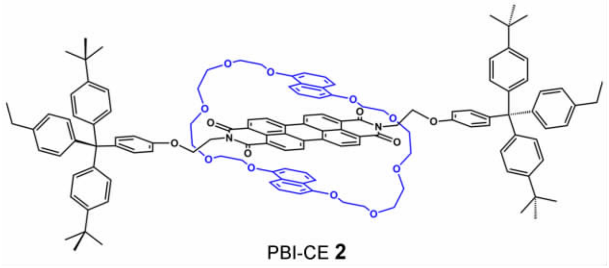
Since the seminal work of Pedersen on CEs in 1967[37], CEs have grown into a field that is undergoing explosive development by a number of groups around the world, because of their unusual abilities to bind cations in a selective fashion[40—42]. For example, it attracts increasing attention over the past two decades that constructing stimuli-responsive supramolecular polymers from CE-based low molecular weight monomers[54—56]. The researches combining PBIs and CEs have also been performed, which are mainly based on the remarkable fluorescence properties of PBIs and excellent binding abilities of CEs to cations[14—19]. For example, Gong and co-workers reported that novel red-light emitting PBI fluorophores with CE units exhibit ionophoric characteristics for various metal ions, resulting from the photo-induced charge transfer (PCT) process[16,17]. The other typical example is that the highly hydrophobic PBIs with the hydrophilic CE substituents can lead to the formation of fluorescent colloidal dyes in water, which is of general interest for scientific applications and avoids the occurrence of sedimentation and flocculation in general dyes[15].

In 2010, we synthesized a PBI-bridged bis-(dibenzo-24-CE-8) molecule (PBI-CE **1**) and a fullerene-modified secondary dibenzylammonium cation (DBA-$C_{60}$), and further constructed a pseudorotaxane system PBI-CE **1**·DBA-$C_{60}$ through complexation of PBI-CE **1** with DBA-$C_{60}$ (Scheme 1)[18]. The binding behavior and photophysical behavior of the obtained PBI-CE **1**·DBA-$C_{60}$ have been investigated by $^1$H NMR and fluorescence spectra. The changes of $^1$H NMR spectra validated formation of PBI-CE **1**·DBA-$C_{60}$ and gave a clear insight into the complex structure between PBI-CE **1** and DBA-$C_{60}$. Meanwhile, the fluorescence intensity of PBI-CE **1** was gradually quenched upon increasing the concentration of DBA-$C_{60}$, which revealed occurrence of a photoinduced electron transfer (PET) between PBI-CE **1** and DBA-$C_{60}$. Furthermore, in view of the binding characteristics of CEs to metal ions, a reversible fluorescence test of PBI-CE **1**·DBA-$C_{60}$ was performed by the alternating addition of $K^+$ or 18-CE-6. When $K^+$ was added to the solution of PBI-CE **1**·DBA-$C_{60}$, the fluorescence quenching of PBIs was restored (91%). To check the reversibility of this process, 18-CE-6 was then added to the resultant solution and the fluorescence quenching was reproduced again, demonstrating that the fluorescence of PBI-CE **1**·DBA-$C_{60}$ can be switched in a reversible manner by external chemical stimuli.



**Scheme 1**　Schematic representation of formation of pseudorotaxane PBI-CE **1**·DBA-$C_{60}$ and its PET process

In 2011, Champness and co-workers also successfully synthesized a [2]-rotaxane PBI-CE **2** by the utilization of PBIs and the naphthyl-based CE (Scheme 2), where the PBI moiety acts as a recognition site for complexation of the CE unit[19]. Importantly, the switchable states of [2]-rotaxane PBI-CE **2** can be controlled by its redox processes. One-electron reduction of PBI-CE **2** leads to the formation of a radical anion based [2]-rotaxane, representing a switchable state of PBI-CE **2**. The second reduction of PBI-CE **2** initiates a dethreading process in the [2]-rotaxane, presumably as a result of electrostatic repulsion between the electron-rich CE and the reduced PBI recognition site.



