

Supramolecular Assembly of Perylene Bisimide with β -Cyclodextrin Grafts as a Solid-State Fluorescence Sensor for Vapor Detection

By Yu Liu,* Ke-Rang Wang, Dong-Sheng Guo, and Bang-Ping Jiang

A nanoscopic supramolecular aggregate is constructed from perylene bisimide-bridged bis-(permethyl- β -cyclodextrins) **1** via π - π stacking interactions. Its self-assembly behavior in organic and aqueous solutions is investigated by UV-Vis, fluorescence, and ^1H NMR spectroscopy. Transmission electron microscopy and scanning electron microscopy images show the 1D nanorod aggregation of **1**, which is birefringent under crossed polarizer conditions and strongly fluorescent as depicted in the fluorescence microscopy image. X-ray powder diffraction measurements indicate that **1** forms a well-ordered crystalline arrangement with a π - π stacking distance of 4.02 Å. Furthermore, the solid-state fluorescence sensing is explored by utilizing the poly(vinylidene fluoride) membrane-embedded **1**, giving that **1**, as a novel vapor detecting material, can probe several kinds of volatile organic compounds and, especially, exhibits high sensitivity to organic amines.

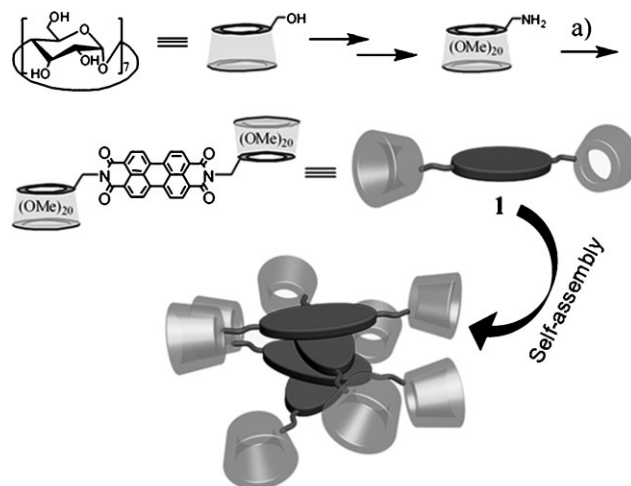
1. Introduction

Solid-state fluorescence sensing has received considerable attention for vapor detection in recent years as one of the simple, expedient detection techniques in chemistry, materials, and environment science.^[1] To design effective solid-state fluorescence sensors based on organic materials, two prerequisites are usually demanded: one is available organic substances that exhibit strong fluorescence in the solid state (most organic materials are strongly fluorescent in solution but not in solid state because of self-quenching), and the other is suitable binding or absorption sites that can capture the analyte molecules.^[1b,2] Since the seminal report by Swager and coworkers that pentyptycene-conjugated polymers were utilized for detecting the vapors of 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT),^[3] several kinds of fluorescence-sensing materials have been fabricated for detecting vapors of volatile organic compounds, which mainly focused on electron-donating materials.^[1a-d,4] By contrast, the corresponding availability of electron-accepting materials is reported much less frequently.^[5] Perylene bisimide and its

derivatives are one robust class of electron-accepting molecules widely used as liquid crystals, organogels, photoinduced electron transfer systems, and organic electronic devices.^[6] More recently, Zang and coworkers successfully developed a new type of fluorescence sensory material based on perylene bisimides for vapor probing of organic amines,^[5b] which further extended the application of perylene bisimides to the field of solid-state optical sensing.^[7]

In this paper, we report a supramolecular assembly fabricated from perylene bisimides and cyclodextrin conjugates (Scheme 1) that can be used as solid-state fluorescence sensing materials for vapor detection. In the building block **1**, perylene bisimides act as a fluorescence probe due to their strong solid-

state fluorescence, photochemical stability, and low quantum yield of intersystem crossing^[7,8] and permethyl- β -cyclodextrin acts as the molecular receptor that provides the binding site for analytes. Cyclodextrins, a class of cyclic oligosaccharides with six to eight D-glucose units linked by α -1,4-glucose bonds, have been extensively investigated in molecular recognition and construction of versatile supramolecular architectures.^[9] Although supramolecular hosts such as calixarenes^[10] have been linked to perylene bisimides



Scheme 1. The synthetic route and structural illustration of **1** and its self-assembly mode. Reagents: a) perylene-3,4,9,10-tetracarboxylic acid bisanhydride, zinc acetate, and pyridine, 100 °C.

[*] Prof. Y. Liu, K.-R. Wang, Dr. D.-S. Guo, B.-P. Jiang
Department of Chemistry,
State Key Laboratory of
Elemento-Organic Chemistry
Nankai University, Tianjin, 300071 (P. R. China)
E-mail: yuliu@nankai.edu.cn

DOI: 10.1002/adfm.200900221

(without studies on complexation), this is the first report about the sensing of the host-linked perylene bisimides.

2. Results and Discussion

2.1. π - π Aggregation of **1** in Solution

The perylene bisimide-bridged bis-(permethyl- β -cyclodextrins) **1** was synthesized by reaction of 6-deoxy-6-amino-permethyl- β -cyclodextrin with 3,4:9,10-perylenetetracarboxylic dianhydride (Scheme 1). Similarly to the reported perylene bisimide derivatives with solubilizing substituents at the imide nitrogens,^[1e,6a] **1** presents the capability of π - π aggregation in both solution and solid state. Benefiting from the grafts of cyclodextrin, the building block **1** possesses benign water solubility and is used to investigate the π -stacking behavior of **1** in aqueous solution. As shown by UV-Vis and fluorescence spectra (Figs. 1a and S5a), **1** exists in the typical non-aggregated state when toluene, chloroform, acetonitrile, and acetone are employed as solvents,^[11] whereas in solutions

of methanol and water, pronounced π - π aggregation of **1** is observed. This results from the enhancement with respect to the 0-0 transition for the transition from ground state to the higher electronic states (0-1, 0-2, and 0-3) as shown by the broadening of a vibrational shoulder beyond 550 nm in the absorption spectra and the quenching of the fluorescence emission. The difference in the solvents is due to the strong π -stacking interactions between perylene bisimide backbones in alcohols and water and equally that the poorly polarizable solvents cannot dissolve the π -surfaces well.^[6a]

The π -stacking behavior of **1** in water is considerably concentration-dependent. The absorption spectral changes of **1** as a function of concentration (Fig. 1b) show that the apparent absorption coefficients (ϵ) of 0-0 (526 nm) and 0-1 (491 nm) electronic transitions decrease while that of the 0-2 (462 nm) electronic transition increases upon gradual augmentation of the concentration, and concurrently a new shoulder at about 560 nm appears as a result of π - π aggregation. The decreasing extent of the 0-0 transition is much more appreciable than that of the 0-1 transition, and the aggregation (or lack thereof) of perylene bisimide derivatives can be determined by comparing the A_{0-0}/A_{0-1} ratio.^[12] At the lower concentration of 3.0×10^{-6} M, the A_{0-0}/A_{0-1} ratio of **1** is 1.36, which is similar to the values in toluene and acetone solvents ($A_{0-0}/A_{0-1} = 1.53$) and considered to be the non-aggregated state according to previous results.^[12] At the higher concentration of 1.0×10^{-4} M, the A_{0-0}/A_{0-1} ratio decreases to 0.66, reflecting the electronic coupling with a face-to-face stacking arrangement, which undoubtedly demonstrates the π - π aggregation of **1** in water. Furthermore, the aggregation constant (K_{agg}) of **1** in water can be obtained using a nonlinear least-square regression analysis of the concentration-dependent UV-Vis spectral data by the isodesmic or equal-K model, in which the formation of 1D aggregates with equal binding constants for the top and bottom faces of the perylene bisimides **1** display moderately strong aggregation in water ($K_{\text{agg}} = 7.3 \times 10^4 \text{ M}^{-1}$).^[13] In addition, the π - π aggregation of **1** is also temperature-dependent in that the present aggregate in water melts with the increase of temperature from 5 to 70 °C (Fig. S5b), which indicates that the self-assembly process is enthalpy driven.^[13b,14]

The fluorescence properties of the monomer and aggregates of **1** are investigated by concentration-dependent steady-state fluorescence spectra and time-resolved fluorescence spectra. From 5.0×10^{-7} M to 9.0×10^{-6} M, the intensity of the fluorescence emission increases with increasing concentration, and the emission band is slightly bathochromically shifted (Fig. S6a). However, the fluorescence emission is quenched with increasing the concentration from 9.0×10^{-6} M to 1.0×10^{-4} M because of the self-quenching effects between the perylene bisimide backbones of the aggregates, indicating the transition of lower aggregates into higher aggregates (Fig. S6b), and the maximum fluorescence emission is bathochromically shifted from 537 nm (9.0×10^{-6} M) to 578 nm (1.0×10^{-4} M).^[15] Stern-Volmer analysis gives insight into the efficiency of the fluorescence self-quenching of **1** with increasing concentration, which is calculated as 3284 M^{-1} by the sphere of action model (Fig. S6c).^[16] The degree of the quenching response is more significant at higher quencher concentration because of the upward curvature in the Stern-Volmer plot. Furthermore, the fluorescence quantum yield of **1** in the monomer form was determined to be 55.1% at 1.0×10^{-6} M, but decreased

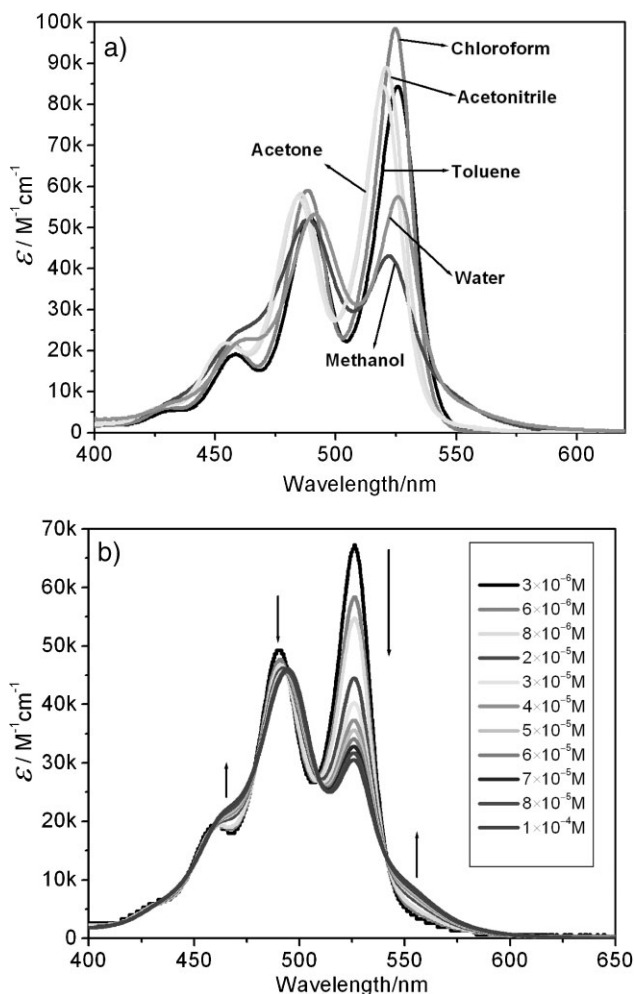


Figure 1. a) UV-Vis spectra of **1** (1.0×10^{-5} M) in different solvents at 25 °C, and b) concentration-dependent UV-Vis spectra of **1** from 3.0×10^{-6} M to 1.0×10^{-4} M in water at 20 °C.

upon increasing the concentration, namely, the quantum yield was 4.4% at 1.0×10^{-4} M (Table S1), where **1** is mainly in the higher aggregated form. To further demonstrate the fluorescence properties of **1** in the monomer and aggregate forms, time-resolved fluorescence measurements were performed (Fig. S7 and Table S1). The fluorescence decays of **1** at 1.0×10^{-6} , 1.0×10^{-5} , 5.0×10^{-5} , and 1.0×10^{-4} M obey the single exponential function, giving a single fluorescence lifetime (4.62, 4.97, 5.43, and 5.96 ns, respectively). Thus, the lifetime of the aggregate form is 1.34 ns higher than that of the monomer form. The prolonged lifetimes upon increasing concentration are attributed to the monomer transfer to aggregates.^[14] On the basis of these characteristic features in the fluorescence and aforementioned absorption spectra, the aggregation behavior can be identified as resulting from the formation of cofacial H-type aggregates in aqueous solution.^[14,17]

The distinguishable aggregation behaviors of **1** in different solvents were also identified by ¹H NMR spectroscopy. As shown in Figure S8, perylene bisimide protons present a simple pattern of sharp signals located in the region of 8.74–8.66 ppm in CDCl₃, indicating that **1** exists in the monomeric form (or at most a very low aggregated form) at a high concentration of 5.0×10^{-3} M. In D₂O, two apparently broad signals (8.55–8.47 ppm and 8.22 ppm) are observed for the perylene bisimide protons, and the protons suffer pronounced upfield shifts because of the π -stack ring current.^[18]

2.2. Solid-State Aggregation Morphology and Fluorescence of **1**

The solid-state packing behavior of **1** was hypothesized upon based on its aggregation characteristics in solution and the morphology of the obtained supramolecular assembly was intuitively reflected in both transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images (Fig. 2a and b), showing a well-ordered 1D nanorod structure. X-ray powder diffraction (XRD) measurements of **1** show three strong peaks at $2\theta = 4.26^\circ$, 8.72° , and 11.46° , with several smaller peaks at 5.74° , 6.84° , 7.56° , 9.78° , 13.02° , 16.34° , and 22.12° (Fig. S9), and the *d* values were determined to be 20.72, 15.38, 12.91, 11.68, 10.13, 9.04, 7.72, 6.79, 5.42, and 4.02 Å from these peaks, which indicates that the building blocks form a well-ordered crystalline arrangement. The π - π stacking distance of **1** was calculated from the wide angle region as 4.02 Å, which is larger than the common π - π stacking distances (≈ 3.50 Å) of perylene bisimide derivatives^[6a] because of the steric hindrance of the permethyl- β -cyclodextrin grafts. According to the steric requirements of the imide substituents, longitudinal, transverse, and rotational offsets may occur between neighboring perylene bisimide derivatives.^[6a] Taking the size of permethyl- β -cyclodextrin (torus height 11.1 Å and outer torus diameter 16.5 Å at the wide rim)^[19] into account, rotational offset was assumed for the building block **1**, leading to the alternating rotation stacking.^[20] The corresponding representation was illustrated in Scheme 1.

The well-organized aggregate of **1** is birefringent when examined under crossed polarizer conditions (Fig. 2c), indicating a high degree of molecular anisotropy within the molecular arrangement and that the optical axis is along the orientation of π - π stacking.^[21] Furthermore, the aggregate of **1** exhibits strong red

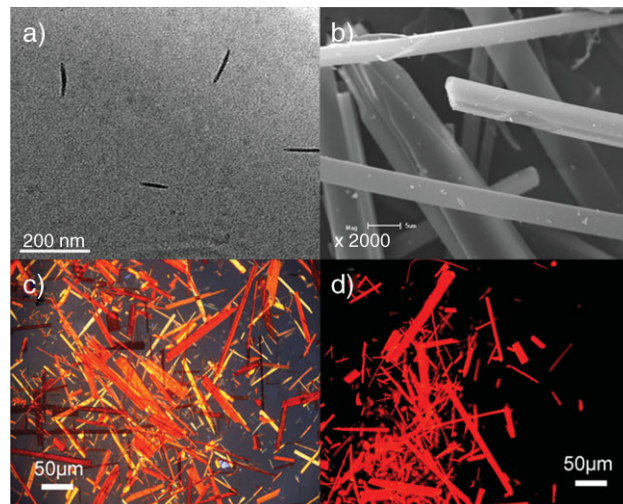


Figure 2. a) TEM image of **1**. b) SEM image of **1**. c) Optical micrograph of **1** under crossed polarizer. d) Fluorescence optical image of **1**.

fluorescence as depicted in the fluorescence microscopy image (Fig. 2d), which indicates that the π - π stacking interactions between the extended aromatic building blocks lead to the formation of collective electronic well-organized materials.^[22] The strong solid-state fluorescence of **1**, as one of the necessary prerequisites, endows it with potential application as a fluorescence sensing material.

2.3. Solid-State Fluorescence Probing for Organic Vapors

To further investigate the solid-state fluorescence sensing for vapor detection, the aggregate of **1** was embedded in the poly(vinylidene fluoride) (PVDF) membrane. The PVDF membrane was immersed in the solution of **1** at 1.0×10^{-4} M for 2 h, and then PVDF membrane was air-dried. This kind of film is conveniently manufactured into devices and easily tailored according to practical need, resembling the pH paper. The UV-Vis spectrum of the PVDF membrane-embedded **1** exhibits the lower assembled excimer-like state, where the A_{0-0}/A_{0-1} ratio (0.88) obviously decreases compared with the spectrum in chloroform ($A_{0-0}/A_{0-1} = 1.67$) (Fig. 3a). Excited at 490 nm, a new emission band appears at 611 nm, while no monomer emission of **1** is observed (Fig. 3b). The PVDF membrane-embedded **1** exhibits hypsochromic emission as comparison with the fluorescence wavelengths of the conventional solid-state perylene bisimide aggregates reported before (around 630–650 nm), which should be reasonably attributed to the relatively weak electronic coupling between the neighboring π -orbitals induced by the steric hindrance of the permethyl- β -cyclodextrin grafts (see the aforementioned π - π stacking distance). Based on the isodesmic or equal-K model, the average dye numbers per stack *N* (average aggregation number) at 1.0×10^{-4} M can be calculated as 3 or 4 from the reported equation.^[13b,14] It is reasonably acceptable that the red fluorescence of the PVDF membrane-embedded **1** observed in the fluorescence optical images mainly originates from the low aggregated crystal state of perylene bisimides.^[22a]

The previous fluorescence sensory material based on perylene bisimides is in virtue of the expedient diffusion of gaseous analyte

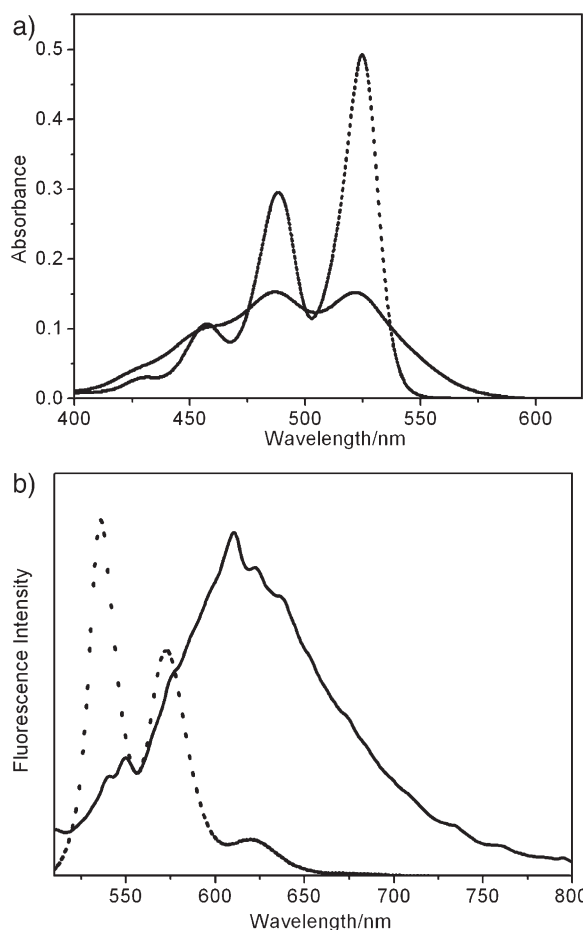


Figure 3. a) UV-Vis spectra of **1** in chloroform (1.0×10^{-5} M, dotted line) and the PVDF membrane-embedded **1** (solid line). b) Fluorescence spectra of **1** in chloroform (1.0×10^{-5} M, dotted line) and the PVDF membrane-embedded **1** (solid line), $\lambda_{\text{ex}} = 490$ nm.

molecules within the matrix of the meshlike, porous film formed by the entangled perylene bisimide nanofibers in which the vapor probing was dominated by the morphology and topology of the obtained material.^[5b] Therefore, one more advantage of the present solid-state fluorescence sensing system is that there are specific binding sites for analytes based on the cyclodextrin receptors. It has been shown that cyclodextrins can capture gaseous molecules in the solid state besides the plentiful reports in solution.^[23] When the PVDF membrane-embedded **1** was exposed to the analyte vapors, the gaseous molecules were immersed and accumulated into the cavities of permethyl- β -cyclodextrins and then induced the fluorescence quenching of perylene bisimide chromophores. The contribution from the absorption of gaseous molecules within the matrix can be ignored as **1** aggregates to trimer or tetramer states in the PVDF membrane.

The PVDF membrane-embedded **1** exhibited fluorescence quenching to several saturated vapors of volatile organic compounds with a response time of 10 s including not only organic amines and nitro-based compounds (*o*-methyl-aniline, aniline, benzylamine, butylamine, triethylamine, hydrazine, nitroethane, nitromethane, and nitrobenzene) but also general organic solvents (chloroform, toluene, chlorobenzene, methanol,

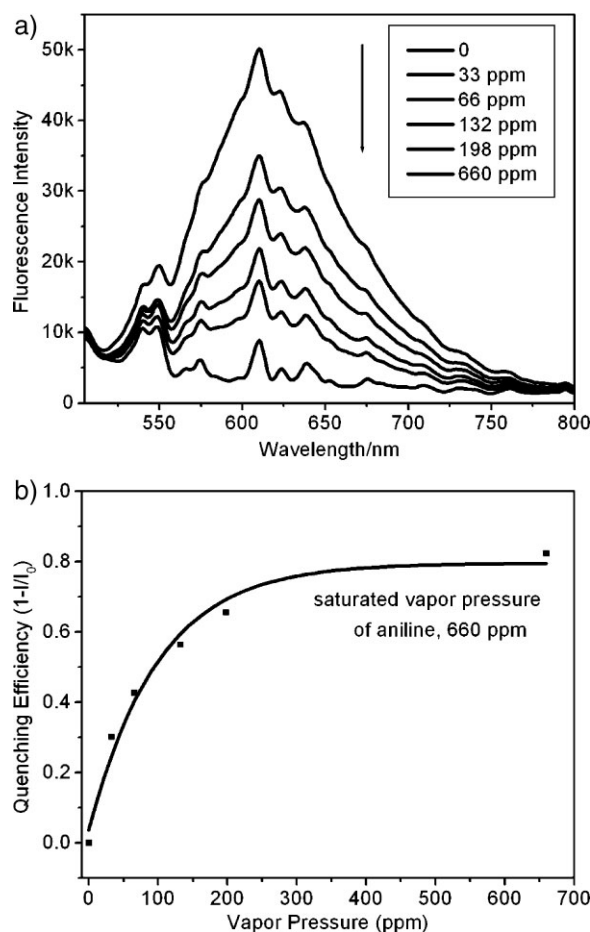


Figure 4. a) Fluorescence spectra of the PVDF membrane-embedded **1** upon exposure to the vapor of aniline at different vapor pressures, $\lambda_{\text{ex}} = 490$ nm. b) The fluorescence quenching efficiency as a function of the vapor pressure of aniline.

and acetonitrile) (Fig. S10). As a result, the fluorescence changes are considered to be attributable to analyte inclusion and concomitant changes in the packing of the dyes in addition to the photoinduced electron transfer reported before.^[5b,7] Inclusion of analytes into the cyclodextrin cavity may change the distance between the perylene backbones and thus alter fluorescence. The probing sensitivities were measured for toluene and aniline and show that the PVDF membrane-embedded **1** is much more sensitive to aniline than toluene. The fluorescence was quenched 30% by aniline with a vapor pressure of 33 ppm (Fig. 4) and 15% by toluene with a vapor pressure of 4100 ppm (Fig. S11). The higher sensitivity to aniline is attributed to photoinduced electron transfer from the reducing reagents to the excited states of chromophores.^[24]

3. Conclusion

In summary, we constructed a supramolecular nanorod aggregate from the perylene bisimide-bridged bis-(permethyl- β -cyclodextrins) **1**, which exhibited strong solid-state fluorescence. Moreover, with the grafts of cyclodextrin, a well-known molecular receptor, **1**

showed promise as a novel fluorescence sensory material with both elegant fluorescence probes and specific binding sites. The obtained results from the vapor detection show that the well-defined aggregate of **1** can probe several kinds of organic vapors and exhibit high sensitivity to organic amines. The reported study introduces an interesting approach to solid-state fluorescence sensing that is based on two innovative ideas: the synthesis of cyclodextrine-linked perylene bisimides and the preparation of analyte-sensitive membranes. Taking the fascinating binding ability and selectivity of cyclodextrins into account, further comprehensive investigation of the solid-state fluorescence sensing based on perylene bisimide-cyclodextrin conjugates is in progress, which will hopefully provide a sophisticated pathway for detecting specialized analytes with high sensitivity and selectivity.

4. Experimental

^1H NMR and ^{13}C NMR spectra were recorded on a Varian 300 Spectrometer. Positive-ion matrix-assisted laser desorption ionization mass spectrometry was performed on an IonSpec QFT-MALDI MS. Elemental analysis was performed on a Perkin-Elmer-2400C instrument. Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu Bio-Rad FTS 135 instrument. UV-Vis spectra were recorded in a quartz cell (light path 5 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. UV-Vis spectra in solid state were recorded using a Shimadzu integrating sphere assembly attached to a Shimadzu UV-3600 spectrophotometer. BaSO_4 was used as the reflectance standard. The steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a VARIAN CARY Eclipse equipped with a VARIAN CARY single cell peltier accessory to maintain the temperature at 25 °C. The fluorescence lifetimes were recorded on an Edinburgh Analytical Instruments FLS920 (Edinburgh Instruments) spectrometer equipped with a NF900 nanosecond flash lamp using the time-correlated single-photon-counting (TCSPC) method. The solid-state fluorescence spectra were recorded with a front surface accessory on an Edinburgh Analytical Instruments FLS920 (Edinburgh Instruments) spectrometer. TEM images were recorded on Philips Tecnai G2 20S-TWIN microscope operating at an accelerating voltage of 200 keV. The sample for TEM measurements was prepared by dropping the solution of **1** (CHCl_3 /petroleum ether = 1:4, 3.1 mmol) onto a copper grid. SEM images were recorded on a HITACHI S-3500N SEM. XRD patterns were obtained using a Rigaku D/max 2500 diffractometer with $\text{Cu K}\alpha$ radiation (40 kV, 100 mA). Fluorescence optical microscopy images were recorded on an OLYMPUS BX51+Mc MP5. Optical polarization was investigated on a Nikon Optophot-Pol XTP-11.

Synthesis of 1: 6-Deoxy-6-amino-permethyl- β -cyclodextrin was synthesized according to the literature procedures from natural β -cyclodextrin [25]. 6-Deoxy-6-amino-permethyl- β -cyclodextrin (0.94 g, 0.67 mmol), perylene-3,4,9,10-tetracarboxylic acid bisanhydride (0.13 g, 0.33 mmol), and zinc acetate (0.073 g, 0.33 mmol) were mixed in pyridine (200 mL). The reaction mixtures were heated at 100 °C under N_2 for 48 h. After cooling to room temperature, the solvent was removed at reduced pressure and the residue was dissolved in chloroform, washed with water, dried over Na_2SO_4 , and evaporated to dryness under vacuum. The residue was purified by silica-gel column chromatography using chloroform/methanol (30:1 v/v) as the eluent to give the product as a red powder (513 mg) at yield of 48%. FTIR (KBr) ν [cm^{-1}]: 1702, 1665, 1596; ^1H NMR (300 MHz, CDCl_3 , δ): 8.71 (m, 8H), 5.28–5.21 (m, 8H), 5.11–5.06 (m, 4H), 4.98 (d, 2H), 4.74–2.68 (m, 204H); ^{13}C NMR (300 MHz, CDCl_3 , δ): 163.5, 134.8, 131.7, 129.7, 126.7, 123.8, 123.3, 99.8, 99.1, 98.8, 85.4, 82.4, 82.2, 81.9, 81.8, 81.0, 80.6, 80.0, 79.7, 79.5, 71.8, 71.69, 71.3, 71.1, 70.6, 69.1, 61.7, 61.6, 61.5, 59.3, 59.2, 59.1, 58.8, 58.6, 42.1; MALDI-MS: calcd for

$\text{C}_{148}\text{H}_{226}\text{N}_2\text{O}_{72}\text{Na}^+$, 3206.3977; found 3206.3965. Anal. calcd for $\text{C}_{148}\text{H}_{226}\text{N}_2\text{O}_{72}$: C 55.81, H 7.15, N 0.88; found: C 55.69, H 7.25, N 0.80.

Acknowledgements

We thank the 973 Program (2006CB932900), NNSFC (No. 20572052, 20721062 and 20703025), and the Tianjin Natural Science Foundation (07QTPTJC29600) for financial support. Supporting Information is available online from Wiley InterScience or from the author.

Received: February 5, 2009

Published online: May 21, 2009

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