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Superbenzene-bridged bis(permethyl-βcyclodextrin) as a convenient and effective probe for trinitrophenol exploder[†]

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A novel planar C_2 symmetrical superbenzene-bridged bis(permethyl- β -CD) was synthesized by grafting two permethyl- β -CD units onto a coronene core. Its self-assembly and luminescent behaviors could be smartly controlled by adjusting the polarity of the environment. Significantly, the resultant self-assembly showed specific fluorescence responses to exploders, especially 2,4,6-trinitrophenol, over various common aromatic compounds, which could be readily distinguished either in solution or on the test paper, and the detection limit of self-assembly towards 2,4,6-trinitrophenol could reach the ppb level. This finding would enable the self-assembly as a convenient and highly efficient fluorescence sensor for the detection of exploders.

As a group of fascinating organic molecules, polycyclic aromatic hydrocarbons (PAHs) have drawn much research interest to investigate their special properties and possible applications.¹ Owing to the strong π - π stacking interactions, many PAHs are inclined to self-assembly to form columnar mesophases, and charge carrier migration will occur among the π - π stacked PAHs.² Therefore, the supramolecular assembly of PAHs has many exciting applications in fields of organic electronics.³ As an important member of PAHs, hexa-peri-hexabenzocoronene (HBC), also named superbenzene, is widely regarded as the smallest graphene unit,⁴ and is attracting increasing attention for applications in organic electronics, photovoltaics, photonics, chemical sensors, anticancer drugs and cellular imaging agents.^{5,6} Kumar et al. synthesized two HBC derivatives for the detection of picric acid.^{6a} Zhang et al. reported a three-dimensional nanographene/triptycene conjugate for the detection of nitroaromatic explosives.^{6d} However, most of these works were performed in organic solvents, which inevitably limits their practical application.

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.⁷ 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.⁸

In this work, we synthesized a superbenzene-bridged bis-(permethyl-β-CD) (**PHBC**, Scheme 1) by attaching two permethylβ-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



Scheme 1 Supramolecular assembly of PHBC.

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Scheme 2 Synthetic route to PHBC.

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-\beta-CD were synthesized in good yields according to the literature reported methods.⁹ C_2 symmetrical compound 4 was obtained by Suzuki coupling reaction of hexaphenylbenzene derivative 3 with 4-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl) phenol. However, owing to the rigid planar and C_2 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 photophysical 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}



Fig. 1 (a) UV-vis spectra of **PHBC** (1.0×10^{-5} M) in different solvents at 25 °C, and (b) emission spectra of **PHBC** (1.0×10^{-6} M) in different solvents at 25 °C ($\lambda_{ex} = 365$ nm).

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.^{4*a*,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, CH₃CN, 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⁺).



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/ $H_2O = 1/9$.



Fig. 3 TEM (a and c) and SEM (b and d) images of PHBC in methanol (a and b) and methanol/ $H_2O = 1/9$ (c and d).

High-resolution transmission electronic microscopy (HR-TEM) and scanning electron microscopy (SEM) were applied to investigate the morphology of the PHBC assembly in methanol and methanol/ water (1:9). The TEM images (Fig. 3a) in methanol showed a number of needle-like nanostructures with average length of 112 nm and an average width of 17 nm. On altering the solvent from methanol to methanol/water (Fig. 3c), the original needlelike nanostructures changed to rod-like ones, and their average length and width increased to 200 nm and 67 nm, respectively. The similar morphological change of PHBC was also observed in SEM images (Fig. 3b and d). A possible reason may be the solvent-dependent self-assembly behaviors of PHBC, that 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 $((I_0 - I)/I_0 \times 100\%)$ 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).^{6a,d} Through a quantitative study, the self-assembly of PHBC gave a K_{sv} constant of $1.7 \times 10^4 \text{ M}^{-1}$ 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.¹² 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.¹³ 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.^{13a} 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-2,4dinitrobenzene) 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. 5 Quenching efficiency of PHBC self-assembly (in $CH_3OH/H_2O = 1/9$) 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^{-5} 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 common aromatic compounds, which was basically consistent with the sensing selectivity of the **PHBC** self-assembly in solution. By using this convenient method, the detection limit of the **PHBC** self-assembly toward **TNP** could reach 1×10^{-8} M (Fig. S28, ESI†).

In conclusion, a novel planar C_2 symmetrical hexa-*peri*-hexabenzocoronene bridged bis(permethyl- β -CD)s was successfully synthesized, and its self-assembly exhibited obvious fluorescence responses, 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.

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Notes and references

- (a) Y. Z. Liao, V. Strong, Y. Wang, X. G. Li, X. Wang and R. B. Kaner, *Adv. Funct. Mater.*, 2012, 22, 726–735; (b) A. Narita, X. Y. Wang, X. L. Feng and K. Müllen, *Chem. Soc. Rev.*, 2015, 44, 6616–6643; (c) L. Q. Qin, Y. A. Zhang, X. Y. Wu, L. Nian, Z. Q. Xie, L. L. Liu and Y. G. Ma, *Small*, 2015, 11, 3028–3034.
- 2 (a) E. W. Meijer and A. Schenning, *Nature*, 2002, 419, 353–354;
 (b) D. Wasserfallen, M. Kastler, W. Pisula, W. A. Hofer, Y. Fogel,
 Z. H. Wang and K. Müllen, *J. Am. Chem. Soc.*, 2006, 128, 1334–1339; (c) M. Kastler, J. Schmidt, W. Pisula, D. Sebastiani and K. Müllen, *J. Am. Chem. Soc.*, 2006, 128, 9526–9534.

