

Supporting Information

for

Host-guest Interactions and Controllable Capture and Release of Proteins based on Cationic Perylene Bisimides

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1. Experimental Section

Measurements

¹H NMR and ¹³C NMR spectra were recorded at 600 MHz. HRMS analysis was performed in MALDI-TOF mode or in positive ion reflection mode or positive ion liner mode. UV–Vis spectra were recorded in a quartz cell (light path 10 mm). Fluorescence spectra were measured on a quartz cell (light path 10 mm). The absolute fluorescence quantum yield was determined by an absolute method using an integrating sphere excited at 499 nm using a 150 W Xenon lamp. The fluorescence

lifetimes were excited with a supercontinuum ultrafast fiber laser, using the time correlated single-photon-counting (TCSPC) method. Typically, 10000 counts were collected at the peak channel, and the decay curves were fitted by least-squares deconvolution with original Edinburgh Instrument software; the quality of the parameters were judged by the reduced χ^2 values and the randomness of the weighted residuals.

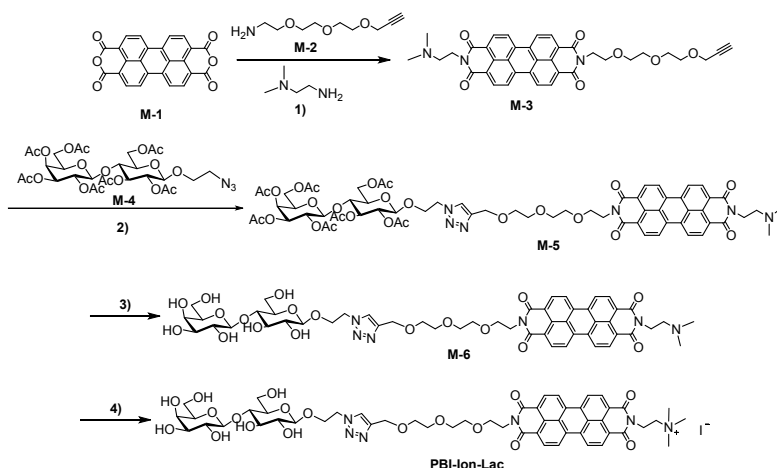
Turbidity assay: Turbidity assays were performed by adding 80 μL of the PNA solution (1 mg/mL) to a dry quartz micro-cuvette (120 μL volume, 1 cm path length). A solution of compound **PBI-Ion-Lac** was quickly added (8 μL at 1.0×10^{-4} M) and mixed vigorously. After 1500 s, a solution of CB[8] (25 μL at 7.0×10^{-5} M) was added to the above mixtures. Then another 5 μL (3.0×10^{-2} M) of ADA was added after another 1500 s. Absorbance data were recorded at 750 nm.

Binding constants (K_b): The binding constant K_b was derived from curve-fitting with Kaleidagraph, using the equation 1:^[1]

$$I_i / I_0 = 1 + (\Delta I / 2I_0) * ([G_0] + [PNA] + K_b - \sqrt{([G_0] + [PNA] + K_b)^2 - 4[G_0][PNA]}) \quad (1)$$

wherein $[G_0]$ is the initial concentration of the fluorescent probe, I_i is the intensity of the sample, I_0 is the initial intensity of the sample, $[PNA]$ is the concentration of the PNA, and ΔI is the total change in the intensity from the free state to the total binding state.

Synthesis procedures and analytical data



Scheme S1. 1) Pyridine, 120 °C, 18%; 2) Sodium ascorbate, CuSO₄, THF/H₂O, 56%; 3) NaOMe, MeOH, 95%; 4) CH₃I, DMF, 80 °C, 98%.

Compound **M-3**: In a single-neck round-bottom flask were suspended 1.0 g (2.55 mmol) of perylenetetracarboxy dianhydride **1**, 477 mg (2.55 mmol) of **M-2**, and 0.27 mL (2.55 mmol) of *N,N*-dimethylethylamine in 40 mL of pyridine, and the mixture was stirred at 120 °C for 12 h under N₂ atmosphere. The solvent was evaporated under vacuum. The residue was purified by silica-gel column chromatography using CH₂Cl₂/CH₃OH (v/v = 17/1) as the eluent to give the compound **M-3** (288 mg) with the yield of 18%. m.p. 162.0-163.6 °C; ¹H NMR (CDCl₃, 600 MHz): δ 2.38 (br, 1H, -CH), 2.42 (s, 6H, -CH₃), 2.75 (t, 2H, *J* = 6.6 Hz), 3.64 (d, 4H, *J* = 1.8 Hz), 3.67 (t, 2H, *J* = 4.8 Hz), 3.76 (t, 2H, *J* = 4.2 Hz), 3.88 (t, 2H, *J* = 6.0 Hz), 4.15 (d, 2H, *J* = 1.8 Hz, -CH₂), 4.35 (t, 2H, *J* = 6.6 Hz), 4.45 (t, 2H, *J* = 5.4 Hz), 8.26 (dd, 4H, *J* = 3.6 Hz, 7.8 Hz, perylene-H), 8.44 (t, 4H, *J* = 8.4 Hz, perylene-H); ¹³C NMR (CDCl₃, 150 MHz): δ 38.1, 39.2, 45.7, 56.9, 58.3, 67.8, 69.1, 70.0, 70.3, 70.6, 74.5, 79.7, 122.3, 122.6, 122.7, 125.1, 128.3, 128.4, 130.5, 133.3, 162.6, 162.7; HRMS: Calcd. for C₃₇H₃₄N₃O₇, 632.2397, found 632.2393.

