Arene-Perfluoroarene Interaction Induced Chiroptical Inversion and Precise ee% Detection for Chiral Acids in a Benzimidazole-Involved Ternary Coassembly

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Experimental Section

Materials

Tartaric acid (**TA**), malic acid (**MA**) and 1-pyrenecarboxylic acid were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Dimethylsulfoxide (DMSO) was purchased from Jinan Saibo Instrument Co., Ltd. O-phenylenediamine and 5-aminoisophthalic acid was bought from Bide Pharmatech Ltd. All water used in this work is deionized (DI) water.

Computational details

Molecular dynamic (MD) simulation

The geometries of **PBI**, *L*-**TA** and **OFN** were optimized by Gaussian View06 program, which were initially optimized, and the electrostatic potential (ESP) was simultaneously calculated by Hartree–Fork method at the B3LYP/6-31G (d) basis. The Antechamber program was used to fit the restrained electrostatic potential (RESP) charge, and then the general amber force field (GAFF) was adopted to parameterize the for subsequent MD simulations. The MD simulation of different assemblies were carried out as following. Take the structure of

PBI/*L*-**TA**/**OFN** (2/6/6 by molar ratio) as example. Firstly, we built a box with a length, width and height of 20, 15, 15 nm, respectively. And we insert 50 **PBI** molecules into the box by free dispersing. Then, 150 *L*-**MA** molecules are introducing into the box with the synergetic effect of H-bonded between **PBI** and *L*-**MA**, π-π stacking between **PBI** as well as the intramolecular and intermolecular H-bonded of *L*-**MA** (with a ~2 Å d-spacing). Next, 150 **OFN** molecules are introducing into the box with the Arene-Perfluoroarene (AP) interaction between pyrene ring and **OFN**. Finally, the box was full of solvent (the water solvent simulated was the SPC216 model). The MD simulations of coassembly systems were carried out for 50 ns with a time step of 0.002 ps per integration step under the ensemble conditions of T = 298 K. All MD simulations were implemented with the GROMACS 2020 program.

Characterizations

If not particularly indicated, all characterizations were carried out at room temperature. Transmission electron microscopy (TEM) images were recorded using a JEM-100CX II electron microscope (100 kV). Samples for TEM were prepared by dropping 20 mL aggregate solution on TEM copper grids, followed by air drying. X-ray diffraction (XRD) patterns were recorded on a PANalytical X′pert3 power diffractometer (40 kV, 40 mA) using Cu Ka radiation (λ = 0.15418 nm). It should be noted that the whole measurement was divided into two parts comprising small angle (0.5–10 degree) and wide angle (10–50 degree) regions. For XRD, assembled systems were centrifuged to remove solvents and non-assembled species, and the obtained aggregates were spread evenly on glass slide and air-dried at room temperature. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a Bruker

Advance 400 MHz instrument. Circular dichroism (CD) and Circular polarized light (CPL) spectra were measured with Applied Photophysics Chirascan.

Sample preparation

Suspension solutions for CD characterization

In order to trigger coassembly, **PBI** and chiral acids (**TA** and **MA**) were dissolved in dimethyl sulfoxide (DMSO) and deionized water as concentrated stock solutions (100 mM), respectively. Then, **PBI** (2 mM) and different concentrations chiral acids aqueous solution were successively added into 5 mL vials. Taking the preparation of **PBI**/*L*-**MA** (**PBI** : *L*-**MA** = 2 mM : 6mM) assemblies as an example, **PBI** (55.4 mg, 0.1 mmol) and *L*-**MA** (15.2 mg, 0.1 mmol) were dissolved in 1 mL DMSO (100 mM) and DI water (100 mM), respectively. Then, **PBI** stock solution (20 μL) were taken out by pipettes into different 5 mL vial, following adding the mixed solution of *L*-**MA** stock solution (60 μL) with DI water (920 μL) by a pipette into the vital. The vial was sealed by a cap, and an aging period at least for 8 h at room temperature was applied.

Emulsion solutions for chiral sensing

PBI and chiral acids (**TA** and **MA**) were dissolved in DMSO as concentrated stock solutions. In order to trigger the co-assembly, a certain amount of stock solutions of **PBI** and chiral acids were added into 5 mL bottle, followed by the addition the DI water. Taking the preparation of **PBI**/*L*-**MA** (**PBI** : ***L*-MA** = 0.5Mm : 5mM) assemblies as an example, **PBI** (55.4 mg, 0.1 mmol) and *L*-**MA** (15.2 mg, 0.1 mmol) were dissolved in 1 mL DMSO (100 mM). Then, **PBI** and *L*-**MA** stock solution (5 μL and 50μL, respectively) were taken out by pipettes into different 5 mL vial, following adding the DI water (945 μL) by a pipette into the vital. The

vial was sealed by a cap, and an aging period at least for 8 h at room temperature was applied.

Solid samples for CPL characterization

In order to preparation CPL samples, co-assembly systems were centrifuged to obtain aggregates, and those aggregates were spread evenly on quartz plate and air-dried at room temperature.