**Scheme 2**　Chemical structure of [2]-rotaxane PBI-CE **2**

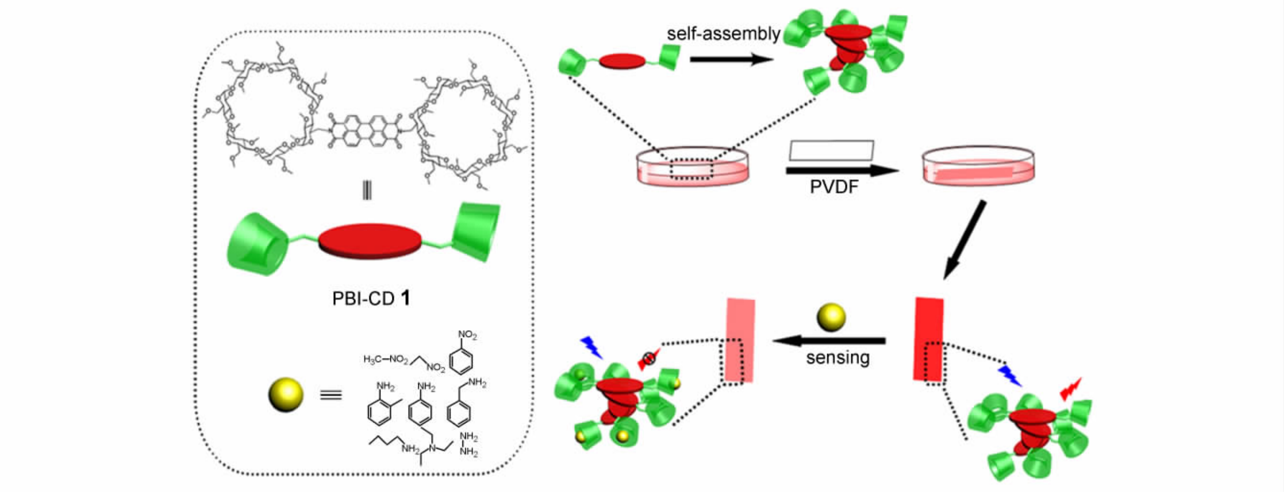
## 3　PBI-CD systems

CDs, a class of cyclic oligosaccharides with 6—8 D-glucose units linked by α-1,4-glucose bonds, have been extensively investigated in molecular recognition and construction of various well-defined nanostructures[44—47]. By virtue of both the outstanding optoelectronic properties of PBIs and unique molecular recognition as well as self-assembly properties of CDs, the introducing CDs into the PBI motifs was also performed, which led to interesting assembly behaviors and remarkable optoelectronic properties, making potential candidates for applications in optoelectronic devices and optical sensors[20—26]. The corresponding works will be detailedly presented in this section.

### 3.1　Assemblies of PBI-CD conjugates as solid-state fluorescence sensors for vapor detection

In 2008, Zang and co-workers employed PBI derivatives as a new electron-acceptor type of fluorescence sensory material for vapor probing of organic amines based on π…π aggregation, which extended the application of PBIs to the field of the solid-state optical sensing[57]. However, it still remains a severe challenge to be addressed that selectively detecting and distinguishing a given gaseous amine from other analogues, due to the lack of specialized binding sites in sensory materials, which may be overcome by the introduction of well-defined receptor sites into building sensory materials, such as CDs.

With this consideration in mind, in 2009, we fabricated a nanoscopic supramolecular assembly from a PBI-CD conjugate (PBI-CD **1**) and explored its sensing behaviors for several kinds of organic vapors (Scheme 3)[20]. The aggregation behaviors of PBI-CD **1** in different solvents were primarily studied, which pronounced π…π aggregation of PBI-CD **1** was observed in water. A moderately strong aggregation constant of PBI-CD **1** in water was further obtained as $K_{agg} = 7.3 \times 10^4\ M^{-1}$ using a nonlinear least-squares regression analysis of the concentration-dependent UV-Vis spectral data by the isodesmic or equal-K model. On the basis of its aggregation characteristics in solutions, the solid-state packing behavior of PBI-CD **1** was investigated. From the X-ray powder diffraction (XRD) measurement, we obtained a π…π stacking distance (4.02 Å) of PBI-CD **1** that is larger than the common π…π stacking distance (3.50 Å) of PBI derivatives, ascribed to the steric hindrance of the permethyl-β-CD grafts. The morphology of the obtained supramolecular assembly was further studied by both transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images, showing a well-ordered 1D nanorod structure. As one of the necessary prerequisites to turn into fluorescence sensory materials, the 1D nanorod assembly of PBI-CD **1** exhibits strong red fluorescence as depicted in the fluorescence microscopy image. Furthermore, to investigate the solid-state fluorescence sensing behaviors for organic vapors, the assembly of PBI-CD **1** was embedded in the poly (vinylidenefluoride) (PVDF) membrane. The results of the vapor detection showed that the assembly of PBI-CD **1** can exhibit high sensitivity to organic amines, which can be attributed to PET from the reducing amines to the excited state of PBIs. However, compared to the previous report[57], the analytes of general organic solvents and nitro-based compounds can also lead to the fluorescence quenching of PBIs, owing to that weak aggregation capability of PBI-CD **1** makes the well-ordered π…π aggregation of PBI backbones easily disturbed by inclusion of analytes into the CD cavity. Thereby, the fluorescence of CD-PBI **1** in the vapor sensing process can be quenched by two factors: one is the PET from analytes to PBIs; the other is that encapsulation of analytes disturbs the π…π stacking of PBIs. The steric hindrance of the permethyl-β-CD grafts to the π-stacking of PBIs is an unfavorable factor for the vapor detection of PBI-CD **1**.



