Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

for

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

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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 mensurated 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** (4×10^{-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 $MnCl_2$, 0.1 mM $CaCl_2$). X-ray powder diffraction (XRD) pattern was performed on a D8 ADVANCE diffractometer (Bruker/Germang) 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) $MeOH/H_2O$, 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 N_2 for 72 hours. After cooling to room temperature, the solvent was removed at reduced pressure, and the residue was dissolved in CH_2Cl_2, washed with water, dried over Na_2SO_4, and evaporated to dryness under vacuum. The residue was purified by silica-gel column chromatography using CH_2Cl_2/CH_3OH (*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 ºC; ^{1}H NMR (600 M Hz, $CDCl_3$, ppm): δ 1.90 (s, 6 H, -$COCH_3$), 1.93 (s, 6 H, -$COCH_3$), 1.99 (s, 6 H, -$COCH_3$), 2.01(s, 6 H, -$COCH_3$), 2.01 (s, 6 H, -$COCH_3$), 2.07 (s, 6 H, -$COCH_3$), 2.11 (s, 6 H, -$COCH_3$), 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); ^{13}C NMR (150 M Hz, $CDCl_3$, 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 H_2O, 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 ºC; ^{1}H NMR (600 M Hz, $(CD_3)_2SO$, 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); ^{13}C NMR (150 M Hz, $(CD_3)_2SO$, 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 $[M+Na]^+$.

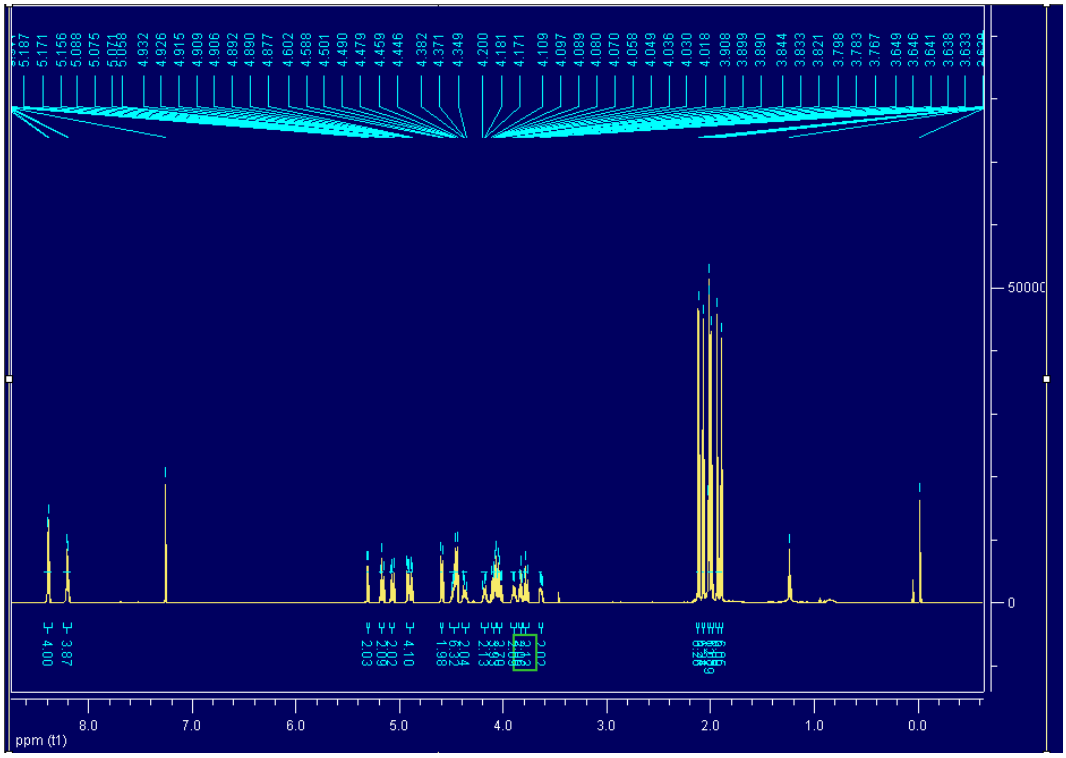

Fig. S1. ^{1}H NMR (600 M Hz, $CDCl_3$) spectrum of **Lac-2**.