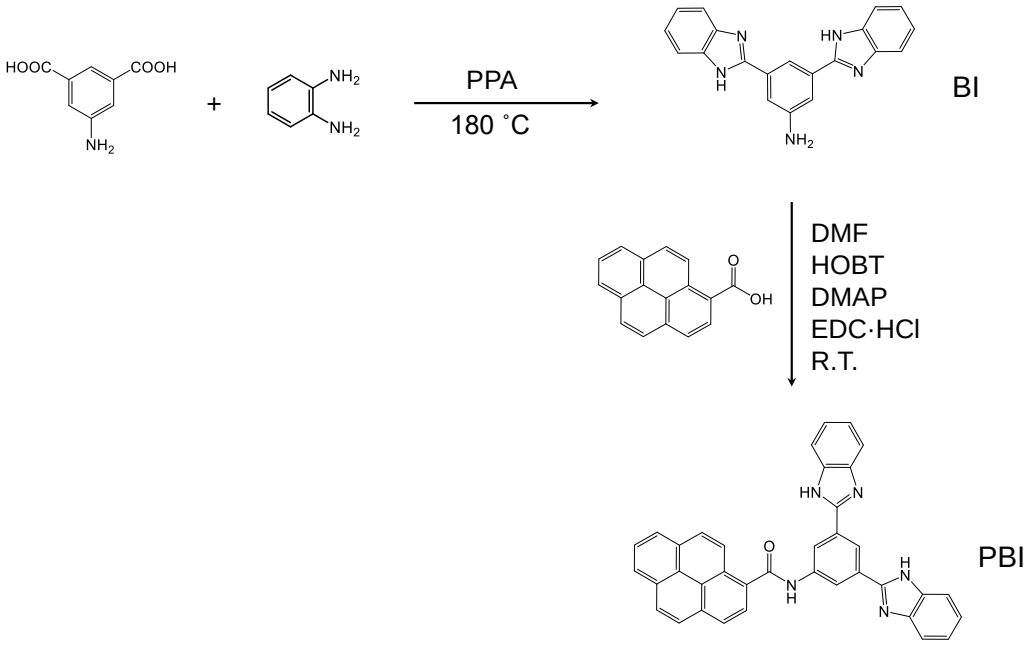
Synthesis of BI

O-phenylenediamine (0.061 mol; 6.57 g) and 5-aminoisophthalic acid (0.028 mol; 5.00 g) were added to 50 mL of polyphosphoric acid in a 100 mL round-bottom flask. The mixture was heated and stirred at 180˚C for 12 h. The resultant-colored melt was poured into 1000 ml of ice-cold water, when a solid precipitated out. The mixture was neutralized with saturation sodium bicarbonate solution with stirring 24 h and filtered. The solid was cleaned by DI water for 12 h and filtered. Finally, the solid recrystallized from methanol to get a clay brown product (8.2 g, yield ~ 90.0 %).

Synthesis of PBI

BI (1.00 g, 3.073 mmol), 1-pyrenecarboxylic acid (0.76 g, 3.073 mmol), triethylamine (1 mL, 7.21 mmol), 1-Hydroxybenzotriazole (HOBt) (0.10 g, 0.740 mmol) and 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC-HCl) (1.5 g, 7.82 mmol) and 4-dimethylaminopyridine (DMAP) (0.10 g, 0.819 mmol) were added to 150 mL of N,N-dimethylformamide in a 250 mL round-bottom flask. The mixed solution was stirred at room temperature overnight. The reaction mixture was washed with DI water for four times (4 × 100 mL). The organic phase was subjected to rotary evaporation to afford the crude product. After purifying by column (DCM/MeOH, 100:1), the final compound **PBI** (yellow powder,

yield ~ 65%) was obtained.



Scheme S1. Synthesis route of **PBI**.

^{1}H NMR (400 MHz, d_6-DMSO, 298K) δ 13.22 (s, 2H, N=C-NH), 11.16 (s, H, C=O-NH), 8.81 (s, 3H, Py-H), 8.65-8.67 (d, 1H, Py-H), 8.26-8.49 (m, 7H, Py-H and Ar-H), 7.16-8.20 (t, 1H, Py-H), 7.73-7.75 (d, 2H, Ar-H), 7.59-7.62 (d, 2H, Ar-H), 7.23-7.31 (m, 4H, Ar-H). ^{13}C NMR (101 MHz, d_6-DMSO, 298K) δ 168.49, 151.25, 144.28, 140.85, 135.75, 132.56, 132.07, 131.84, 131.23, 130.69, 129.09, 128.54, 127.74, 127.23, 126.58, 126.34, 126.03, 125.00, 124.87, 124.35, 124.14, 123.27, 122.36, 120.83, 120.23, 119.41, 112.13, 49.07. HR-MALDI-MS: calcd. for $[M+H]^+$, 554.19. Found: 554.20.

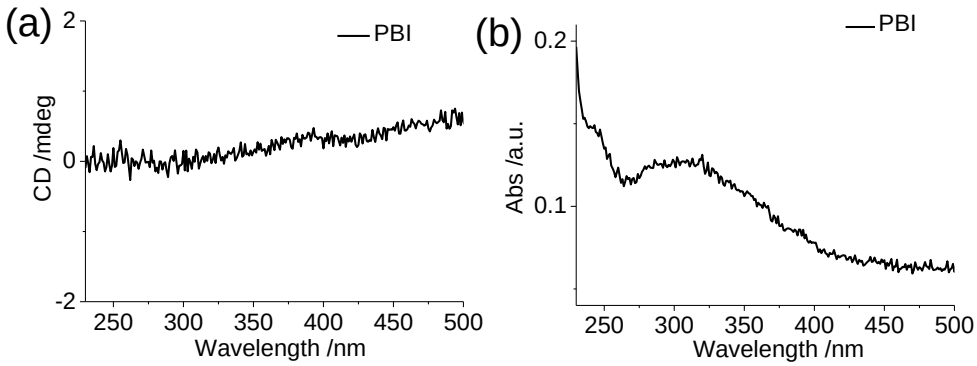


Figure S1. CD and UV spectra of **PBI** (a,b) individual assemblies.