**Scheme 3** Schematic illustration of the vapor sensing process of the PVDF-embedded PBI-CD **1**

In order to avoid the steric hindrance of CDs to the π-stacking of PBIs, PBI-CD **2** with the elongation of spacers between CDs and PBIs (Fig. 1) was synthesized[23], which exhibits much stronger aggregation capability relative to PBI-CD **1**, demonstrated by both the aggregation constant ($K_{agg} = 2.1 \times 10^6\ M^{-1}$) and $\pi \cdots \pi$ stacking distance (3.34 Å) of PBI-CD **2**. Stronger π-stacking not only prevents encapsulation of analytes from disturbing the $\pi \cdots \pi$ stacking of PBIs, but also promotes facile exciton migration to be effectively disturbed by less occupation of integrated receptor units, enabling amplification in fluorescence quenching. Prior to sensing studies, the aggregate of PBI-CD **2** was embedded in the PVDF membrane and a benign solid-state emission was observed. The vapor sensing results showed that the anti-interference capability of PBI-CD **2** is dramatically improved in contrast to PBI-CD **1** (Fig. 1), because the compact π-stacking of PBIs can hardly be disturbed by the entrapment of common organic reagents. Moreover, from the sensing results for the saturated vapors of various amines (Fig. 1), PBI-CD **2** exhibits high selectivity to aniline, benefiting from both the stronger binding affinity of CDs for aniline and more effective PET efficiencies between PBIs and aniline compared with other amines. It is the first time that fluorescence response of solid-state sensory materials has been successfully used to distinguish various amines. In previous works from Zang and our groups[20,57], amine analogues always gave rise to extremely similar responses. Furthermore, an satisfactory detection limit of PBI-CD **2** for aniline (as low as 80 ppb) can be obtained, thanks to the amplification effect endowed by the aggregation of PBI-CD **2**. Especially, the thermodynamically reversible host-guest inclusion of CDs leads to the excellent sensing reversibility of PBI-CD **2** for aniline. Therefore, in comparison of results based on PBI-CD **1**, the PBI-CD **2** system achieves pronounced improvements of selectivity, sensitivity, and reversibility.

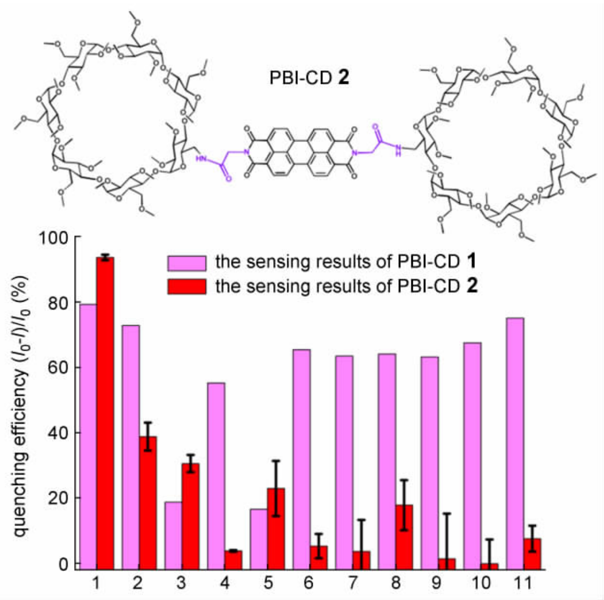
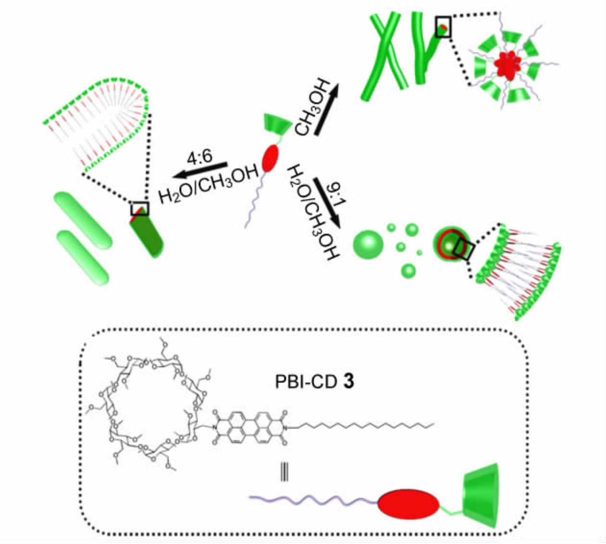


**Fig. 1** The chemical structure of PBI-CD **2** and fluorescence response of the PVDF-embedded PBI-CD **1** and PBI-CD **2** to the saturated vapors of various amines, nitro-based compounds, and general organic solvents with response time of 10 s: 1, aniline; 2, butylamine; 3, benzylamine; 4, triethylamine; 5, hydrazine hydrate; 6, toluene; 7, methanol; 8, chloroform; 9, nitromethane; 10, nitroethane; 11, acetonitrile. Error bar: standard deviation

As parts of our ongoing program concerning supramolecular assemblies of PBI-CD conjugates as solid-state fluorescence sensors for vapor detection, in 2010, the solid-state fluorescence sensing behaviors based on different aggregation morphologies were also comparatively studied by employing an asymmetrical, amphiphilic PBI-CD conjugate (PBI-CD **3**), which was synthesized by grafting a permethyl-β-CD at one side and an octadecyl chain at the other side[21]. Differing from PBI-CD **1** and PBI-CD **2**[20,23], PBI-CD **3** does not dissolve in pure water, possibly because of two factors: one is the unfavorably hydrophobic effect of long alkyl chain, and the other is the very strong π-stacking ability of PBI backbone in water. Therefore, the aggregation behaviors of PBI-CD **3** were investigated in water/methanol binary solvents with different volume ratios. With increase of water components from 0∶0 to 9∶1, the UV-Vis changes of PBI-CD **3** indicated the occurrence of more and more strong aggregation. A special case appeared in 4∶6 water/methanol where PBI-CD **3** is precipitated from mother liquor. Meanwhile, a significant color change of fluorescence takes place, with yellow emission in pure methanol and red emission in 9∶1 water/

