Superbenzene-bridged bis(permethyl-β-cyclodextrin) as a convenient and effective probe for trinitrophenol exploder†

Jie Yu, a Yong Chen, a Jing-Jing Li a and Yu Liu* ab

On the other hand, cyclodextrins (CDs), a kind of cyclic oligosaccharides, possess good water solubility and low toxicity and are widely applied in many fields, such as drug delivery, cellular imaging and fluorescence sensing. Recently, in our group, a series of supramolecular assemblies was constructed from cyclodextrin modified perylene, which can be used as fluorescence sensing probes for organic vapor detection.

In this work, we synthesized a superbenzene-bridged bis-(permethyl-β-CD) (PHBC, Scheme 1) by attaching two permethyl-β-CD units to a HBC core. A comprehensive investigation by means of UV-vis spectroscopy, fluorescence spectroscopy, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) demonstrated that the self-assembly and luminescent behaviors of PHBC could be smartly controlled by adjusting the polarity of the environment. It is noteworthy that the resultant self-assembly showed specific fluorescence responses to exploders including 2,4,6-trinitrophenol (TNP), 2,4-dinitrophenol, and 1-methyl-2,4-dinitrobenzene, which could be readily distinguished either in solution or on the test paper. Significantly, the detection limit of self-assembly towards 2,4,6-trinitrophenol reached 306 ppb in solution and 2 ppb on the test paper, which would enable the potential...
application of PHBC as a highly sensitive and highly selective probe for the detection of nitroaromatic exploders.

The synthetic route to superbenzene-bridged bis(permethyl-β-CD) is shown in Scheme 2. Therein, hexaphenylbenzene derivative 3 and 6-deoxy-6-azido-permethyl-β-CD were synthesized in good yields according to the literature reported methods. C2 symmetrical compound 4 was obtained by Suzuki coupling reaction of hexaphenylbenzene derivative 3 with 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenol. However, owing to the rigid planar and C2 symmetrical properties of compound 4, which was insoluble in many common organic solvents, and the attached phenol group in compound 4, which makes it liable to oxidation, compound 4 was directly used without further purification for the reaction with 3-bromo-1-propyne in the presence of K2CO3 to give the intermediate 5. Subsequently, by means of "click chemistry" method, the intermediate 5 reacted with an excess amount of 6-deoxy-6-azido-permethyl-β-CD in the presence of CuI to give permethyl-β-CD-modified hexaphenylbenzene 6 in 78% yield. Finally, through a Scholl oxidation reaction catalyzed by anhydrous FeCl3, PHBC was successfully synthesized from 6 in 63% yield. The composition and structure of 6 and PHBC were fully characterized by 1H NMR, 13C NMR and MALDI-TOF (Fig. S1–S8, ESI†).

Owing to the good solubility of permethyl-β-CD, the photo-physical properties of PHBC in different solvents could be conveniently investigated by means of UV-vis and fluorescence spectroscopy. As shown in Fig. 1a, the UV-vis spectrum of PHBC exhibited three typical absorption bands (α, β and p bands), which was consistent with the report by Müllen et al.2c

Typically, PHBC displayed an absorption maximum peak at 360 nm and fine absorption peaks at the p band in dichloromethane, indicating the existence of un-aggregated PHBC monomers in dichloromethane.4c,10 Moreover, similar absorption features of PHBC were observed in acetone and methylbenzene, but the intensity of the absorption decreased. These results might be attributed to the π-π stacking interaction leading to partial aggregation in acetone and methylbenzene. Furthermore, with the increasing of solvent polarity, an obvious decrease of absorption intensity was observed, accompanied by the disappearance of fine absorption peaks (from 300 nm to 450 nm), probably owing to the aggregation of PHBC in polar solvents such as acetonitrile, methanol and methanol/H2O.10

Similarly, the fluorescence spectra of PHBC also showed the fine structures in the wavelength region of 450–540 nm in dichloromethane, acetone and methylbenzene (Fig. 1b and Fig. S10, ESI†), where the emission peaks at 470 nm and 493 nm maybe assigned to the fluorescence of PHBC monomers.11 However, when the solvent became more polar, these emission peaks red-shifted to 525 nm, assigned to the excimer emission, accompanied by the disappearance of fine structures.11 In addition, the polarity-induced change of aggregation state could readily be distinguished by the naked eye. As seen in Fig. 2, the color of the PHBC solution varied from green to yellow with the increase of solvent polarity. Furthermore, the fluorescence lifetime of PHBC was also investigated in different solvents, including PhCH3, DCM, acetone, CH2CN, CH3OH and CH3OH/H2O (1/9). The results showed that PHBC displayed a significantly longer lifetime and a non-monoexponential fluorescence decay especially in methanol/water (1/9), indicating the higher interchain interactions (e.g. with the formation of weakly-coupled aggregates or excimers) and reduced rigidity (Fig. S29, ESI†).
The similar morphological change of PHBC tended to exist as monomers in the weakly polar solvents but tended to form large self-assemblies through the π–π interactions among planar superbenzene molecules in the polar solvents, leading to the different morphologies in the different environments.