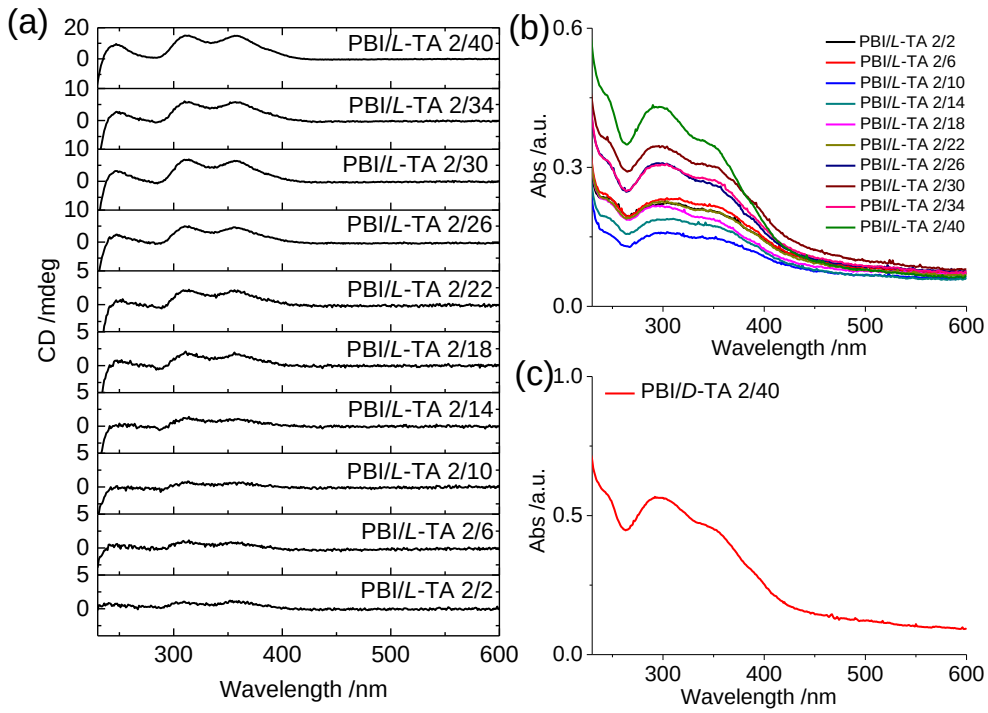
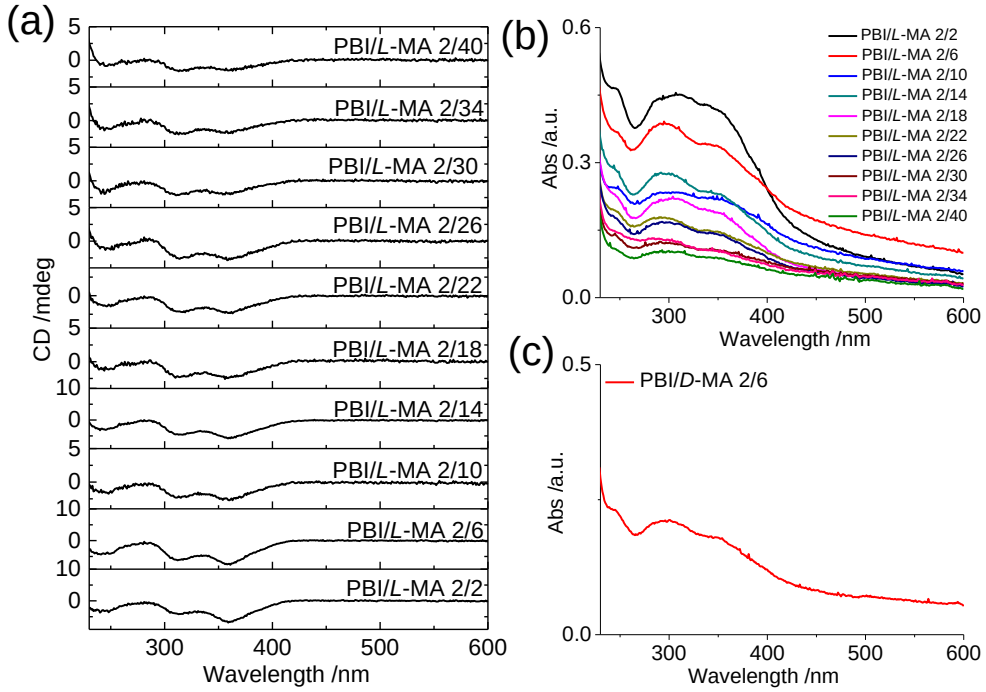


Figure S2. CD and UV spectra of **PBI** in the presence different concentrations of *L*-**TA** (a,b) as well as the UV spectra of **PBI**/*D*-**LA** (2/40 by molar ratio) (c).



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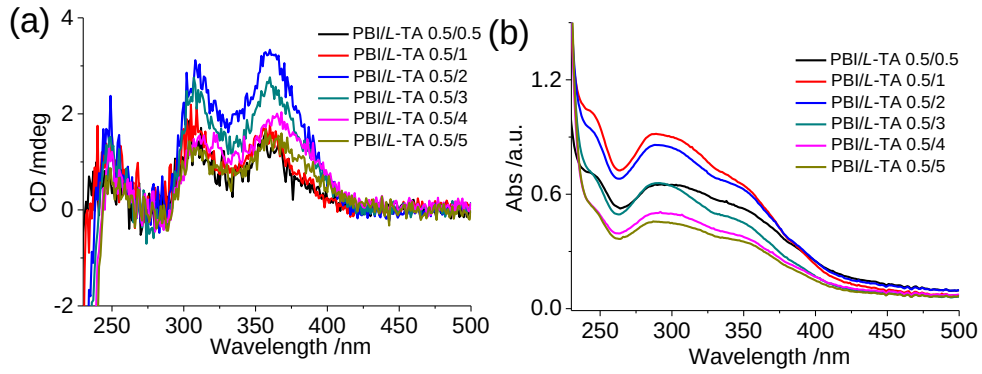
2 Figure S3. CD and UV spectra of **PBI** in the presence different concentrations of *L*-**MA** (a,b)

3 as well as the UV spectra of **PBI**/*D*-**MA** (2/6 by molar ratio) (c).



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5 Figure S4. CD and UV spectra of **PBI** in the presence different concentrations of *L*-**TA** (a,b).

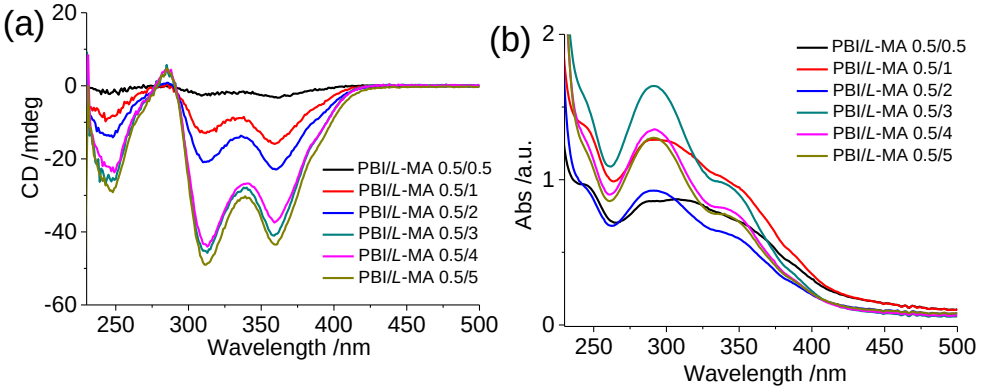

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Figure S5. CD and UV spectra of **PBI** in the presence different concentrations of *L*-**MA** (a,b).

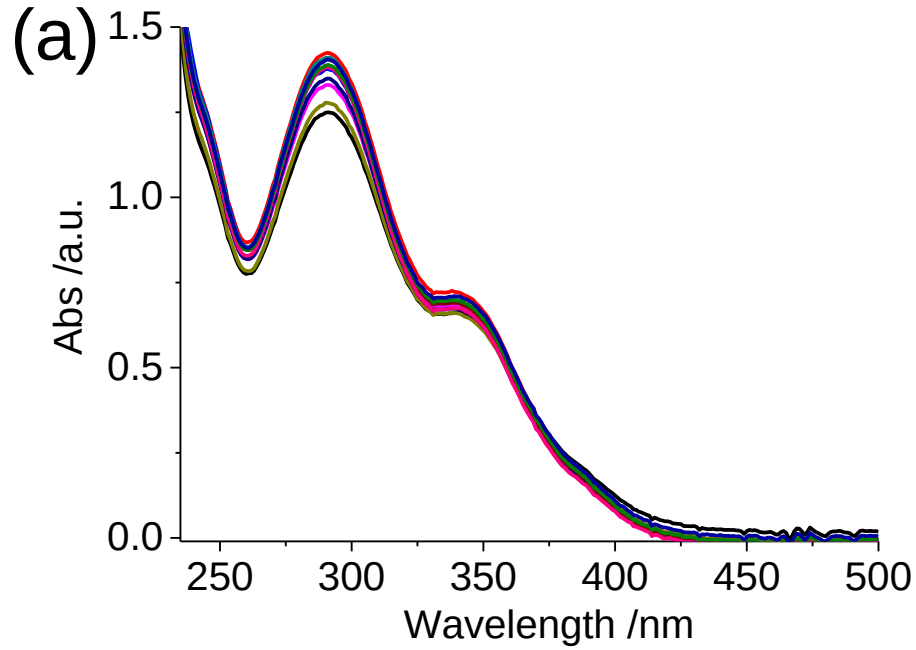

Figure S6. UV spectra of **PBI**/**MA** (0.5/5 by molar ratio) (a).

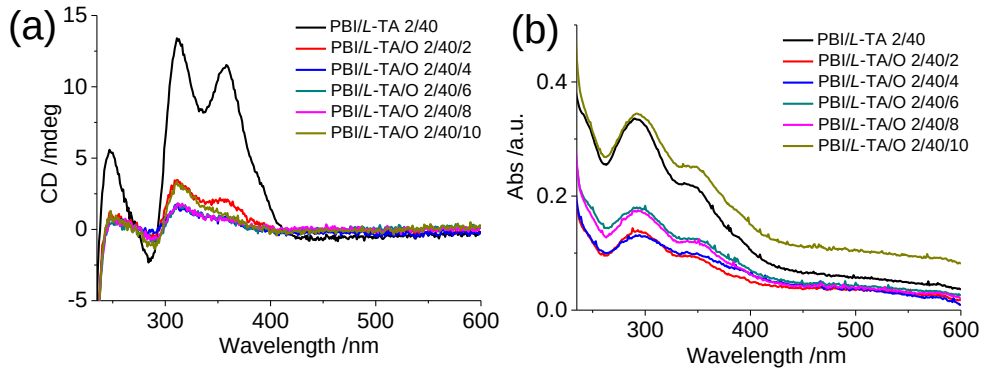

Figure S7. CD and UV spectra of **PBI**/*L*-**TA** (2/40) in the presence different concentrations of **OFN** (a,b).

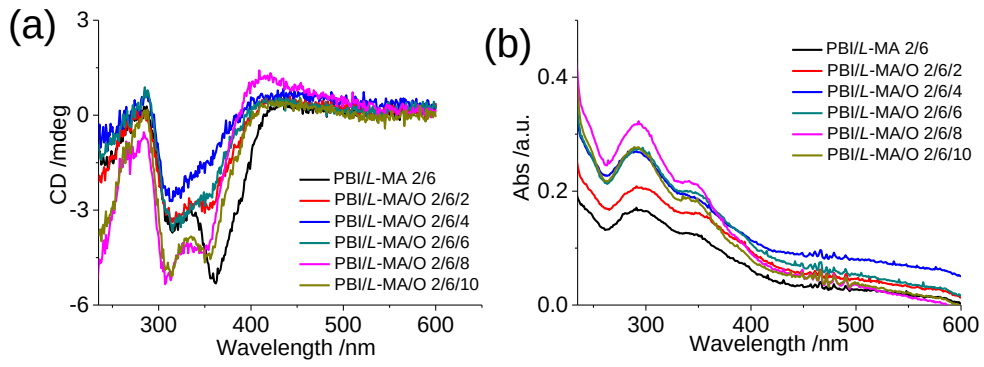

Figure S8. CD and UV spectra of **PBI**/*L*-**MA** (2/6) in the presence different concentrations of **OFN** (a,b).

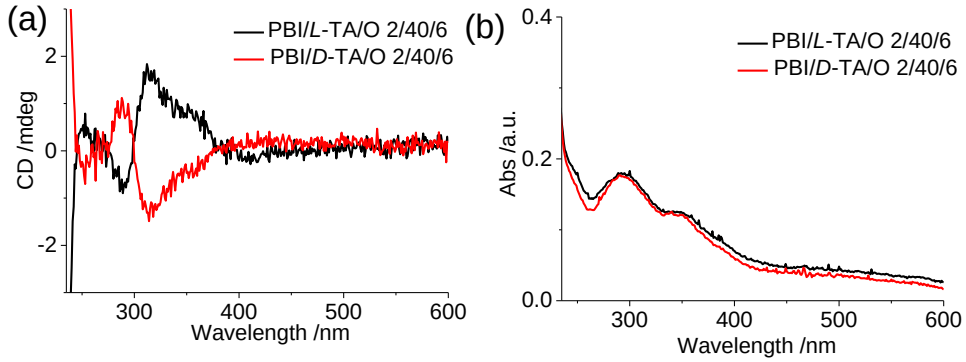

Figure S9. CD and UV spectra of **PBI**/*L*-**TA/OFN** (2/40/6) (a,b).

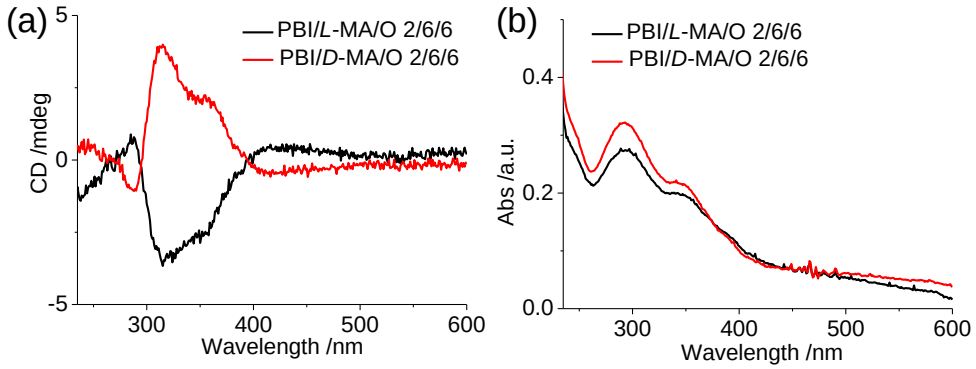

Figure S10. CD and UV spectra of **PBI**/*L*-**MA/OFN** (2/6/6) (a,b).

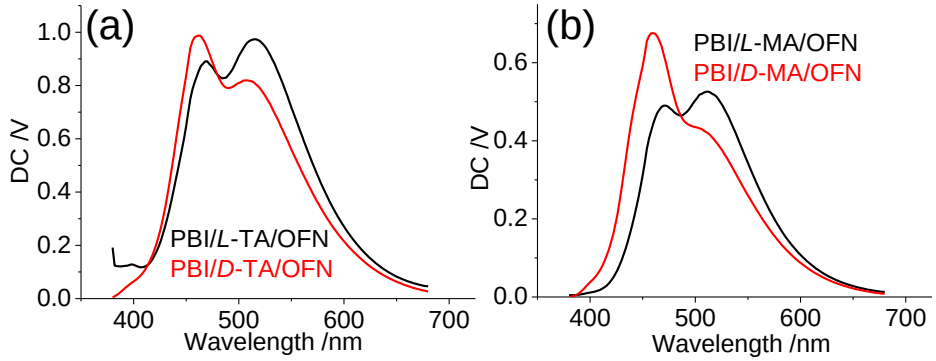

Figure S11. Fluorescence spectra of **PBI**/*L*-**TA**/**OFN** (2/40/6) and **PBI**/*L*-**MA**/**OFN** (2/6/6) (a,b).

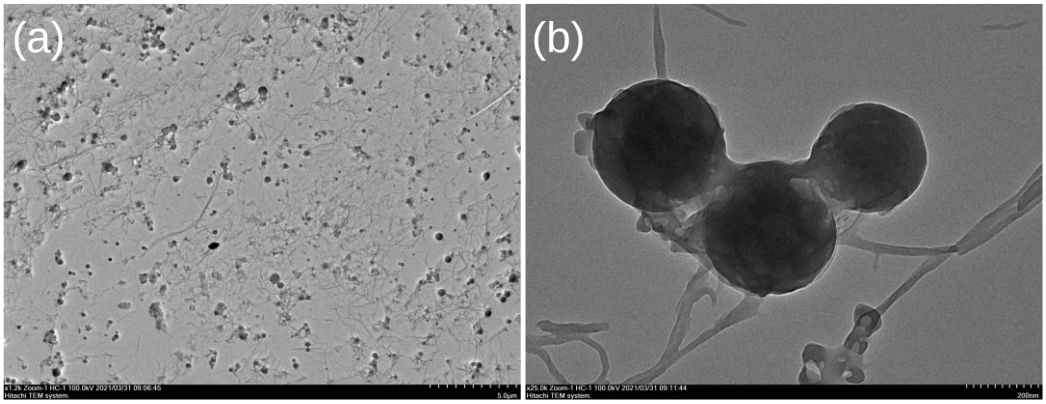

Figure S12. TEM images of **PBI** (2 mM).

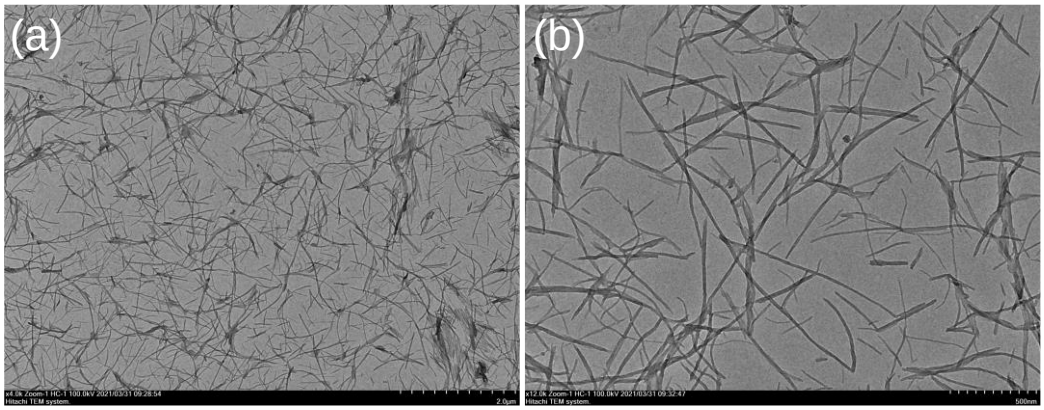

Figure S13. TEM images of **PBI**/*L*-**TA** (2/40 by molar ratio).

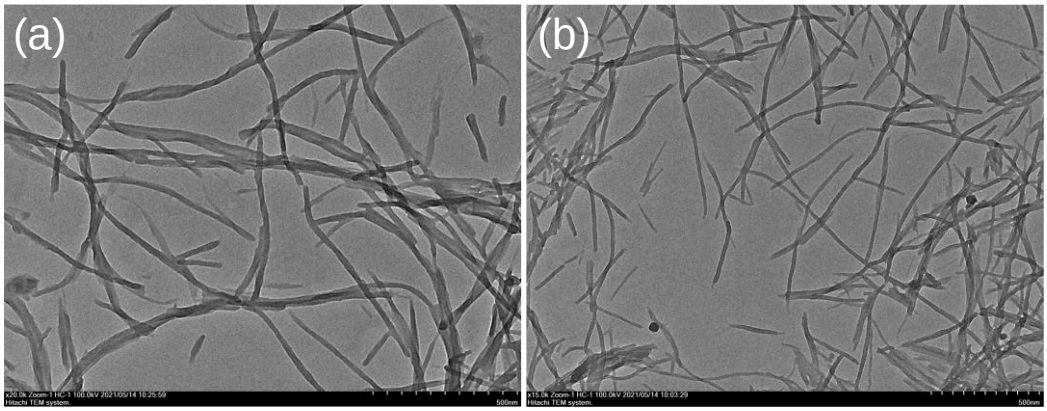

Figure S14. TEM images of **PBI**/*D*-**TA** (2/40 by molar ratio).