methanol, implying the formation of oligomer aggregate upon increase in water components. The morphologies of PBI-CD **3** in different solvents were studied by TEM and SEM measurements, which the solvent-dependent morphological changes of PBI-CD **3** are found. PBI-CD **3** shows nanorod aggregation in pure methanol, chunky nanostructure in 4∶6 water/methanol, and spherical morphology in 9∶1 water/methanol, as illustrated in Scheme 4. Furthermore, the differently morphological aggregates of PBI-CD **3** were embedded in PVDF membrane and employed as the solid-state fluorescence sensors for organic amine vapors (Fig. 2), which appreciable difference of the solid-state fluorescence sensing results was observed due to the distinguishable aggregation states. For most substrates, the fluorescence quenching of the PBI-CD **3** from 9∶1 water/methanol is more pronounced than that of the PBI-CD **3** from methanol, exhibiting better sensitivity. It can be reasonably interpreted as that stronger π…π interaction of the PBI-CD **3** from 9∶1 water/methanol enables more notable amplification in fluorescence quenching. Moreover, comparing the sensing results of the PBI-CD **3** from 9∶1 water/methanol with those of PBI-CD **1**, we found that the background interference of common organic reagents is effectively inhibited, ascribed to that stronger π…π interaction of the PBI-CD **3** from 9∶1 water/methanol more effectively prevents the inclusion of analytes into the CD cavities from altering the π-stacking of PBIs than that of PBI-CD **1**.



**Scheme 4** Schematic illustration of assembly models of PBI-CD **3** in water/methanol mixed solvents with various compositions.

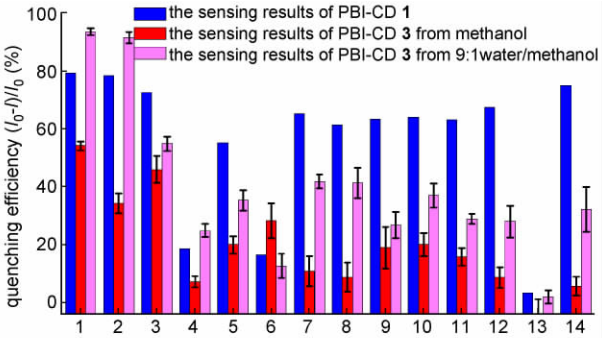
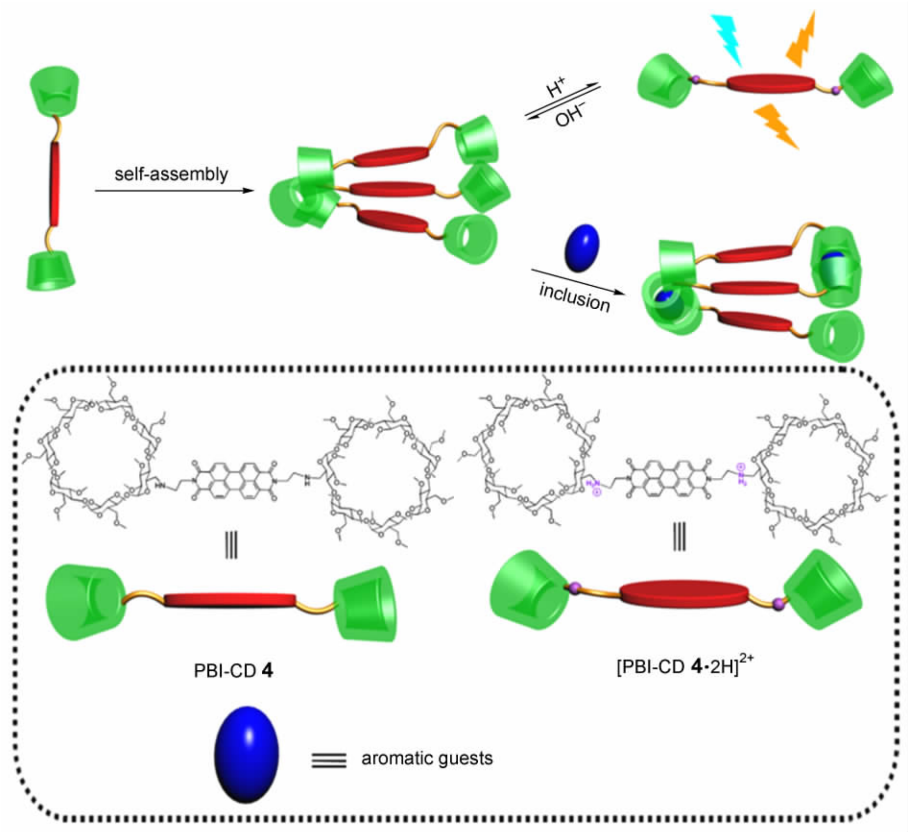