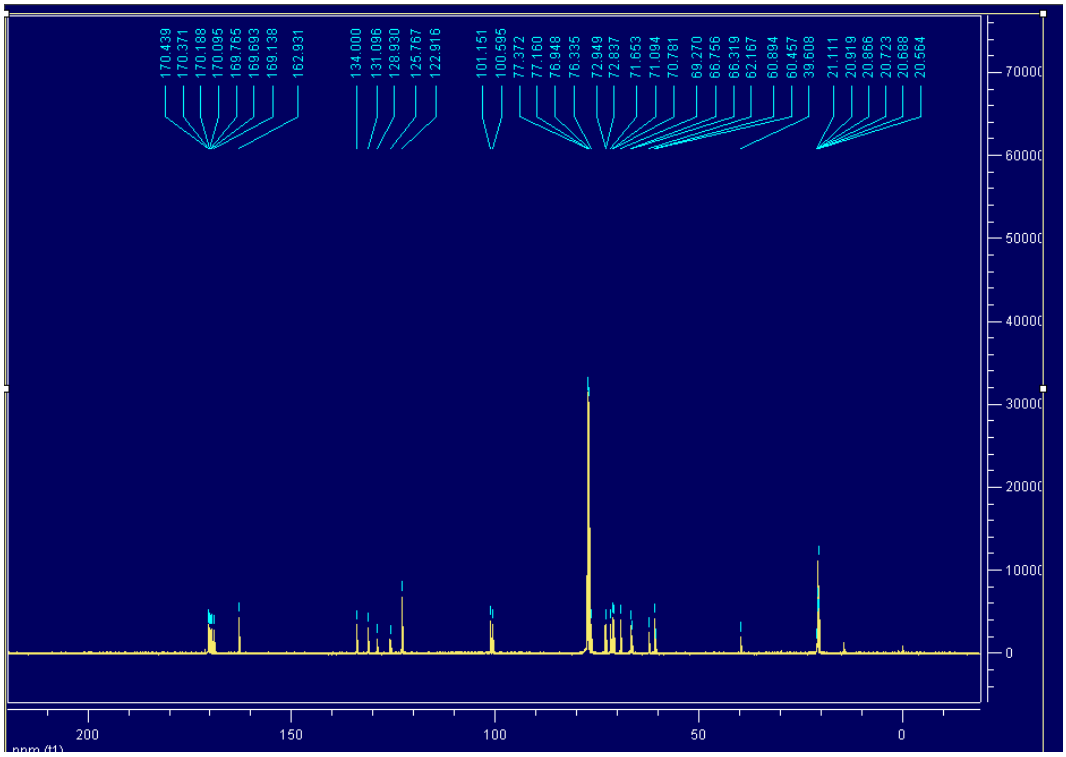

Fig. S2. ^{13}C NMR (150 M Hz, $CDCl_3$) spectrum of **Lac-2**.

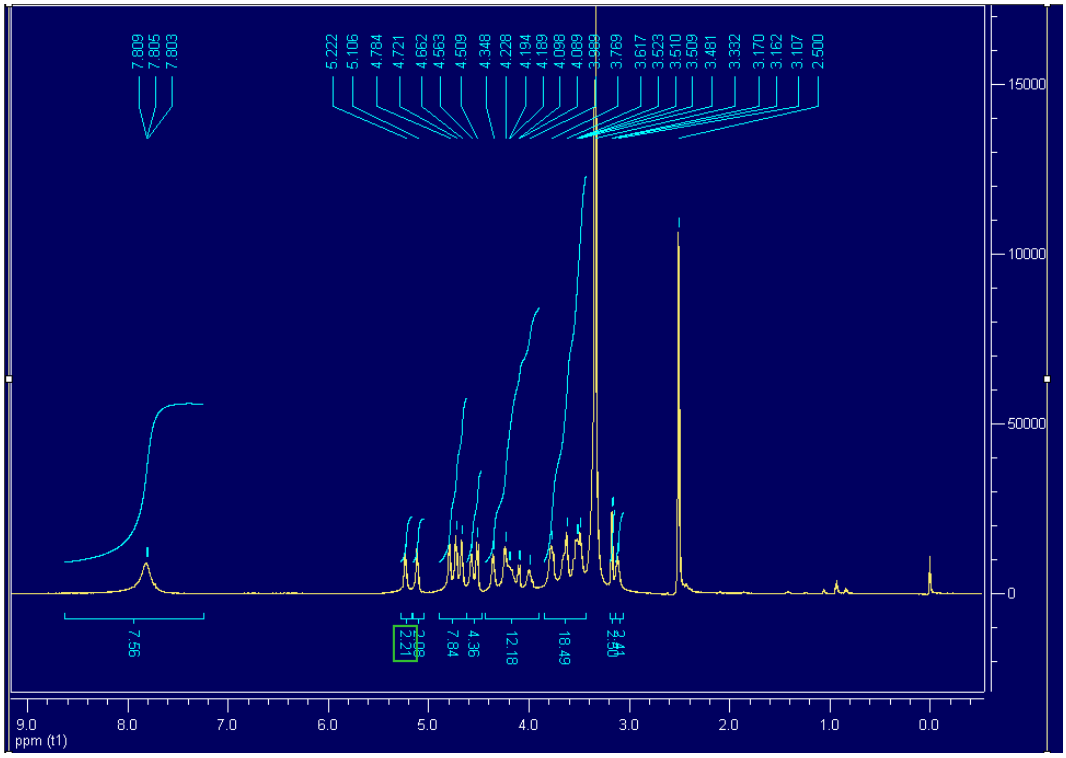

Fig. S3. ^{1}H NMR (600 M Hz, DMSO-d_6) spectrum of compound **PBI-Lac**.

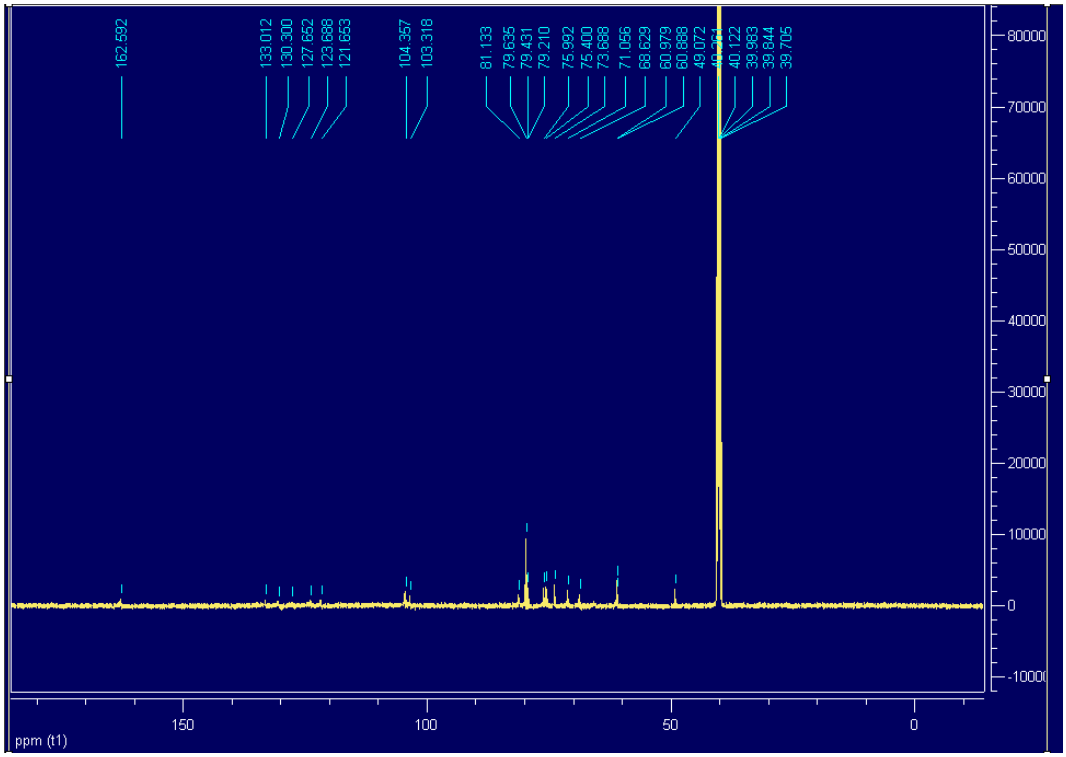

Fig. S4. ^{13}C NMR (150 M Hz, DMSO-d_6) spectrum of compound **PBI-Lac**.