Subsequently, the molecular recognition of exploders by PHBC was investigated by means of fluorescence spectroscopy using 2,4,6-trinitrophenol (TNP) as a model substrate. Typically, with the addition of TNP (0–120 eq.), the fluorescence of PHBC was gradually quenched, which could be easily observed by either fluorescence spectroscopy or the naked eye (Fig. 2 and Fig. 4). Moreover, the color of the solution turned from colorless to yellow (Fig. 2). The quenching efficiency ([I_0 - I]/I_0 × 100%) in different solvents were also calculated under the same conditions, and the highest quenching efficiency was up to 94.3% in methanol/water (1:9). A possible reason for the fluorescence quenching may be attributed to the penetration of TNP into the self-aggregated PHBC via the π–π stacking interactions, leading to the charge transfer from PHBC (electron donor) to the adjacent TNP (electron acceptor).

Through a quantitative study, the self-assembly of PHBC gave a $K_{SV}$ constant of $1.7 \times 10^4$ M$^{-1}$ and a detection limit up to 306 ppb (Fig. S22 and S23, ESI†) for TNP in methanol/water (1:9), which was lower than the corresponding value of reduced graphene oxide. It was reported that the exciton migration would be enhanced by the longer-range molecular aggregation (due to the stronger π–π interactions), then fewer analyte molecules could effectively disturb the exciton migration and further result in the fluorescence quenching. In addition, the intermolecular distance might also be influenced by the inclusion of analytes into the permethyl-β-CD cavity, which then caused the change of fluorescence. As a result, the highly self-aggregated PHBC exhibited good quenching behavior, great Stern–Volmer constants and low detection limit in methanol/water.

It is also important to examine the detection universality and selectivity towards various exploders. Fig. 5 illustrates the fluorescence quenching efficiency of PHBC self-assembly at 525 nm in the presence of various aromatic compounds, including exploders (such as TNP, 2,4-dinitrophenol and 1-methyl-2,4-dinitrobenzene) and possible competing aromatic compounds (such as aniline and phenol) when the PHBC self-assembly was used as an exploder sensor. As shown in Fig. 5, the quenching efficiencies of the PHBC self-assembly towards the common aromatic compounds (such as aniline and phenol) were less than 40%, and this quenching efficiency in no case approached

![Fig. 2](image_url) **Fig. 2** The color of PHBC in different solvents under (a) visible light and (b) UV light (365 nm): (A) toluene, (B) dichloromethane, (C) acetone, (D) acetonitrile, (E) methanol, and (F) methanol/H$_2$O = 1/9.

![Fig. 3](image_url) **Fig. 3** TEM (a and c) and SEM (b and d) images of PHBC in methanol (a and b) and methanol/H$_2$O = 1/9 (c and d).

![Fig. 4](image_url) **Fig. 4** (a) Quenching efficiency of PHBC (1.0 × 10$^{-6}$ M, $\lambda_{ex} = 365$ nm) with TNP in different solvents. (b) Emission spectra of PHBC (1.0 × 10$^{-6}$ M in CH$_3$OH/H$_2$O = 1/9, $\lambda_{ex} = 365$ nm) with TNP at various concentrations.

![Fig. 5](image_url) **Fig. 5** Quenching efficiency of PHBC self-assembly (in CH$_3$OH/H$_2$O = 1/9) towards various exploders.
the corresponding values observed for exploders (more than 70%),
especially the fairly high value for TNP (94.3%). Among the examined
exploders, the PHBC self-assembly gave the highest quenching
efficiency towards TNP, which was the most electron-deficient. In
the control experiment, either the absorbance intensity change or
the fluorescence intensity change of TNP with the gradual addition
of free PM-β-CD were too little to calculate the association constant
(page S22, Fig. S30, ESI†), indicating that the association of the
PM-β-CD cavity with TNP was very weak and could be negligible.
There we deduced that the charge transfer between PHBC
(donor) and TNP (acceptor) may play an important role in the
fluorescence quenching.

Besides in solution, the PHBC self-assembly also exhibited good
fluorescence sensing ability for exploders on the test paper, which
could be readily distinguished under UV light. Like the widely used
pH paper, the test paper was facilely prepared by immersing filter
paper in a solution of PHBC (5 × 10⁻² M in CH₃OH:H₂O 1:9) for
20 min, and then drying for 4 h in the dark. As can be seen in
Fig. S28 (ESI†), nearly all of the fluorescence intensity of the PHBC-
containing test paper was quenched when a very small amount of
TNP solution (1 μL) was dripped on, accompanied by the appearance
of clear dark spots, but the test paper hardly responded to the
TNP-containing test paper was quenched when a very small amount of
TNP (donor) and TNP (acceptor) may play an important role in the
fluorescence quenching.

Significantly, the detection limit of the self-assembly towards
was not obviously affected by common aromatic compounds.
either in solution or on test paper, and this fluorescence sensing
ability for exploders on the test paper, which
could reach 1 × 10⁻⁸ M (Fig. S28, ESI†).

In conclusion, a novel planar C₄ symmetrical hexa-peri-hexa-
benzocoronene bridged bis(permethyl-β-CD)s was successfully
synthesized, and its self-assembly exhibited obvious fluorescence
resonces, which could be readily monitored by both the naked eye and fluorescence spectroscopy, to various exploders
either in solution or on test paper, and this fluorescence sensing
was not obviously affected by common aromatic compounds.
Significantly, the detection limit of the self-assembly towards
TNP could reach 306 ppb in solution and 2 ppb on the test paper.
Considering its easy preparation and fabrication, convenience in
exploder-detection, and high sensing specificity for TNP over other
competing reagents, this assembly is expected to meet the practical
requirements of exploder detection.

We thank NNSFC (21432004, 21672113 and 91527301) for
financial support.

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