**Fig. 2** Fluorescence response of PBI-CD **1** and PBI-CD **3** to the saturated vapors of various amines, nitro-based compounds and general organic solvents with a response time of 10 s: 1, aniline; 2, *o*-methyl-aniline; 3, butylamine; 4, benzylamine; 5, triethylamine; 6, hydrazine hydrate; 7, toluene; 8, chlorobenzene; 9, methanol; 10, chloroform; 11, nitromethane; 12, nitroethane; 13, nitrobenzene; 14, acetonitrile. Error bar: standard deviation

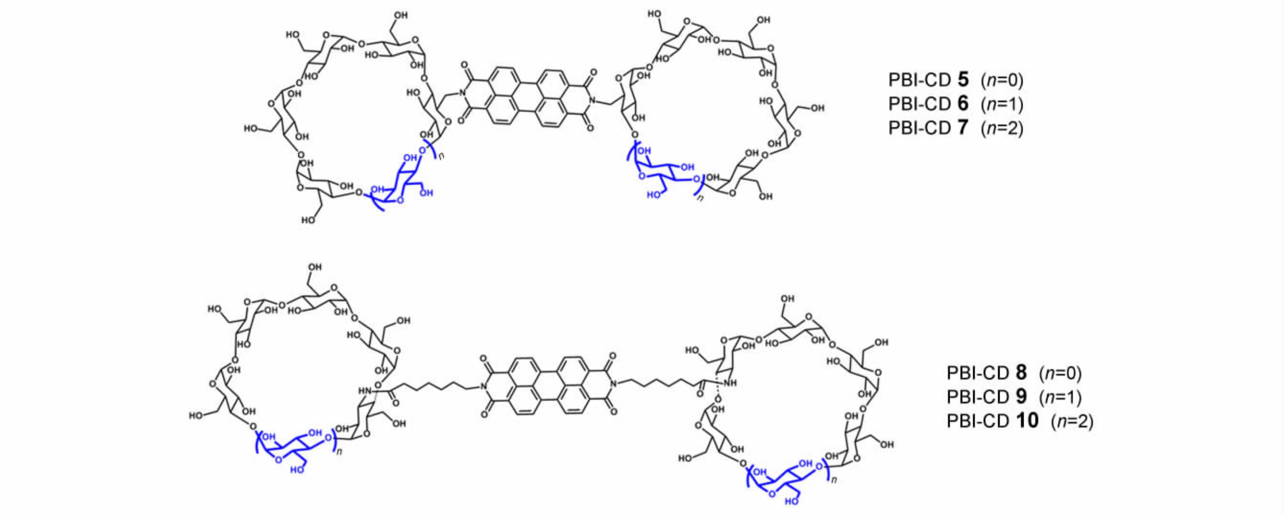
### 3.2 The modulation of molecular aggregation behaviors and fluorescence properties of PBI-CD conjugates

It is well-known that creating adaptive systems, whose structures and functions can be manipulated by external stimuli, is one extraordinarily fascinating topic in the field of supramolecular chemistry[58—60]. However, to date, the regulation of aggregation and disaggregation of PBIs has received much less attention, due to lack of effective stimulation methods[61]. With the exception of focusing the assemblies of PBI-CD conjugates on the solid-state fluorescence sensing for organic amine vapors, we also exploited the aggregation behaviors and fluorescence properties of PBI-CD conjugates to be tuned in aqueous solution, such as PBI-CD **4** (Scheme 5)[22], which shows much stronger π…π stacking in water than the organic solvents as the same as other PBI-CD conjugates[20,21,23]. The most attractability of PBI-CD **4** is its ionization equilibrium of the imino groups in aqueous solution, which may assume either the intrinsically neutral form PBI-CD **4** or the protonated dicationic form [PBI-CD **4**·2H]$^{2+}$. Thereby, the pH changes will extraordinarily influence over the aggregation behaviors of PBI-CD **4**. The experiment results verified that the aggregation ability of PBI-CD **4** in the neutral form is nearly 1 order of magnitude stronger than that of [PBI-CD **4** · 2H]$^{2+}$ in the protonated form, because the electrostatic repulsion between the protonated imino groups plays a certainly unfavorable role in the π⋯π stacking of PBI backbones. Moreover, both the monomer and oligomer of [PBI-CD **4**·2H]$^{2+}$ exhibit stronger fluorescence than those of PBI-CD **4**, ascribed to the effective inhibition of the intramolecular electron transfer process from the imino groups to the PBI backbones. Furthermore, by virtue of the binding sites of grafted CDs, the hierarchical self-assembly of PBI-CD **4** was investigated via inclusion of a series of aromatic guests, clearly showing electronic interactions between PBI backbone of PBI-CD **4** and 1-pyrenebutyric acid sodium salt, as well as 2-anthracenecarboxylate sodium salt.