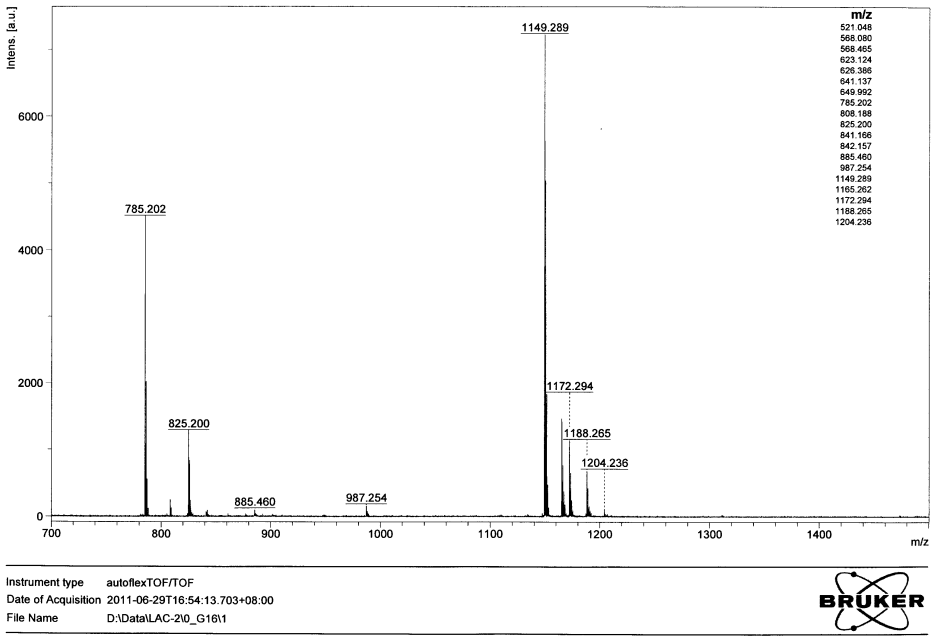

Fig. S5. MS spectrum of compound **PBI-Lac**.

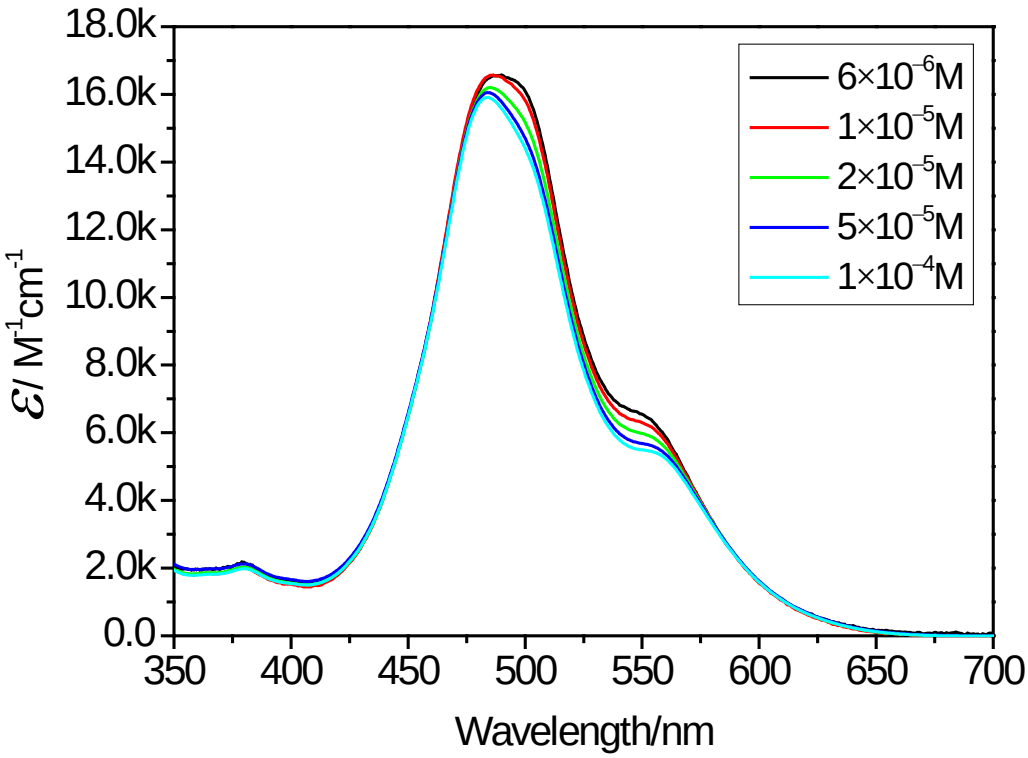

Fig. S6. Concentration-dependent UV–Vis spectra of **PBI-Lac** in water at 25 °C, concentration range from 6.0×10^{-6} M to 1.0×10^{-4} M.