- 3 (a) W. Pisula, A. Menon, M. Stepputat, I. Lieberwirth,
 U. Kolb, A. Tracz, H. Sirringhaus, T. Pakula and K. Müllen,
 Adv. Mater., 2005, 17, 684–689; (b) L. Zhang, A. Fonari, Y. Liu,
 A. L. M. Hoyt, H. Lee, D. Granger, S. Parkin, T. P. Russell,
 J. E. Anthony, J. L. Bredas, V. Coropceanu and A. L. Briseno,
 J. Am. Chem. Soc., 2014, 136, 9248–9251.
- 4 (a) J. P. Hill, W. S. Jin, A. Kosaka, T. Fukushima, H. Ichihara, T. Shimomura, K. Ito, T. Hashizume, N. Ishii and T. Aida, *Science*, 2004, **304**, 1481–1483; (b) D. Lungerich, J. F. Hitzenberger, M. Marcia, F. Hampel, T. Drewello and N. Jux, *Angew. Chem.*, *Int. Ed.*, 2014, **53**, 12231–12235.
- 5 (a) W. W. H. Wong, T. Khoury, D. Vak, C. Yan, D. J. Jones, M. J. Crossley and A. B. Holmes, *J. Mater. Chem.*, 2010, 20, 7005–7014; (b) J. S. Wu, W. Pisula and K. Müllen, *Chem. Rev.*, 2007, 107, 718–747; (c) Y. Yamamoto, T. Fukushima, Y. Suna, N. Ishii, A. Saeki, S. Seki, S. Tagawa, M. Taniguchi, T. Kawai and T. Aida, *Science*, 2006, 314, 1761–1764; (d) Y. Yamamoto, G. X. Zhang, W. S. Jin, T. Fukushima, N. Ishii, A. Saeki, S. Seki, S. Tagawa, T. Minari, K. Tsukagoshi and T. Aida, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, 106, 21051–21056.
- 6 (a) V. Vij, V. Bhalla and M. Kumar, ACS Appl. Mater. Interfaces, 2013, 5, 5373–5380; (b) X. Q. Xiong, L. Gan, Y. Liu, C. Zhang, T. Y. Yong, Z. Y. Wang, H. B. Xu and X. L. Yang, Nanoscale, 2015, 7, 5217–5229; (c) C. Zhang, Y. Liu, X. Q. Xiong, L. H. Peng, L. Gan, C. F. Chen and H. B. Xu, Org. Lett., 2012, 14, 5912–5915; (d) P. C. Zhu, L. N. Luo, P. Q. Cen, J. T. Li and C. Zhang, Tetrahedron Lett., 2014, 55, 6277–6280.
- 7 (a) Y. H. Zhang, Y. M. Zhang, Y. Yang, L. X. Chen and Y. Liu, *Chem. Commun.*, 2016, 52, 6087–6090; (b) Q. Zhao, Y. Chen, M. Sun, X. J. Wu and Y. Liu, *RSC Adv.*, 2016, 6, 50673–50679.
- 8 (a) B. P. Jiang, D. S. Guo and Y. Liu, J. Org. Chem., 2011, 76, 6101–6107; (b) Y. Liu, K. R. Wang, D. S. Guo and B. P. Jiang, Adv. Funct. Mater., 2009, 19, 2230–2235.
- 9 (a) M. Gille, A. Viertel, S. Weidner and S. Hecht, Synlett, 2013, 259–263; (b) M. T. Reetz and S. R. Waldvogel, Angew. Chem., Int. Ed., 1997, 36, 865–867.
- 10 J. M. Hughes, Y. Hernandez, D. Aherne, L. Doessel, K. Müllen, B. Moreton, T. W. White, C. Partridge, G. Costantini, A. Shmeliov, M. Shannon, V. Nicolosi and J. N. Coleman, *J. Am. Chem. Soc.*, 2012, **134**, 12168–12179.
- 11 (a) J. M. Englert, F. Hauke, X. L. Feng, K. Müllen and A. Hirsch, *Chem. Commun.*, 2010, 46, 9194–9196; (b) M. Kastler, W. Pisula, D. Wasserfallen, T. Pakula and K. Müllen, *J. Am. Chem. Soc.*, 2005, 127, 4286–4296; (c) A. Farcas, G. Tregnago, A.-M. Resmerita, S. T. Dehkordi, S. Cantin, F. Goubard, P.-H. Aubert and F. Cacialli, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, 52, 460–471.
- 12 D. Dinda, A. Gupta, B. K. Shaw, S. Sadhu and S. K. Saha, *ACS Appl. Mater. Interfaces*, 2014, **6**, 10722–10728.
- 13 (a) B. P. Jiang, D. S. Guo and Y. Liu, J. Org. Chem., 2010, 75, 7258–7264; (b) T. M. Swager, Acc. Chem. Res., 2008, 41, 1181–1189; (c) S. W. Thomas, G. D. Joly and T. M. Swager, Chem. Rev., 2007, 107, 1339–1386.