**Scheme 5**　Schematic illustration of pH-dependent assembly models of PBI-CD **4** and the possible complex formation between PBI-CD **4** and aromatic guests

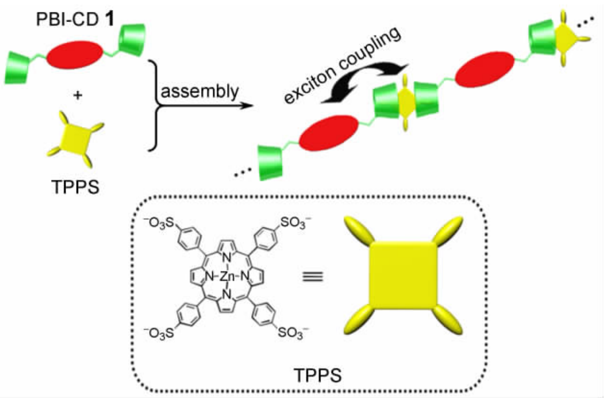
In 2012, Harada and co-workers reported another example of adaptive systems based on PBI-CD conjugates that specific emission properties are achieved, which depend on the type of CDs[25]. PBI-CD **5**, PBI-CD **6**, and PBI-CD **7**, in which the native α, β, and γ-CD units are directly introduced into the PBI units in the narrow rims of CDs without spacers (Scheme 6), respectively, do not show different emission with the type of CD units in aqueous solution. However, among the PBI-CD **8**, PBI-CD **9**, and PBI-CD **10** in which the native α, β, and γ-CD units and PBI units are linked in the wide rims of CDs with spacers (Scheme 6), PBI-CD **9** displays a bright yellow emission and PBI-CD **10** has a weak emission in aqueous solution. The specific emission properties of PBI-CD **8**, PBI-CD **9**, and PBI-CD **10** can be interpreted as that appropriate size of CD nanocavity can effectively prevent self-aggregate and self-quenching of PBIs by encapsulating PBIs into CD nanocavity. Furthermore, polyvinyl alcohol (PVA) films woven with PBI-CD **8**, PBI-CD **9**, and PBI-CD **10** were prepared. Even in PVA films, they also show selective emission behaviors in a similar way to them in aqueous solution.



**Scheme 6** Chemical structures of various PBI-CD conjugates modified by native CDs

### 3.3 Photo- and electro-active assemblies based on PBI-CD conjugates

As a result of excellent optoelectronic properties of PBIs, PBIs and its derivatives have been widely used in the construction of interesting optoelectronic supramolecular systems, leading to various kinds of photo- and electro-active PBI assemblies[5,62]. In most of such supramolecular systems, the photo- and electro-active components are usually connected by covalent linkages, which synthetic procedures are complicated. And hence a convenient approach is to non-covalently link PBI units with other components. Recently, we constructed a novel supramolecular self-assembly of PBI-CD **1** and [5,10,15,20-tetrakis-(4-sulfonatophenyl) porphinato] zinc (Ⅱ) (TPPS) by exploiting strong binding ability of permethyl-β-CD to porphyrin through host-guest interactions, which strong excitonic interactions between PBI backbones and adjacent porphyrins are found in the ground state (Scheme 7)[24]. Combining the results of the Job's plot and dynamic light scattering (DLS), the binding stoichiometry of PBI-CD **1** with TPPS was postulated as *n*∶*n*. Furthermore, the complex structure of PBI-CD **1** and TPPS was determined by 2D NOESY spectroscopy, and obvious cross-peaks of the protons of the CD and porphyrin were observed, indicating that TPPS is deeply included into the cavity of PBI-CD **1**. Both resultant UV-Vis spectra and color changes of PBI-CD **1** upon addition of TPPS demonstrated the strong excitonic interactions between PBI backbones and porphyrins in the ground state. Moreover, the fluorescence of PBI-CD **1** upon addition of 2 equiv. TPPS is almost completely quenched due to a PET from porphyrin to excited PBIs. It can be therefore inferred that the presence of strong excitonic interactions between PBI backbones and adjacent porphyrins can endow supramolecular self-assembly of PBI-CD **1** and TPPS with application potentials in fabrication of photovoltaic cells and electrical data storage. In 2012, Chen and co-workers also reported an example of PBI-CD conjugate non-covalently assembling with single-walled carbon nanotubes (SWCNTs), which was further applied to detect 9-anthracenecarboxylic acid by electrochemical methods[26]. The results showed that the functional assembly is excellent sensing materials for the electrochemical determination of 9-



**Scheme 7** Schematic illustration of the assembly model of PBI-CD **1** and TPPS

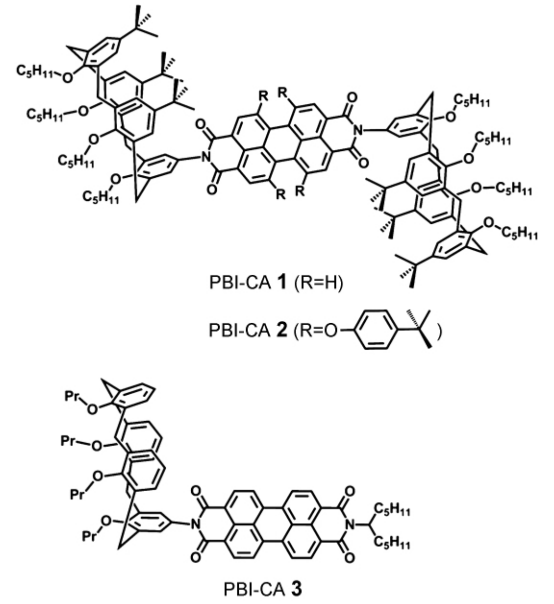
anthracenecarboxylic acid.