Compound **M-5**: Then the mixture **M-3** (300 mg, 0.48 mmol) and compound **M-4** (204 mg, 0.72 mmol) were dissolved in THF (30 mL), and an aqueous solution of CuSO₄·5H₂O (114 mg, 0.54 mmol) and sodium ascorbate (102 mg, 0.54 mmol) were added, respectively. The mixture was stirred for 10 h at 55 °C. The solvent was evaporated under vacuum. The residue was purified by silica-gel column chromatography using CH₂Cl₂/CH₃OH (v/v = 17/1) as the eluent to give compound **M-5** (360 mg) with the yield of 56.0%. m.p. 174.7-176.1 °C; ¹H NMR (CDCl₃, 600 MHz): δ 1.89 (s, 6H, -CH₃), 1.97-1.98 (9H, -CH₃), 2.05 (s, 3H, -CH₃), 2.07 (s, 3H, -CH₃), 2.45 (s, 6H, -CH₃), 2.79 (br, 2H), 3.57-3.58 (8H), 3.68 (t, 2H, *J* = 4.8 Hz), 3.72 (t, 1H, *J* = 9.6 Hz), 3.79-3.83 (4H), 3.98-4.03 (m, 2H), 4.05 (dd, 1H, *J* = 6.0 Hz, 11.4 Hz), 4.11 (m, 1H), 4.30 (br, 2H), 4.34 (t, 2H, *J* = 5.4 Hz), 4.40 (d, 1H, *J* = 7.8 Hz), 4.43 (m, 2H), 4.50-4.55 (3H), 4.82 (t, 1H, *J* = 7.8 Hz), 4.90 (dd, 1H, *J* = 3.6 Hz, 10.2 Hz), 5.03 (dd, 1H, *J* = 8.4 Hz, 12.0 Hz), 5.10 (t, 1H, *J* = 9.6 Hz), 5.28 (d, 1H, *J* = 3.6 Hz), 7.54 (s, 1H, Trizole-H), 8.08 (m, 4H, perylene-H), 8.28 (dd, 4H, *J* = 6.6 Hz, 22.8 Hz); ¹³C NMR (CDCl₃, 150 MHz): δ 20.5, 20.6, 20.7, 20.8, 30.9, 38.2, 39.3, 45.6, 49.9, 53.4, 56.9, 60.7, 61.7, 64.5, 66.6, 67.8, 67.9, 69.1, 69.7, 70.1, 70.4, 70.6, 70.7, 70.9, 72.5, 72.9, 76.1, 100.4, 101.0, 122.8, 122.8, 122.9, 125.6, 128.8, 128.8, 130.9, 133.9, 163.0, 163.0, 169.0, 169.6, 169.6, 170.0, 170.1, 170.3; HRMS: Calcd. for C₆₅H₇₂N₆NaO₂₅, 1359.4445, found 1359.4445.

Compound **M-6**: Compound **M-5** (334 mg, 0.25 mmol) was dissolved in MeOH (30 mL), MeONa (45 mg, 0.83 mmol) was added, and the reaction mixture was stirred at room temperature until disappearance of the starting material. The

solution was put in a cellulose dialysis tube (cutoff 1000), dialyzed against water for 2 days, and lyophilized to give the desired solid **M-6** (240 mg) with the yield of 92%. m.p. 175.6-177.0 °C; ¹H NMR (DMSO-d₆+D₂O, 600 MHz): δ 2.25 (s, 6H, -CH₃), 2.44 (br, 2H), 3.05 (t, 1H, *J* = 7.8 Hz), 3.32 (m, 5H), 3.47-3.62 (20H), 3.79 (d, 1H, *J* = 10.8 Hz), 3.85 (s, 2H), 3.92-3.97 (4H), 4.11 (m, 1H), 4.22 (d, 1H, *J* = 6.6 Hz), 4.34 (d, 1H, *J* = 7.8 Hz), 4.52-4.58 (5H), 7.41-7.50 (8H, perylene-H), 8.15 (s, 1H, Triazole-H); ¹³C NMR (DMSO-d₆+D₂O, 150 MHz): δ 45.1, 49.5, 55.8, 60.2, 63.4, 66.4, 67.3, 67.9, 68.9, 69.5, 69.6, 70.4, 72.2, 72.8, 73.0, 74.6, 74.8, 75.4, 80.4, 102.4, 103.7, 120.3, 120.4, 122.5, 124.6, 126.1, 128.9, 128.9, 131.5, 143.7, 161.3, 161.4; HRMS: Calcd. for C₅₁H₅₈N₆NaO₁₈, 1065.3705, found 1065.3702.

Compound **PBI-Ion-Lac**: In a single-neck round-bottom flask were suspended 50 mg (0.048 mmol) of compound **M-6** and 7.5 mL (3.3 mmol) of CH₃I in 5 mL of DMF, and the mixture was stirred at 80 °C for 12 h under N₂ atmosphere. The deposited solid was collected by filtration and washed with CH₂Cl₂. Compound **PBI-Ion-Lac** (51 mg) was obtained with the yield of 90%. m.p. 183.3-184.6 °C; ¹H NMR (DMSO-d₆+D₂O, 600 MHz): δ 3.27-3.29 (12H), 3.43 (s, 3H), 3.54-3.66 (14H), 4.04 (br, 2H), 4.14-4.27 (8H), 4.47 (br, 2H), 4.78 (m, 4H), 7.91-8.17 (8H, perylene-H), 8.78 (s, 1H, Triazole-H); ¹³C NMR (DMSO-d₆+D₂O, 150 MHz): δ 34.1, 34.2, 38.0, 52.6, 52.8, 53.3, 54.8, 59.8, 60.3, 61.2, 62.0, 66.0, 66.7, 69.7, 69.6, 69.7, 74.8, 75.4, 80.4, 102.3, 103.7, 121.3, 121.5, 123.7, 130.2, 130.3, 132.6, 133.6, 134.1, 139.9, 162.1, 162.3; HRMS: Calcd. for C₅₂H₆₁N₆O₁₈, 1057.4037, found 1057.4050.

2. NMR spectra and additional figures

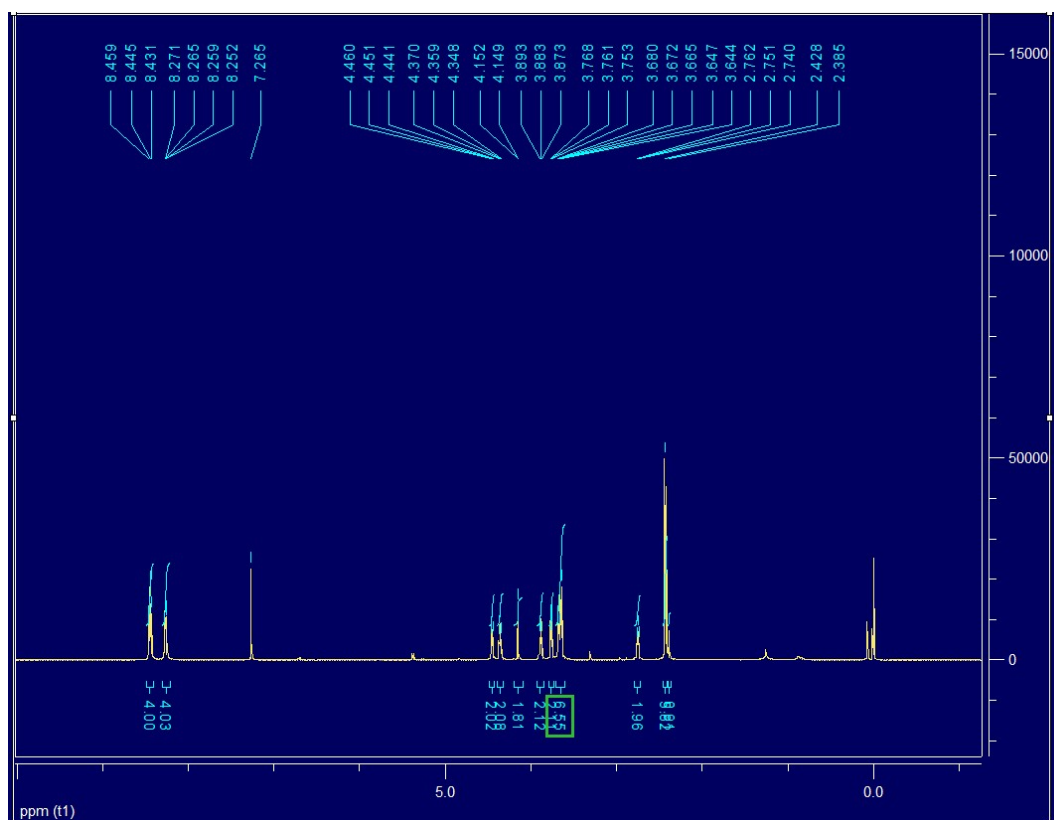


Fig. S1 ¹H NMR (CDCl₃, 600 MHz) of compound **M-3**.

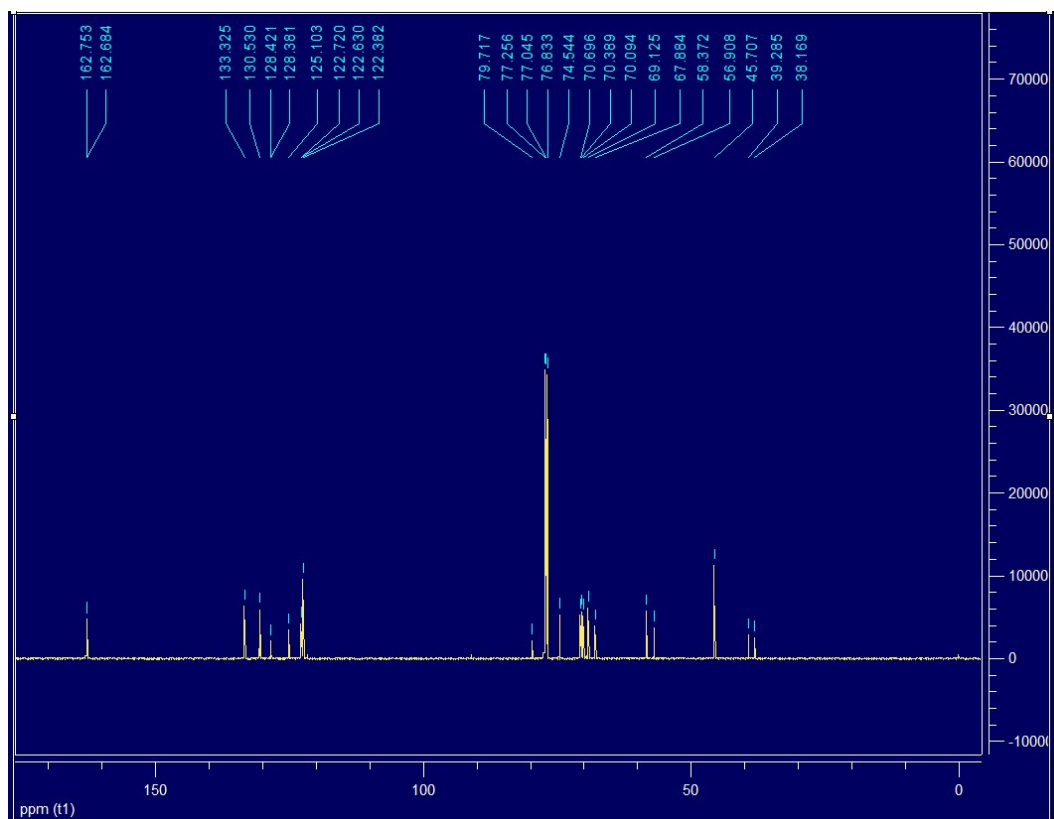


Fig. S2 ¹³C NMR (CDCl₃, 150 MHz) of compound **M-3**.

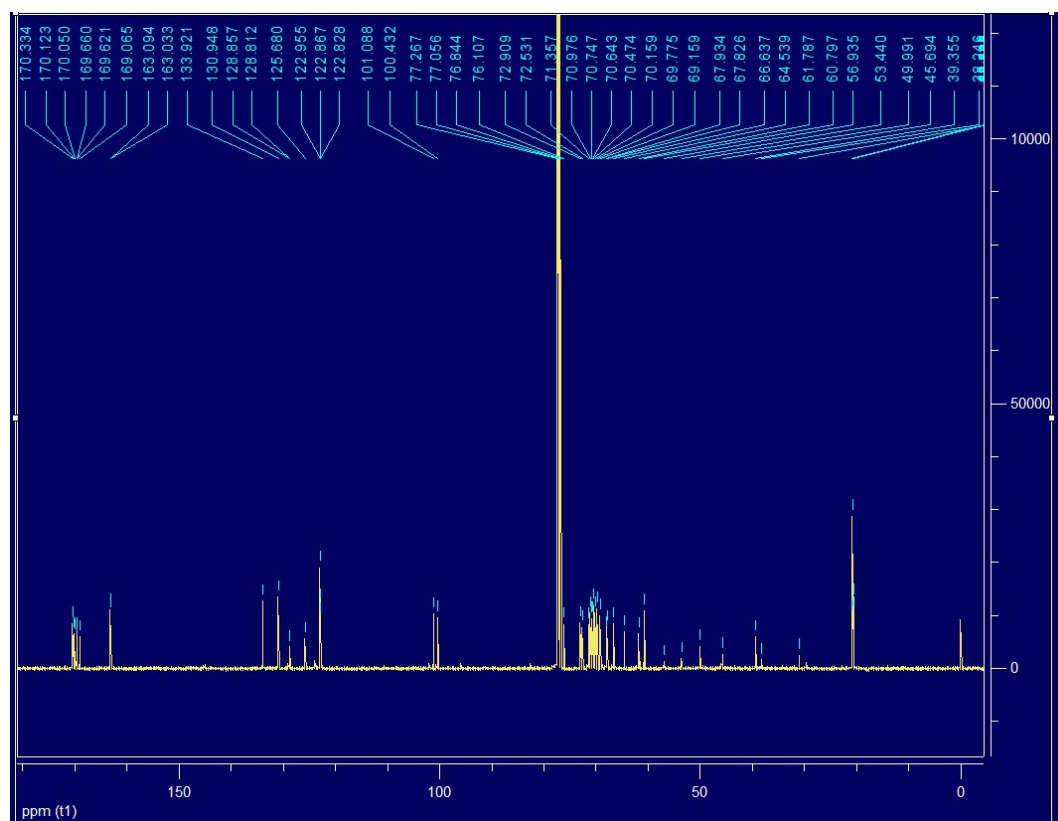


Fig. S5 ^{13}C NMR (CDCl_3 , 150 MHz) of compound **M-5**.

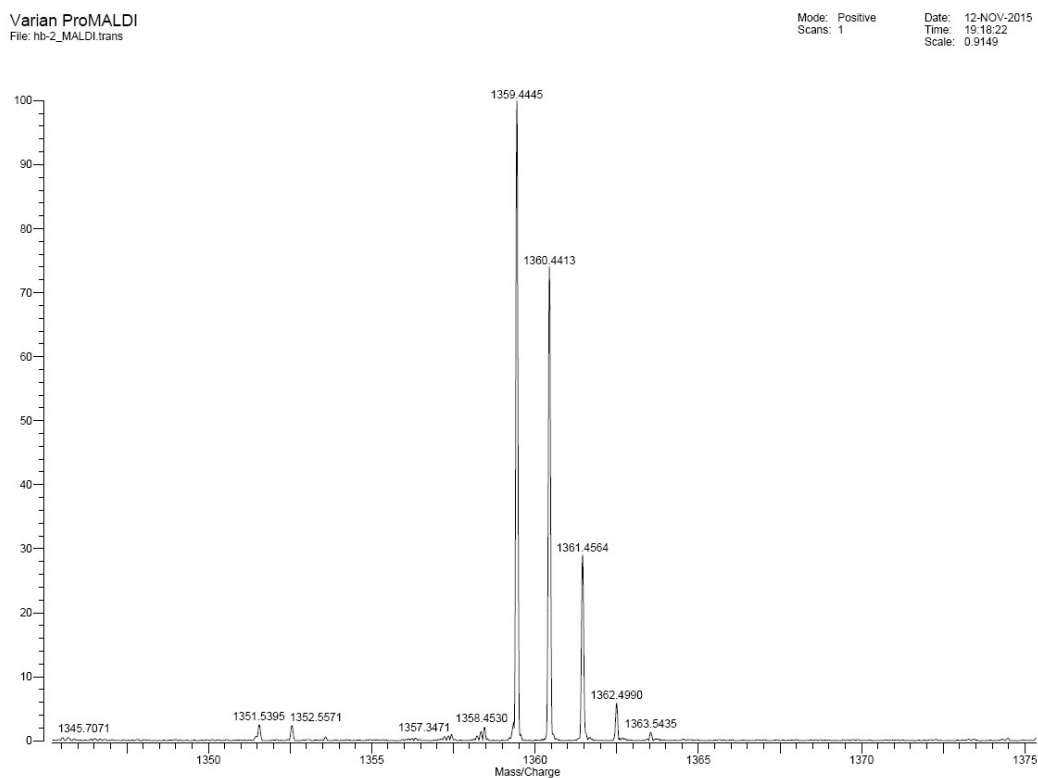


Fig. S6 HRMS of compound **M-5**.

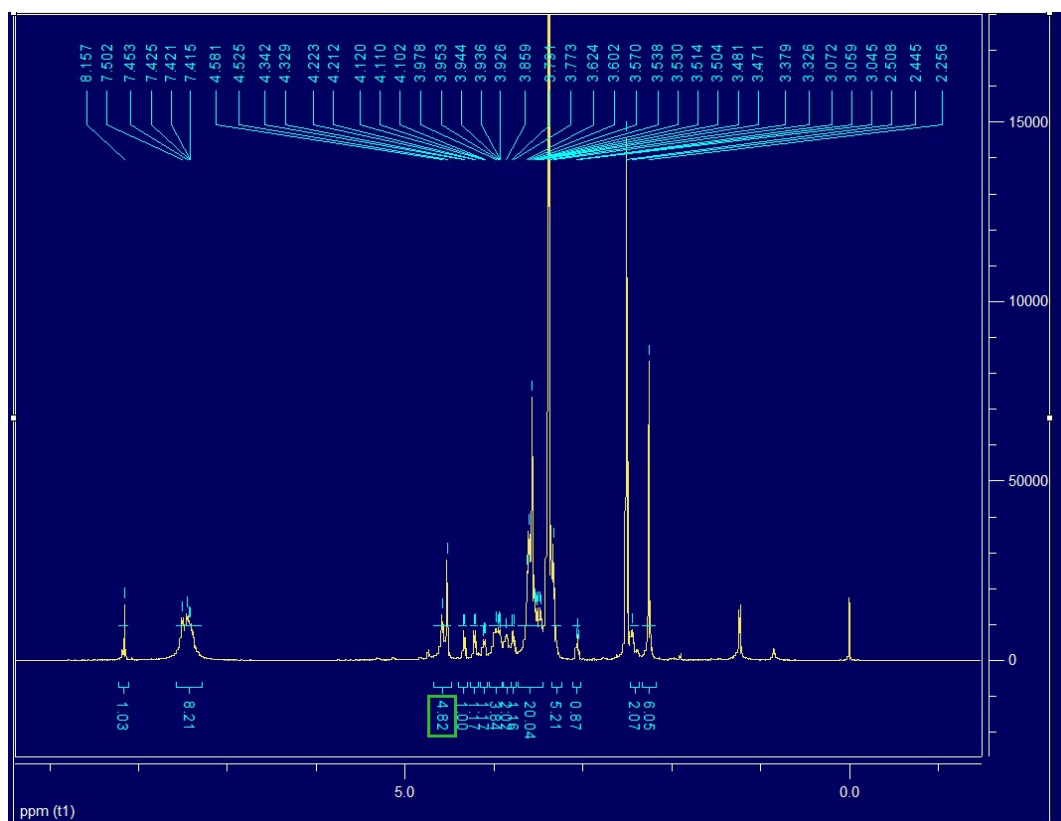


Fig. S7 ^1H NMR ($\text{DMSO-d}_6 + \text{D}_2\text{O}$, 600 MHz) of compound **M-6**.

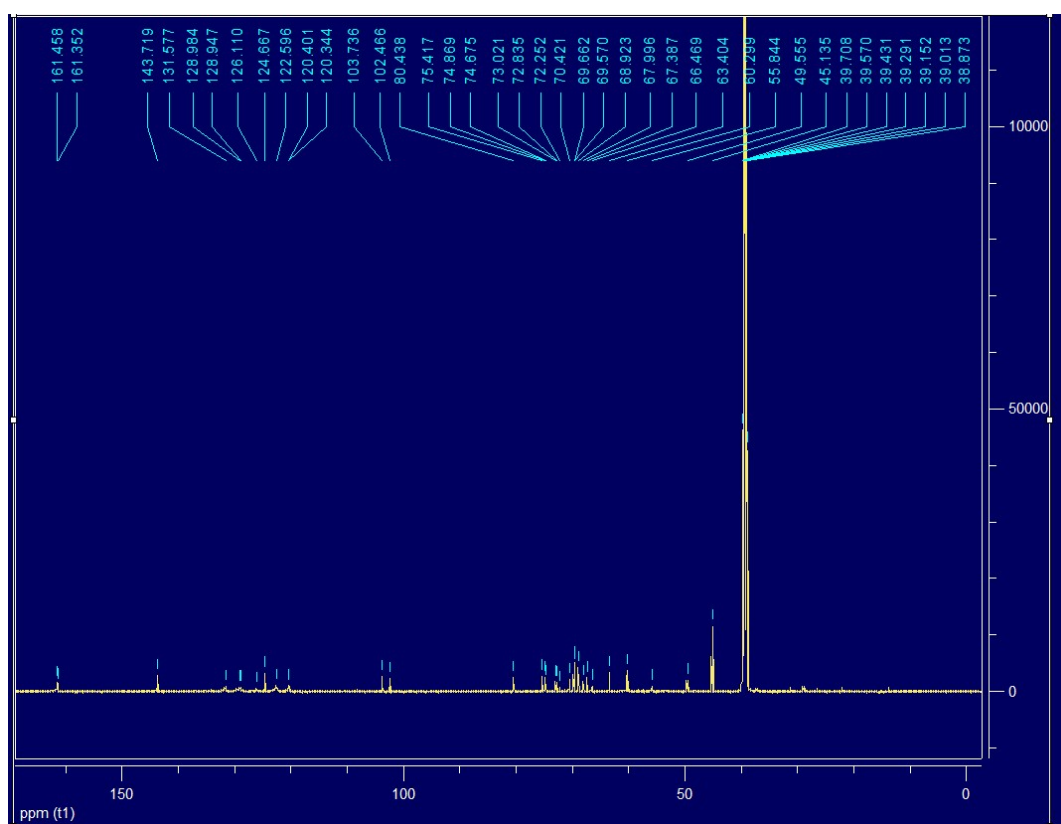


Fig. S8 ^{13}C NMR ($\text{DMSO-d}_6 + \text{D}_2\text{O}$, 150 MHz) of compound **M-6**.

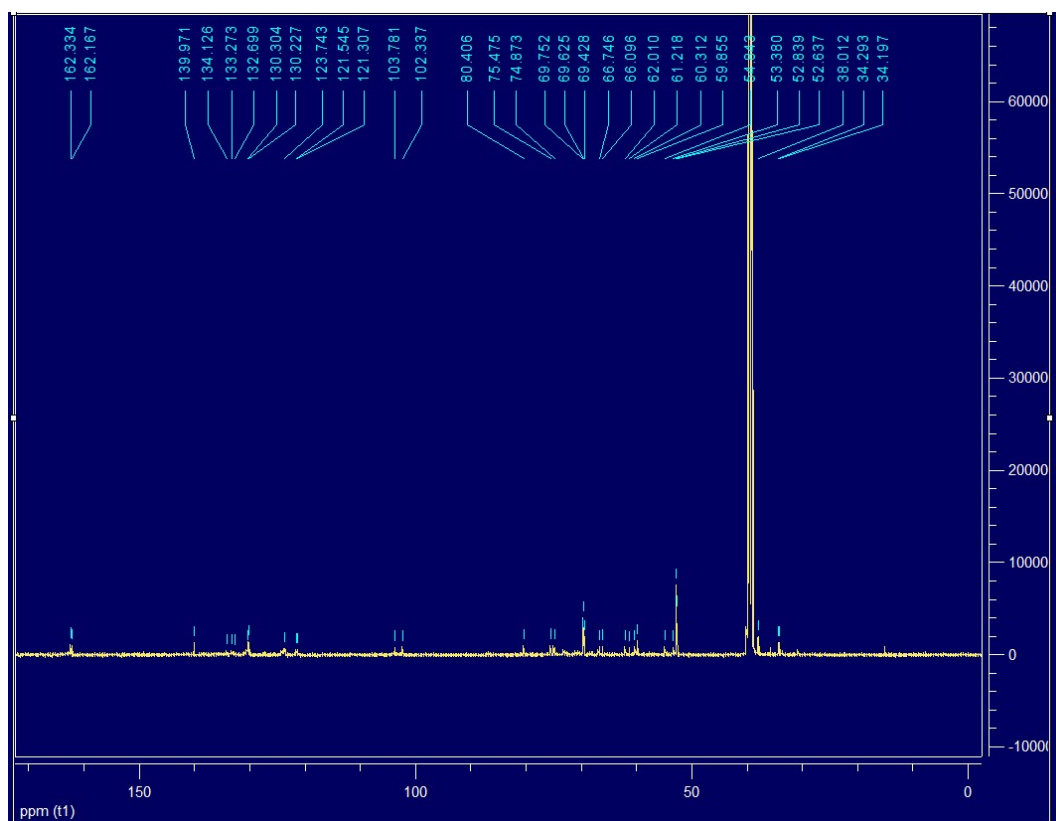


Fig. S11 ¹³C NMR (DMSO-d₆ + D₂O, 150 MHz) of compound **PBI-Ion-lac**.

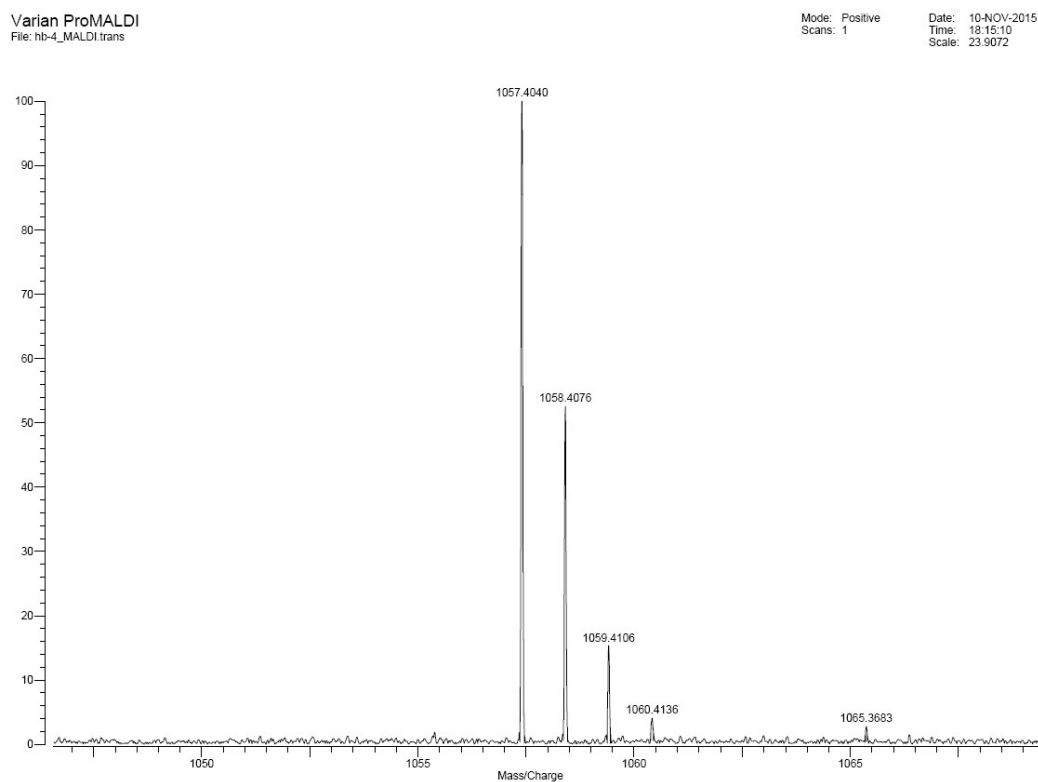


Fig. S12 HRMS of compound **PBI-Ion-Lac**.

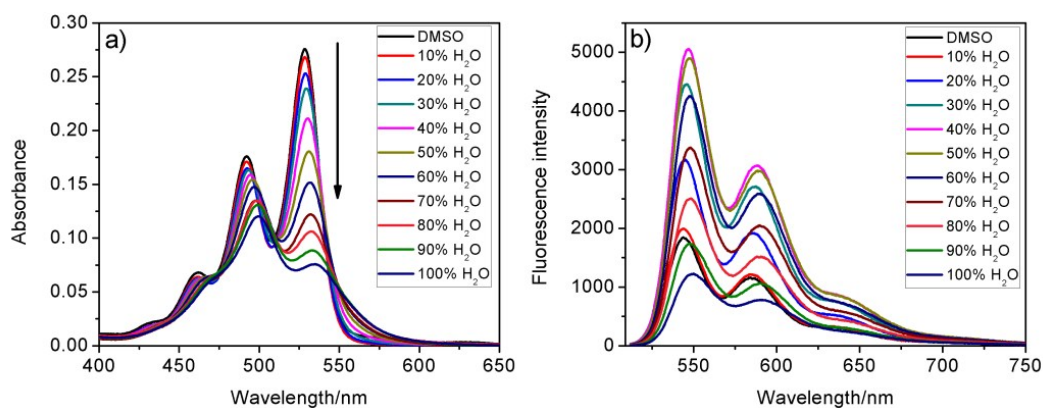


Fig. S13 UV-Vis (a) and fluorescence (b, $\lambda_{\text{ex}} = 500 \text{ nm}$) spectroscopy of **PBI-Ion-Lac** ($1 \times 10^{-5} \text{ M}$) in different volume ratios of DMSO/H₂O at 20 °C.

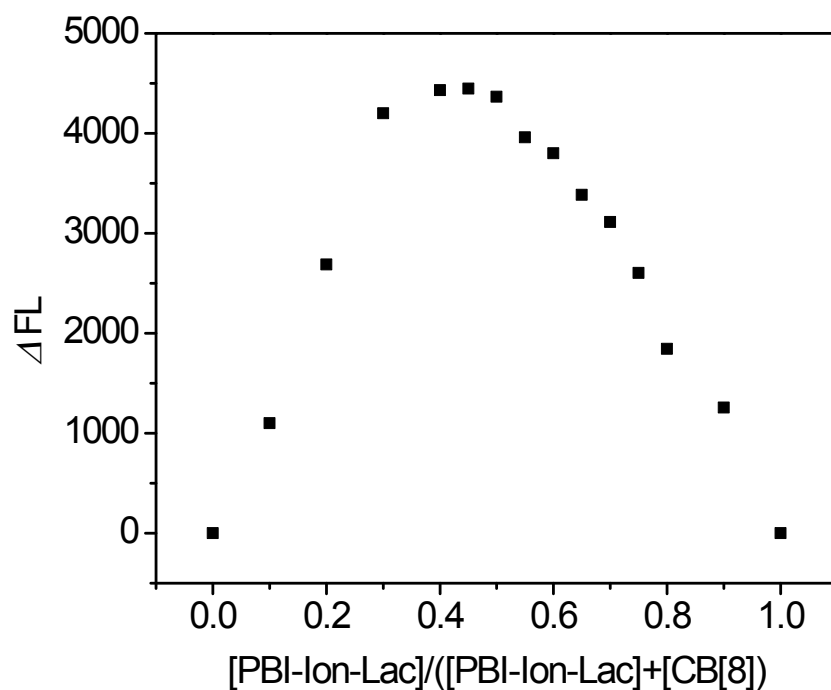


Fig. S14 Job plot of **PBI-Ion-Lac** with CB[8] at the concentration of $2 \times 10^{-5} \text{ M}$ in water containing 0.1 mM CaCl₂ and MnCl₂ at 20 °C.

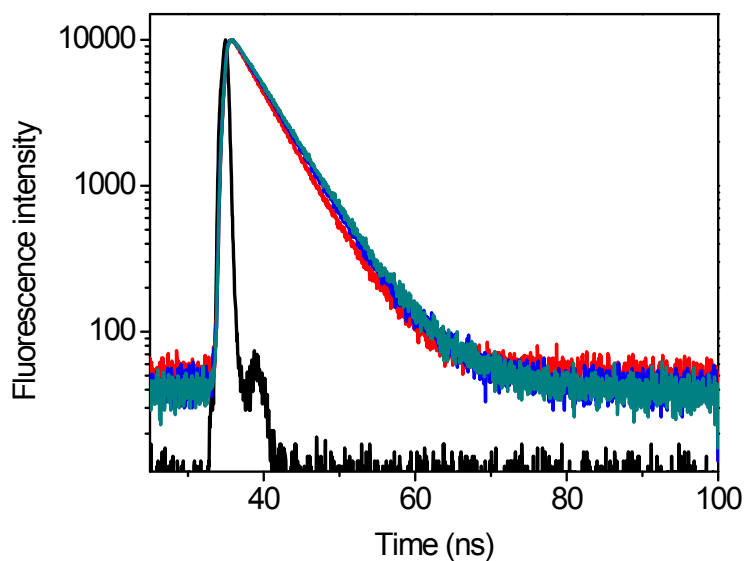


Fig. S15 Fluorescent life time curves of compound **PBI-Ion-Lac** ($\lambda_{\text{ex}} = 500 \text{ nm}$, $1 \times 10^{-5} \text{ M}$) with 1 equivalent CB[8] and 3 equivalent CB[8] in water containing 0.1 mM CaCl_2 and MnCl_2 at 20 °C.

Table S1. Fluorescence lifetimes and quantum yields of compound **PBI-Ion-Lac** ($\lambda_{\text{ex}} = 500 \text{ nm}$, $1 \times 10^{-5} \text{ M}$) upon addition different concentrations of CB[8] ($\lambda_{\text{ex}} = 500 \text{ nm}$) in water at 20 °C.

Compounds	τ (ns)	χ^2	Φ (%)
PBI-Ion-Lac	4.63	1.16	19.2
PBI-Ion-Lac + 1CB[8]	4.96	1.23	37.9
PBI-Ion-Lac + 3CB[8]	5.14	1.28	51.7

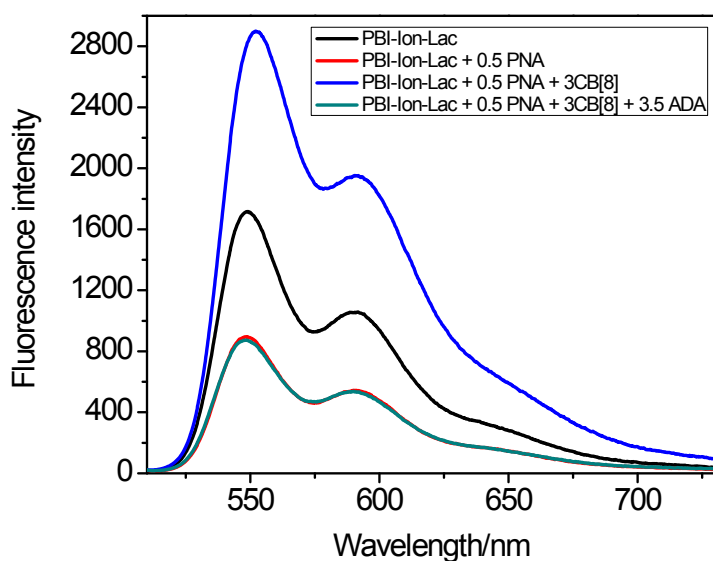


Fig. S16 Fluorescence spectra of **PBI-Ion-Lac** (5×10^{-6} M, $\lambda_{\text{ex}} = 500$ nm, black line) upon addition PNA (0.5 equiv., red line), and then addition CB[8] (3 equiv., blue line), at last addition ADA (3.5 equiv., green line) in water containing 0.1 mM CaCl_2 and MnCl_2 at 20 °C.

[1] (a) Y. Inoue, K. Yamamoto, T. Wada, S. Everitt, X. M. Gao, Z. J. Hou, L. H. Tong, S. K. Jiang, H. M. Wu, *J. Chem. Soc. Perkin Trans. 2*, 1998, 1807; (b) K. R. Wang, D. S. Guo, B. P. Jiang, Z. H. Sun, Y. Liu, *J. Phys. Chem. B*, 2010, **114**, 101; (c) K. R. Wang, D. S. Guo, B. P. Jiang, Y. Liu, *Chem. Commun.*, 2012, **48**, 3644.