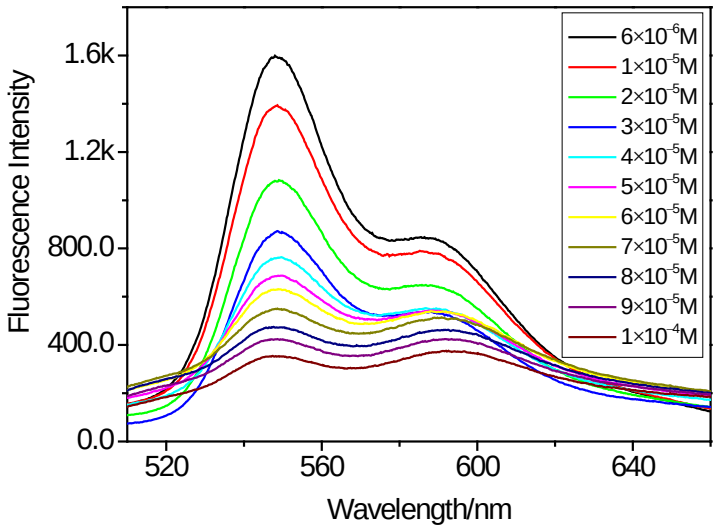

Fig. S7. Concentration-dependent fluorescence spetra of **PBI-Lac** in water, concentration range from 6.0×10^{-6} M to 1.0×10^{-4} M.

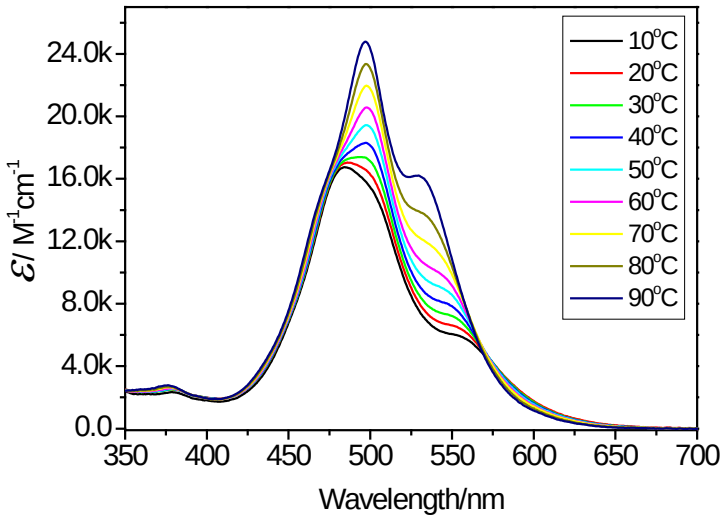

Fig. S8. Temperature-dependent UV-Vis spectra of **PBI-Lac** (1.0×10^{-5} M) from 10 °C to 90 °C.