## 4 PBI-CA systems

CAs, as the third generation of supramolecular macrocyclic hosts, possess three-dimensional, flexible, π-election rich cavities, which have been extensively used as versatile scaffolds to organize various desired dye functionalities such as nonlinear optical dyes, electrophores, and fluorophores[63,64]. To utilize these outstanding properties, the introduction of CAs into PBIs has been reported, and we will detailedly describe recent progresses in this field.

### 4.1 Properties of PBI-CA conjugates

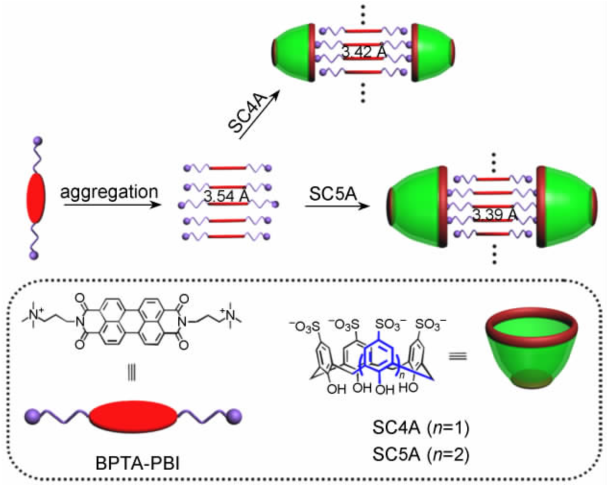
The combination of CAs and PBIs by covalent linkages generated a kind of interesting supramolecular systems, where both lifetimes and quantum yields of the attached PBI chromophores dramatically change upon substitution of the CA units because of PET process from CAs to PBIs[27—34]. In 2002, Böhmer and co-workers reported two PBI-CA conjugates (PBI-CA **1** and PBI-CA **2**) that connect CA units with PBI units via imide linkages in the wide rim of CAs (Scheme 8), which fluorescence of PBIs is distinctly quenched, because the electron-rich CAs in PBI-CA **1** and PBI-CA **2** act as fluorescence quenchers, most probably via PET from CAs to PBIs[27]. After that work, in order to more deeply study photophysical behaviors of PBI-CA systems, Würthner and co-workers designed and synthesized a series of PBI-CA conjugates by changing numbers of CA units and PBI units, modifying bay-areas of PBIs, and introducing other fluorophores into CA scaffolds. They found that the π-stacked conformation and orientation of PBIs and CAs remarkably influence over electron and energy transfer processes[28—33]. After these investigations on photophysical behaviors of PBI-CA systems, they further used a PBI-CA conjugate (PBI-CA **3**) (Scheme 8) as a novel molecular probe of polymer properties[34]. The fluorescence of PBI-CA **3** is strongly quenched in soft media but very bright in solid matrices, owing to the strong dependence of the PET process on medium reorganization. Therefore, PBI-CA **3** is successfully employed as a single-molecule probe of the changes that occur when a polymer is taken through its glass transition.



**Scheme 8** Chemical structures of PBI-CA **1**, PBI-CA **2**, and PBI-CA **3**

### 4.2 CA-induced aggregation of PBI

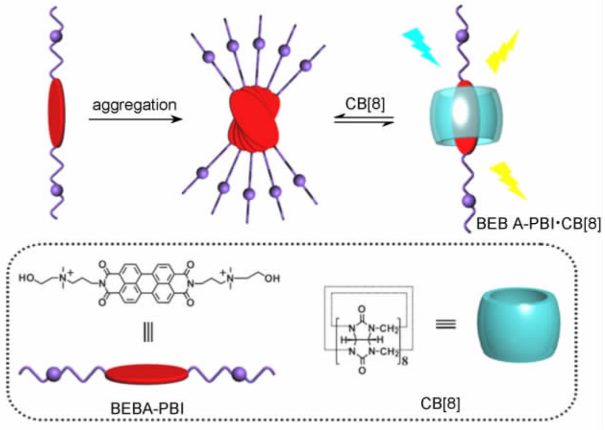
Much more attention has been paid to covalent PBI-CA conjugates, however, up to now, the corresponding investigation on the complex of PBIs and CAs, formed by non-covalent linkages, has been reported much less frequently. Recently, to refine the aggregation properties of PBIs, we investigated the interactions between *p*-sulfonatocalix[*n*]arenes (SC*n*As, *n* = 4—8) and a PBI derivative BPTA-PBI, as illustrated by Scheme 9[35]. The improvements of aggregation of BPTA-PBI were observed from the changes of BPTA-PBI absorption upon addition of SC*n*As, where the absorption bands broadened, the corresponding absorptivities reduced, and especially, the absorption band at 541 nm underwent a bathochromic shift to around 565 nm. The changes of BPTA-PBI emission also proved the strong interactions between BPTA-PBI and SC*n*As. Upon addition of SC*n*As, the monomeric fluorescence of BPTA-PBI disappeared, ascribed to that all of BPTA-PBI molecules were complexed to form aggregates. The binding stoichiometries of BPTA-PBI with SC4A and SC5A are 4∶2 and 5∶2 shown by the Job's plots, respectively, exceeding the conventional 1∶1 stoichiometry as a result of "calixarene-induced aggregation (CIA)” effect, which can lead to highly ordered aggregates. By assuming two BPTA-PBI molecules as one binding unit for simplicity, we calculated the obvious binding stability constants ($K_S$) of BPTA-BPI with SC4A and SC5A as $1.8 \times 10^6$ and $5.9 \times 10^6 M^{-1}$ utilizing nonlinear least-squares analysis of the UV-Vis spectral titration data by the isodesmic or equal-K model, which are 2-3 orders of magnitude larger than those with quaternary ammonium guests owing to the multiple interactions between BPTA-PBI and SC*n*As. Furthermore, the highly ordered structures of the SC5A + BPTA-PBI complex were demonstrated as nano-rod structures by DLS, TEM, SEM, and atomic force microscope (AFM). Moreover, the XRD measurements showed that the π⋯π aggregation distances of PBIs in the highly ordered structures are effectively modulated by different SC*n*As, where the π⋯π stacking distance of free BPTA-PBI is 3.54 Å, and the distances of the BPTA-PBI + SC4A and BPTA-PBI + SC5A complexes are 3.42 and 3.39 Å, respectively.



**Scheme 9** Schematic illustration of the complex-induced aggregation of BPTA-PBI by SC4A and SC5A

## 5 PBI-CB systems

The macrocyclic family CB[*n*], comprising 5—10 glycoluril units, allow them to form stable inclusion complexes with a wide variety of guest molecules, because of their hydrophobic cavities and identical carbonyl-laced portals[52,53]. Although a great of researches on controlling aggregation behaviors of organic dyes by CB[n] have been performed in solution[65,66], the investigation on PBI-CB systems was reported until 2012. Scherman and co-workers demonstrated a facile supramolecular approach that utilized the CB[8] to modulate the aggregation and fluorescent properties of PBI dyes (BEBA-PBI) in aqueous media, where CB[8] can encapsulate PBI inside its cavity, leading to a dramatic increase in the fluorescence quantum yield of the dye while ensuring high photochemical and chemical stability of BEBA-PBI (Scheme 10)[36]. The method retains the spectral properties of the parent PBI chromophore and offers opportunities for versatility through labeling of the diimide functional groups. Furthermore, the resultant complexes can reversibly switch the fluorescence response through additional chemical and electrochemical stimulus, respectively. The fluorescence of BEBA-PBI is instantly turned off upon addition of 1.0 equiv of the strong competitive guest adamantine amine to the BEBA-PBI·CB[8] complex, whereas the addition of excess CB[8] restores fluorescence. As a good electron acceptor, BEBA-PBI is capable of undergoing many reduction-oxidation cycles without structural degradation, which can be (electro) chemically switched between the non-fluorescent reduced states and fluorescent (re) oxidized states. Moreover, 1∶1∶1 ternary complexes can be formed upon addition of suitable dicationic or electron-rich second guests, which can be utilized for the reversible formation of higher-order supramolecular



**Scheme 10** Schematic illustration of reversible deaggregation of BEBA-PBI stacks in water upon addition of CB[8]

architectures in water.

## 6 Conclusion

This mini review mainly summarizes the recent progresses in exploring the PBI-macrocyclic systems. The combination of PBIs and macrocyclic hosts directs the formation of the desirable PBI superstructures, and has received considerable attention. However, it still remains an insufficient research to construct functional PBI supramolecular architectures based on macrocyclic hosts, compared to the development of PBI derivatives in other aspects, where they have been established as an outstanding class of functional materials. Therefore, enormous research efforts are required to further perfect PBI-macrocyclic systems. In the future respect, two investigation directions of PBI-macrocyclic systems are promised to deserve particular attention: one is assembly behaviors, for instance, the construction of stimuli-responsive supramolecular architectures utilizing the thermodynamically reversible binding property of macrocyclic hosts; the other is novel functions of assemblies, which can be improved or endowed by introducing macrocyclic hosts, such as sensing and optoelectronic properties, etc.

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# 苝酰亚胺和大环化合物的超分子组装

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**摘　要**　苝酰亚胺及其衍生物是一类具有良好的 π…π 堆积能力和优良的光电性能的 n 型半导体材料，通过该类化合物与大环化合物构筑纳米超分子组装体是近年来化学、材料科学和纳米科学等领域备受关注的研究之一。本文主要论述了近年来以共价或非共价的方法将超分子大环化合物引入到苝酰亚胺体系构筑出各种纳米功能超分子组装体的研究进展，可以认为超分子大环化合物与苝酰亚胺的组装不仅可以调节苝酰亚胺的光物理行为，而且还可以赋予超分子组装体很多新颖的物理化学特性，使其在传感材料和光电器件等方面展现出很大的潜在应用价值。这些研究极大地拓展了构筑新颖苝酰亚胺纳米超分子组装体的方法。我们相信本文对于进一步构筑具有特定结构和功能的苝酰亚胺-大环化合物超分子组装体将起到积极的促进作用。

**关键词**　自组装体　超分子结构　苝酰亚胺　大环化合物　非共价键作用力　π…π 堆积

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