Supporting Information

for

Chiral Self-assembly of Lactose Functionalized Perylene Bisimides as Multivalent Glycoclusters

Ke-Rang Wang, Hong-Wei An, Ling Wu, Jin-Chao Zhang, Xiao-Liu Li*

*a Key Laboratory of Chemical Biology of Hebei Province, College of Chemistry and Environmental Science, Hebei University, Baoding 071002, China

Tel & Fax: (+86)312-5971-116; E-mail: lixl@hbu.cn

Experiment Section

Analysis: $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker 600 or Bruker 400 spectrometer. Positive-ion matrix-assisted laser desorption ionization mass spectrometry was performed on an IonSpec QFT-MALDI MS. UV–Vis spectra were recorded in a quartz cell (light path 10 mm or 5 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a S-1700 temperature controller. Turbidimetry assay$^1$ of the ligand-protein binding was measured on a Shimadzu UV-3600 spectrophotometer with quartz micro-cuvette (100 µL volume, 1 cm path length). Scanning electron microscopic (SEM) image was recorded on JSM-7500F (JEOL). The sample was prepared by dissolution of PBI-Lac ($4 \times 10^{-5}$ M) in pure water, and then the equivalent volume of MeOH was addition. The agglomerates can be
obtained after filtration. The sample of the complexes of the self-assembly of PBI-Lac and PNA were prepared by adding 100 µL of the solution of PBI-Lac (5 × 10^{-4} M) into 1 mL of the solution of PNA (1 mg/mL) in the PBS buffer (pH = 7.4, 10 mM, 0.1 mM MnCl₂, 0.1 mM CaCl₂). X-ray powder diffraction (XRD) pattern was performed on a D8 ADVANCE diffractometer (Bruker/Germany) with Cu Kα radiation (40 kV, 100 mA). Circular dichroism spectra were performed on MOS-450 (BioLogic).

**Materials:** 3,4:9,10-perylenetetracarboxylic dianhydride was purchased from Alfa Aesar. Concanavalin A (Con A) lectin and Peanut agglutinin (PNA) lectin were purchased from Sigma-Aldrich. Bovine serum albumin (BSA) was purchased from Sangan Biotech (Shanghai). Unless otherwise indicated, all reagents and solvents were obtained from commercial suppliers, and were used without further purification.

**Synthesis:**

**Scheme S1:** Reagents and conditions: a) 3,4:9,10-perylenetetracarboxylic dianhydride, Zn(OAc)₂, pyridine, 100 °C, 60%; b) MeOH/H₂O, NaOH, 95%.

**Lac-2:** 2’-aminoethyl hepta-O-acetyl-β-D-lactoside (Lac-1) was synthesized
according to the literature procedures from D-Lactose.2

**Synthesis of Lac-2:** Lac-1 (1.70 g, 2.5 mmol), 3,4:9,10-perylenetetracarboxylic dianhydride (0.39 g, 1 mmol) and zinc acetate (0.22 g, 1 mmol) were mixed in pyridine (250 mL). The reaction mixtures were heated at 100 °C under N₂ for 72 hours. After cooling to room temperature, the solvent was removed at reduced pressure, and the residue was dissolved in CH₂Cl₂, washed with water, dried over Na₂SO₄, and evaporated to dryness under vacuum. The residue was purified by silica-gel column chromatography using CH₂Cl₂/CH₃OH (v/v = 15/1) as the eluent to give the product as a red powder (1.03 g) at yield of 60%. m. p. 211.5-213.7 °C; ¹H NMR (600 M Hz, CDCl₃, ppm): δ 1.90 (s, 6 H, -COCH₃), 1.93 (s, 6 H, -COCH₃), 1.99 (s, 6 H, -COCH₃), 2.01(s, 6 H, -COCH₃), 2.01 (s, 6 H, -COCH₃), 2.07 (s, 6 H, -COCH₃), 2.11 (s, 6 H, -COCH₃), 3.62-3.64 (m, 2H), 3.78 (t, J = 9.0 Hz, 2 H), 3.83 (t, J = 6.6 Hz, 2 H), 3.88-3.91 (m, 2H), 4.01-4.10 (m, 6 H), 4.16-4.20 (m, 2H), 4.34-4.39 (m, 2H), 4.44-4.50 (m, 6H), 4.60 (d, J = 8.4 Hz, 2 H), 4.87-4.93 (m, 4H), 5.07 (dd, J = 7.8 Hz, 10.2 Hz, 2 H), 5.17 (t, J = 9.6 Hz, 2 H), 5.31 (d, J = 3.0 Hz, 2 H), 8.21 (d, J = 8.4 Hz, 4 H, Ph), 8.38 (d, J = 7.8 Hz, 4 H); ¹³C NMR (150 M Hz, CDCl₃, ppm), δ : 20.58, 20.68, 20.72, 20.86, 20.91, 39.60, 60.89, 62.16, 66.31, 66.75, 69.27, 70.78, 71.09, 71.65, 72.83, 72.94, 76.33, 100.59, 101.15, 122.91, 125.76, 128.93, 131.09, 134.00, 162.93, 169.13, 169.69, 169.76, 170.09, 170.18, 170.37, 170.43.