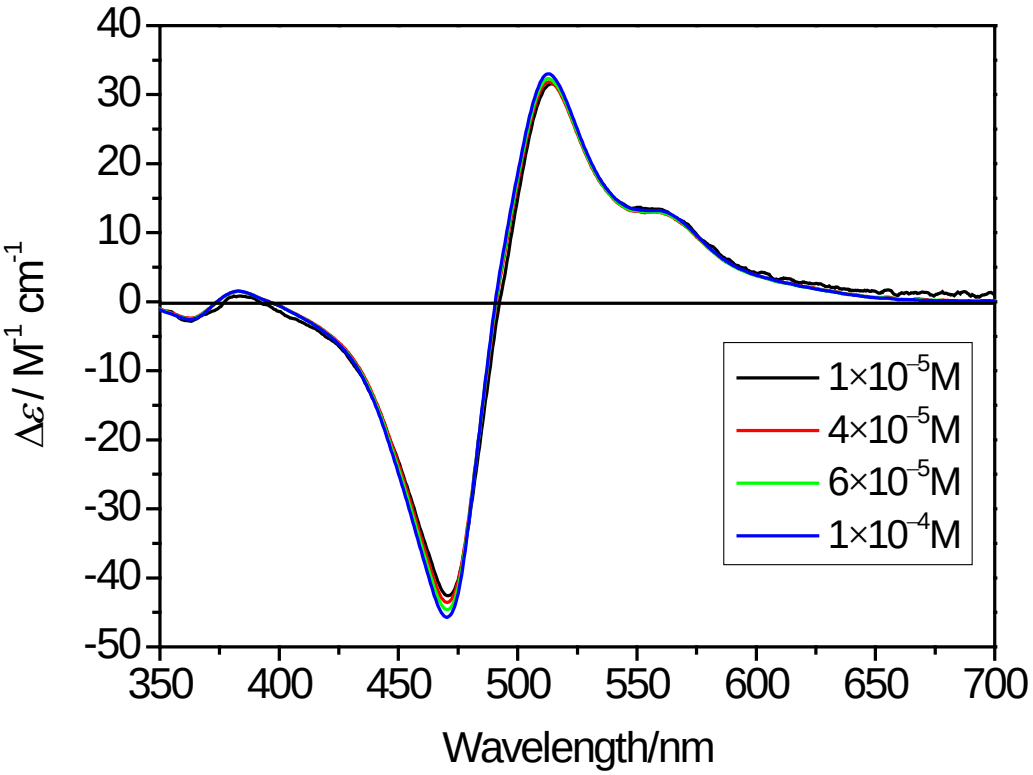

Fig. S9. Concentration-dependent CD spectra of **PBI-Lac** in water, concentration range from 1.0×10^{-5} M to 1.0×10^{-4} M.

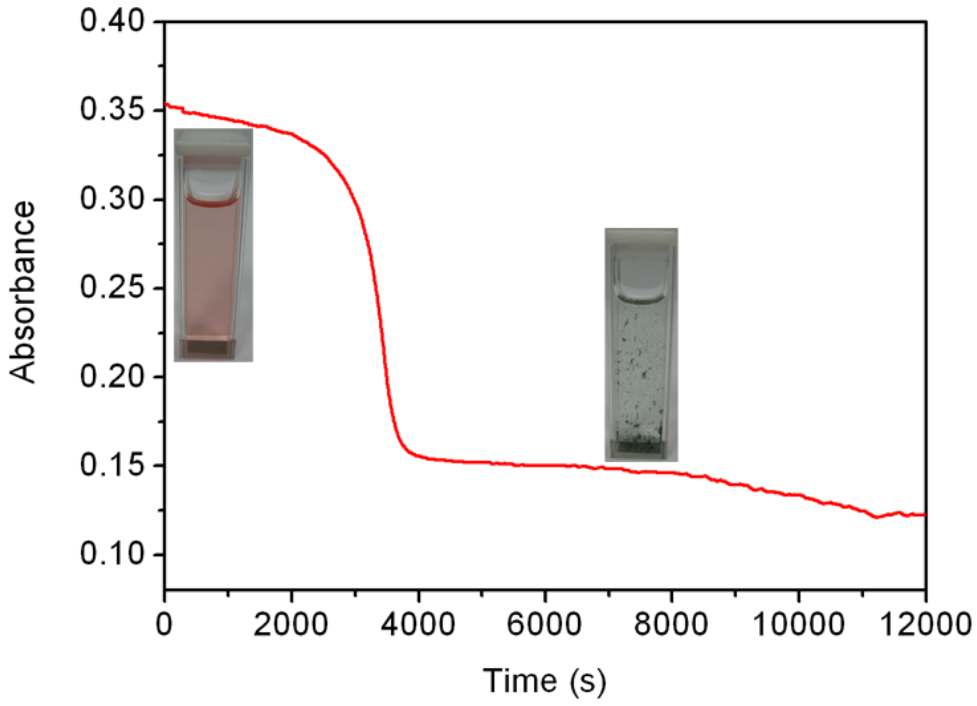

Fig. S10. Kinetic plot for the aggregation of **PBI-Lac** (2.0×10^{-5} M) in H_2O/MeOH (50/50), λ = 494 nm. The inset shows the photographs of **PBI-Lac** at the triggering state and the aggregation state**.**

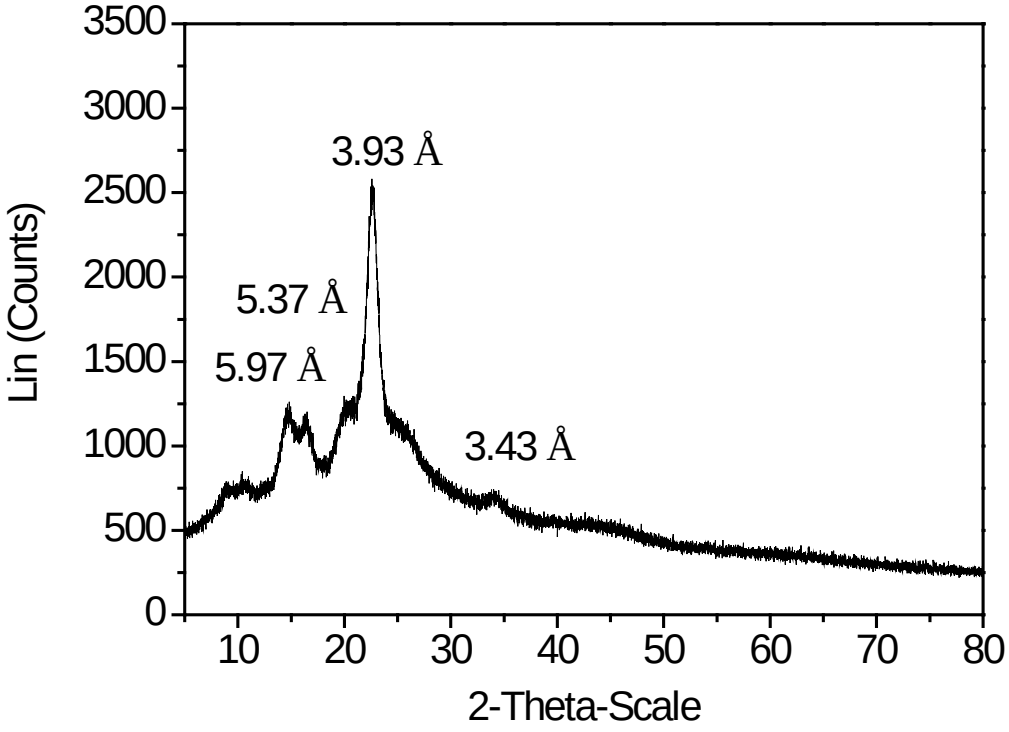

Fig. S11. XRD data of **PBI-Lac**.

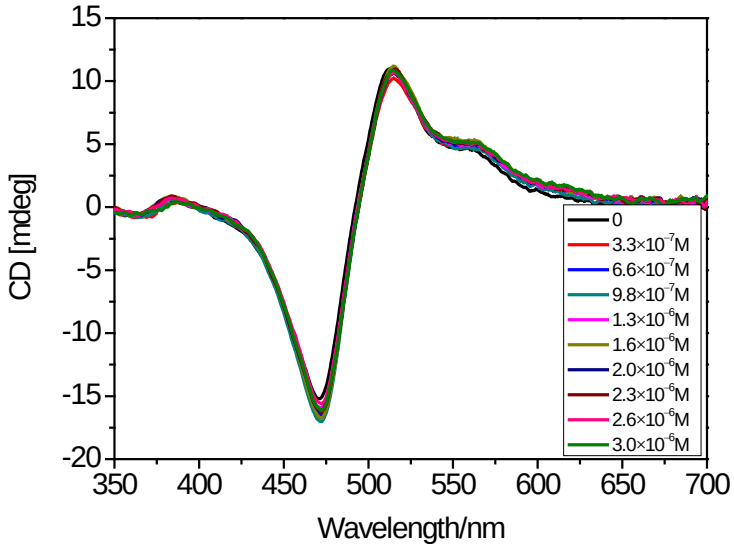

Fig. S12. CD spetra of **PBI-Lac** (1.0×10^{-5} M) upon addition of PNA (from 3.3×10^{-7} M to 3.0×10^{-6} M).

Reference:

1 C. W. Cairo, J. E. Gestwicki, M. Kanai, L. L. Kiessling, *J. Am. Chem. Soc.* 2002, **124**, 1615.

2 (a) Ni, J., Singh, S., and Wang, L.X. *Bioconjug. Chem.*, 2003, **14**, 232; (b) M. D. Disney and P. H. Seeberger, *Chem. Biol.*, 2004, **11**, 1701; (c) A. V. Demchenko, G. J. Boons., *J. Org. Chem.*, 2001, **66**, 2547.