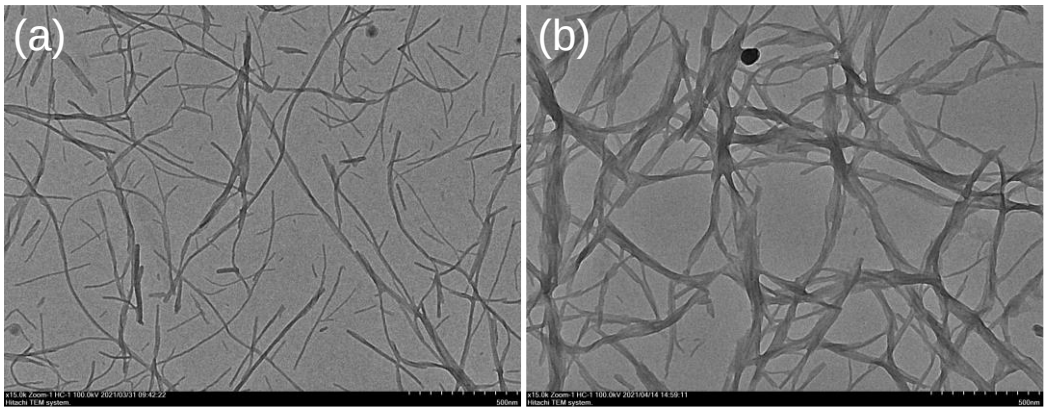

Figure S15. TEM images of **PBI/***L*-**MA** (2/6 by molar ratio).

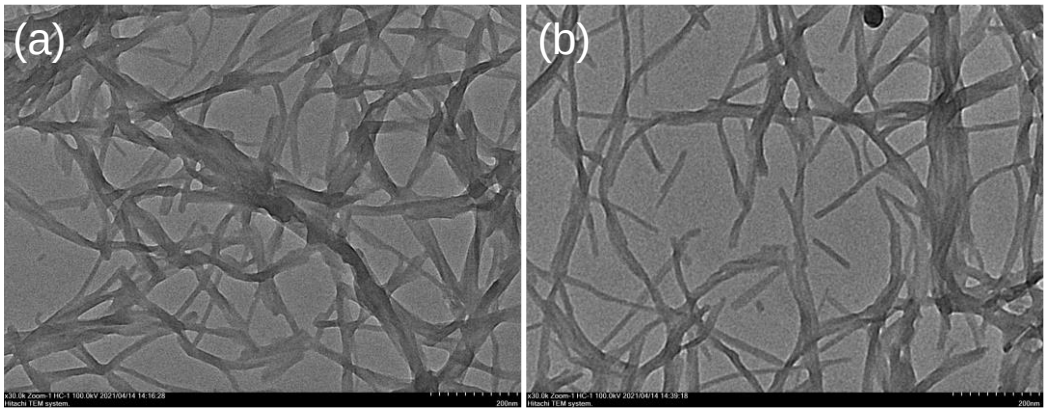

Figure S16. TEM images of **PBI/***D*-**MA** (2/6 by molar ratio).

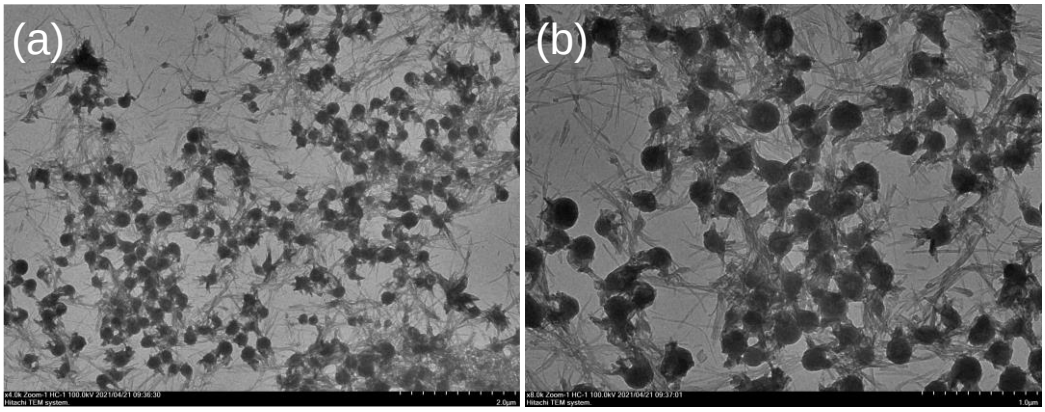

Figure S17. TEM images of **PBI/***L*-**TA** (2/40/6 by molar ratio).

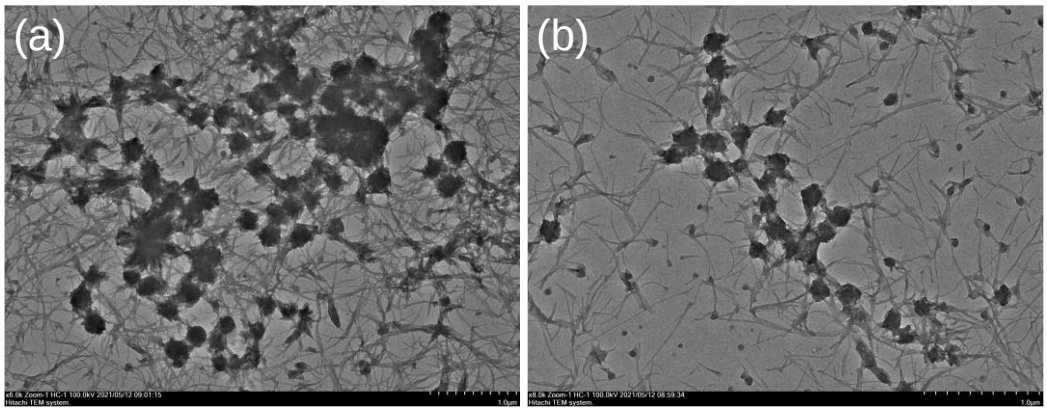

Figure S18. TEM images of **PBI**/*L*-**MA** (2/6/6 by molar ratio).

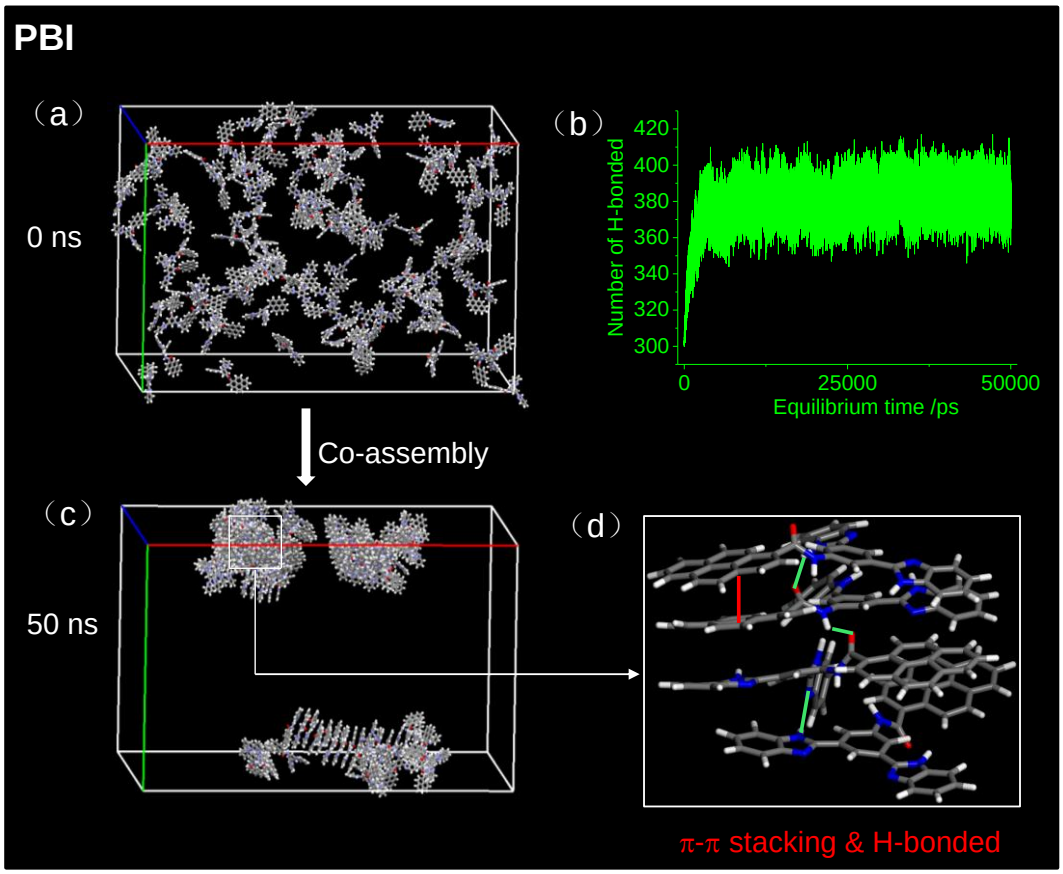

Figure S19. (a-d) The detailed MD snapshots of **PBI** at 0 and 50ns, respectively and the number of H-bonded along with simulation time.

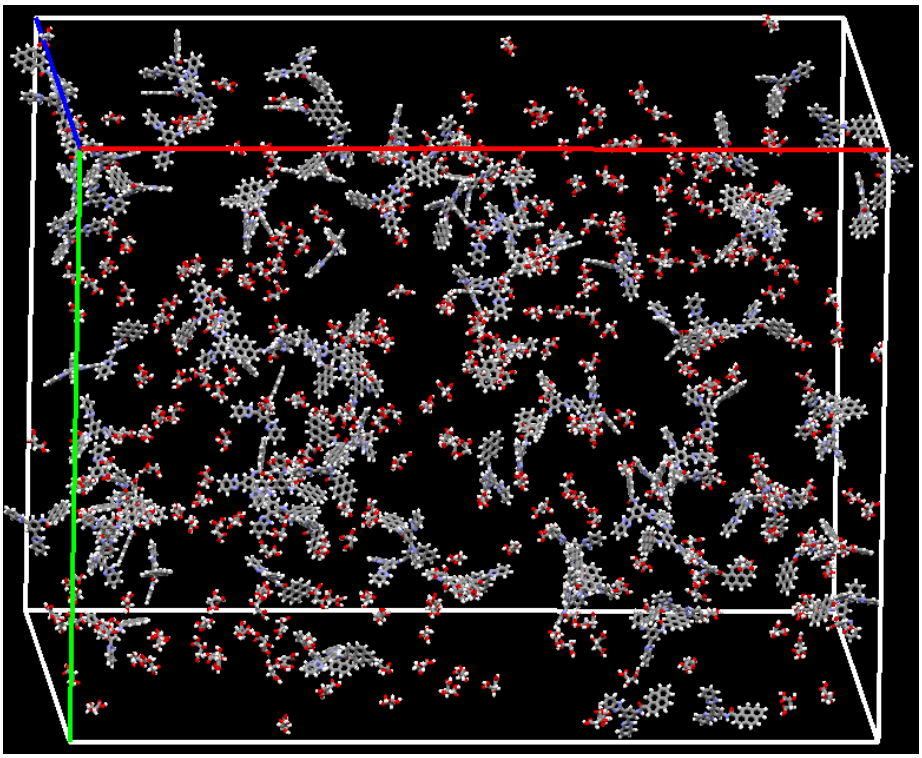

Figure S20. (a,c,d) The detailed MD snapshots of **PBI** at 0 ns.

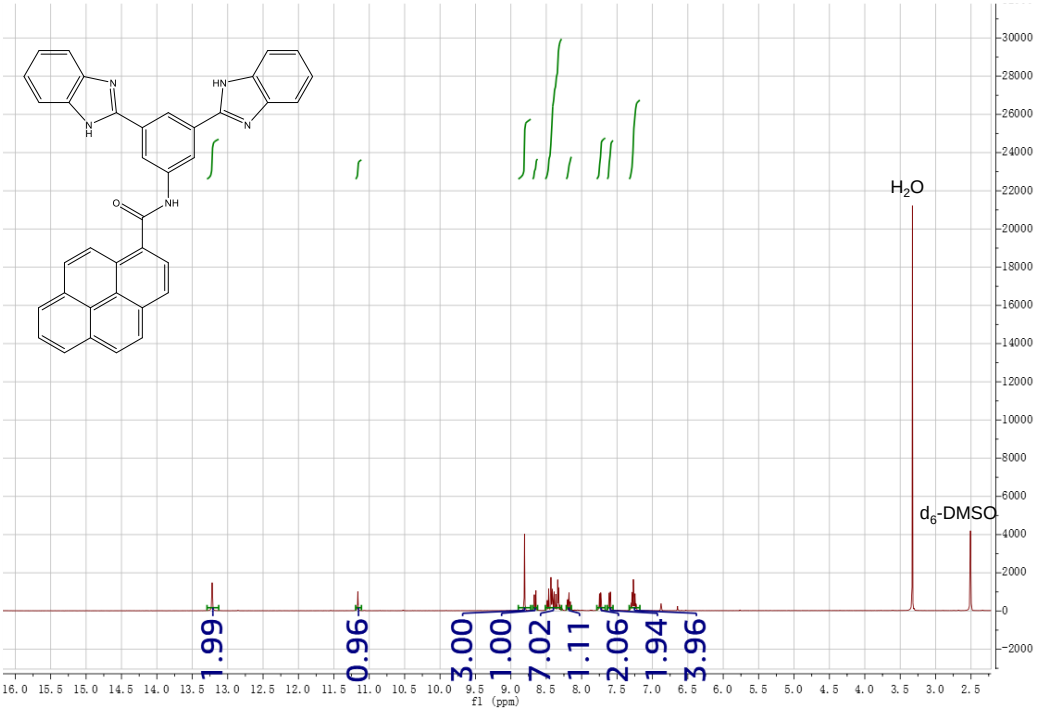

Figure S21. ^{1}H-NMR spectrum (400 MHz, d_6-DMSO, 298 K) of **PBI**.

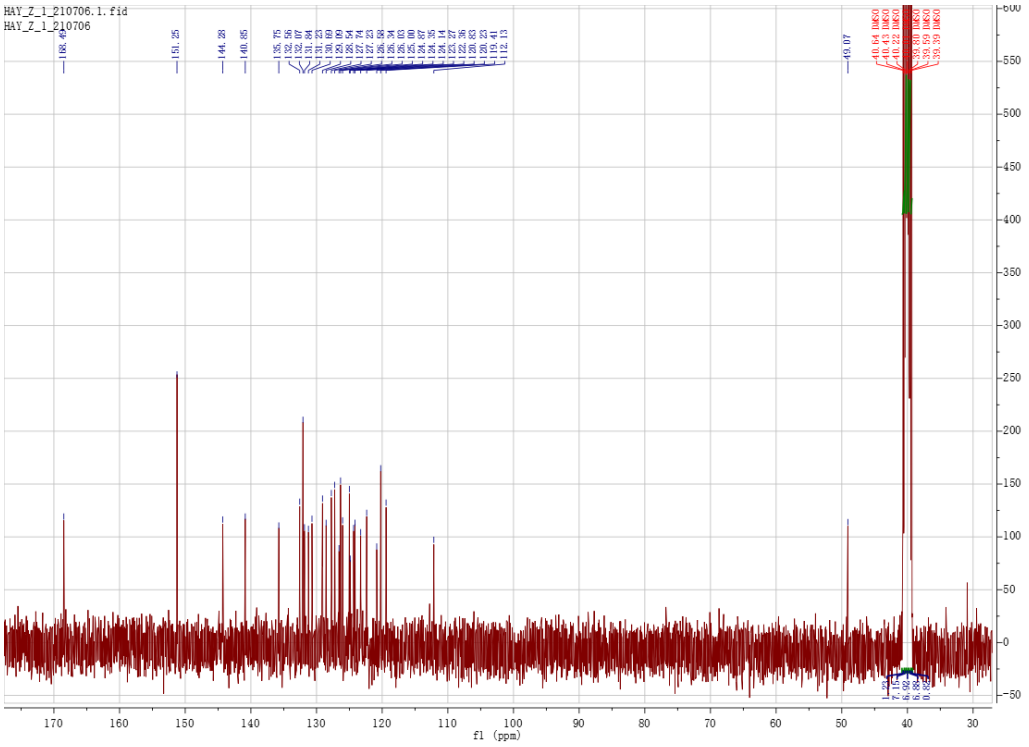

Figure S22. ^{13}C-NMR spectrum (101 MHz, d_6-DMSO, 298 K) of **PBI**.

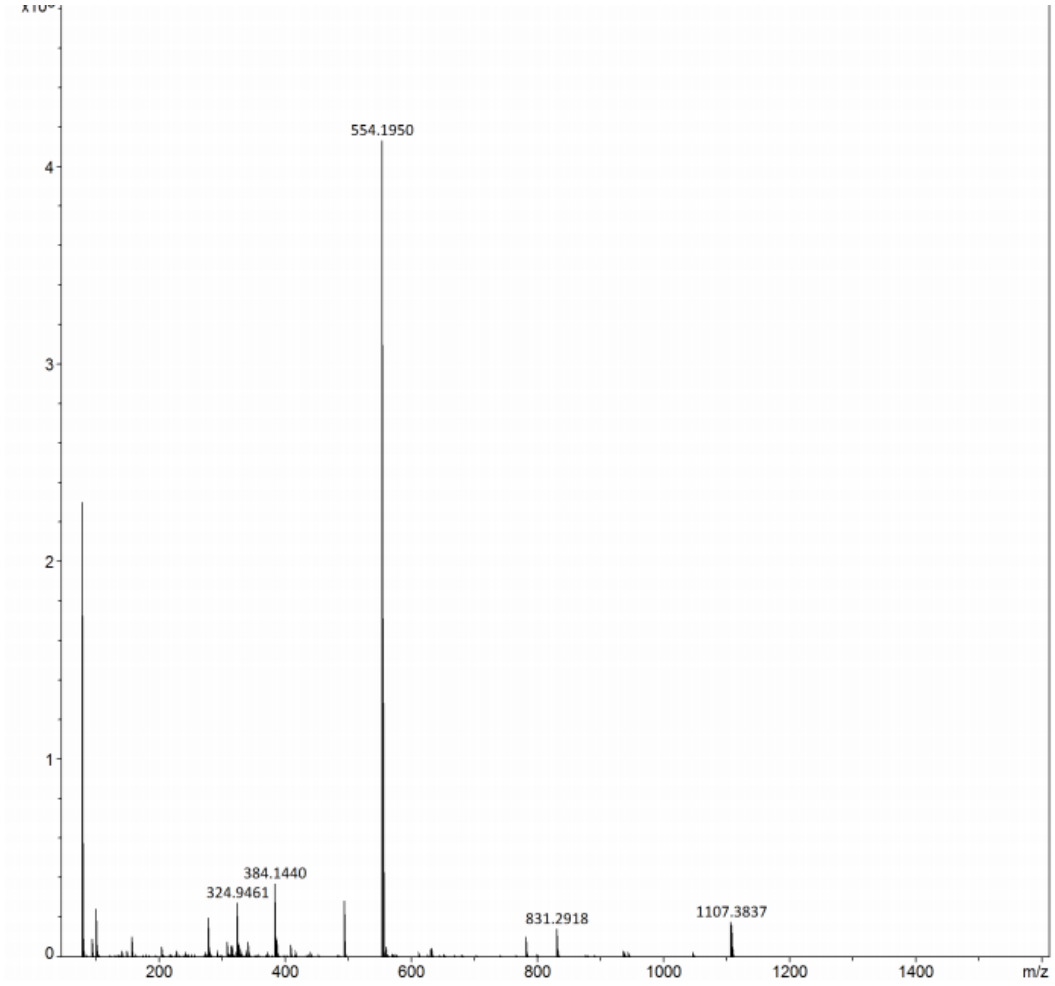

Figure S23. HR-MALDI-TOF mass spectrum of **PBI**.