**Synthesis of PBI-Lac:** Compound Lac-2 (0.86 g, 0.5 mM) was dissolved in MeOH (20 mL), a solution of sodium hydroxide (2.0 mL, 8 mM in H₂O, 16 equiv.) was added, and the reaction mixture was stirred at room temperature until disappearance of the starting material. The solid was filtered, washed with MeOH. PBI-Lac (0.53 g) was obtained with yield of 95%. m. p. 159.9-162.3 °C; ¹H NMR (600 M Hz, (CD₃)₂SO, ppm): δ 3.10 (s, 2H), 3.16 (d, J = 4.8 Hz, 2H), 3.48-3.76 (m, 18H), 3.98-4.34 (m, 12H), 4.50-4.78 (m, 12H), 5.10 (s, 2H), 5.22 (s, 2H), 7.80 (m, 8H); ¹³C NMR (150 M Hz, (CD₃)₂SO, ppm): δ 49.07, 60.88, 60.97, 68.62, 71.05, 73.68, 75.40, 75.99, 79.21, 79.43, 79.63, 81.13, 103.31, 104.35, 121.65, 123.68, 127.65, 130.30, 133.01, 162.59. MS (MALDI-TOF): 1149.289 [M+Na]⁺.
Fig. S1. $^1$H NMR (600 M Hz, CDCl$_3$) spectrum of Lac-2.

Fig. S2. $^{13}$C NMR (150 M Hz, CDCl$_3$) spectrum of Lac-2.
Fig. S3. $^1$H NMR (600 MHz, DMSO-$d_6$) spectrum of compound PBI-Lac.

Fig. S4. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectrum of compound PBI-Lac.
Fig. S5. MS spectrum of compound PBI-Lac.

Fig. S6. Concentration-dependent UV–Vis spectra of PBI-Lac in water at 25 °C, concentration range from $6.0 \times 10^{-6}$ M to $1.0 \times 10^{-4}$ M.
Fig. S7. Concentration-dependent fluorescence spectra of PBI-Lac in water, concentration range from $6.0 \times 10^{-6}$ M to $1.0 \times 10^{-4}$ M.

Fig. S8. Temperature-dependent UV-Vis spectra of PBI-Lac ($1.0 \times 10^{-5}$ M) from 10 °C to 90 °C.
Fig. S9. Concentration-dependent CD spectra of PBI-Lac in water, concentration range from $1.0 \times 10^{-5}$ M to $1.0 \times 10^{-4}$ M.
Fig. S10. Kinetic plot for the aggregation of PBI-Lac (2.0 \times 10^{-5} \text{ M}) in H_{2}O/MeOH (50/50), \lambda = 494 \text{ nm}. The inset shows the photographs of PBI-Lac at the triggering state and the aggregation state.

![Kinetic Plot](image)

Fig. S11. XRD data of PBI-Lac.

![XRD Data](image)

Fig. S12. CD spectra of PBI-Lac (1.0 \times 10^{-5} \text{ M}) upon addition of PNA (from 3.3 \times 10^{-7} \text{ M} to 3.0 \times 10^{-6} \text{ M}).

![CD Spectra](image)
Reference:
