1. Experimental Section

Measurements

$^1$H NMR and $^{13}$C 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 \( \chi^2 \) values and the randomness of the weighted residuals.

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

\[
\frac{I_i}{I_0} = 1 + \frac{\Delta I}{2I_0} \ast \left( \frac{[G_0] + [PNA] + K_b}{\sqrt{([G_0] + [PNA] + K_b)^2 - 4[G_0][PNA]}} \right) \tag{1}
\]

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 \(\Delta I\) 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, CuSO$_4$, THF/H$_2$O, 56%; 3) NaOMe, MeOH, 95%; 4) CH$_3$I, 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 N$_2$ atmosphere. The solvent was evaporated under vacuum. The residue was purified by silica-gel column chromatography using CH$_2$Cl$_2$/CH$_3$OH (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; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 2.38 (br, 1H, -CH), 2.42 (s, 6H, -CH$_3$), 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, -CH$_2$), 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); $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 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 C$_{37}$H$_{34}$N$_3$O$_7$, 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 CuSO$_4$·5H$_2$O (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 CH$_2$Cl$_2$/CH$_3$OH (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; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 1.89 (s, 6H, -CH$_3$), 1.97-1.98 (9H, -CH$_3$), 2.05 (s, 3H, -CH$_3$), 2.07 (s, 3H, -CH$_3$), 2.45 (s, 6H, -CH$_3$), 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); $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 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, 122.9, 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 C$_{65}$H$_{72}$N$_6$NaO$_{25}$, 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-d$_6$+D$_2$O, 600 MHz): δ 2.25 (s, 6H, -CH$_3$), 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-d$_6$+D$_2$O, 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, 129.9, 131.5, 143.7, 161.3, 161.4; HRMS: Calcd.
for C$_{51}$H$_{58}$N$_6$NaO$_{18}$, 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 CH$_3$I in 5 mL of
DMF, and the mixture was stirred at 80 °C for 12 h under N$_2$ atmosphere. The
deposited solid was collected by filtration and washed with CH$_2$Cl$_2$. **Compound PBI-Ion-Lac** (51 mg) was obtained with the yield of 90%. m.p. 183.3-184.6 °C; **1H** NMR
(DMSO-d$_6$+D$_2$O, 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-d$_6$+D$_2$O, 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 C$_{52}$H$_{61}$N$_6$O$_{18}$, 1057.4037, found 1057.4050.
2. NMR spectra and additional figures

Fig. S1 $^1$H NMR (CDCl$_3$, 600 MHz) of compound M-3.

Fig. S2 $^{13}$C NMR (CDCl$_3$, 150 MHz) of compound M-3.
Fig. S3 HRMS of compound M-3.

Fig. S4 $^1$H NMR (CDCl$_3$, 600 MHz) of compound M-5.
Fig. S5 $^{13}$C NMR (CDCl$_3$, 150 MHz) of compound M-5.

Fig. S6 HRMS of compound M-5.
Fig. S7 $^1$H NMR (DMSO-$d_6$ + D$_2$O, 600 MHz) of compound M-6.

Fig. S8 $^{13}$C NMR (DMSO-$d_6$ + D$_2$O, 150 MHz) of compound M-6.
Fig. S9 HRMS of compound M-6.

Fig. S10 $^1$H NMR (DMSO-d$_6$ + D$_2$O, 600 MHz) of compound PBI-Ion-Lac.
Fig. S11 $^{13}$C NMR (DMSO-$d_6 + D_2O$, 150 MHz) of compound PBI-Ion-lac.

Fig. S12 HRMS of compound PBI-Ion-Lac.
Fig. S13 UV-Vis (a) and fluorescence (b, $\lambda_{ex} = 500$ nm) spectroscopy of **PBI-Ion-Lac** (1 × 10^{-5} M) in different volume ratios of DMSO/H$_2$O at 20 °C.

Fig. S14 Job plot of **PBI-Ion-Lac** with CB[8] at the concentration of 2 × 10^{-5} M in water containing 0.1 mM CaCl$_2$ and MnCl$_2$ at 20 °C.
**Fig. S15** Fluorescent life time curves of compound **PBI-Ion-Lac** ($\lambda_{ex} = 500$ nm, $1 \times 10^{-5}$ 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** ($\lambda_{ex} = 500$ nm, $1 \times 10^{-5}$ M) upon addition different concentrations of CB[8] ($\lambda_{ex} = 500$ nm) in water at 20 °C.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\tau$ (ns)</th>
<th>$\chi^2$</th>
<th>$\Phi$ (%)</th>
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</thead>
<tbody>
<tr>
<td>PBI-Ion-Lac</td>
<td>4.63</td>
<td>1.16</td>
<td>19.2</td>
</tr>
<tr>
<td>PBI-Ion-Lac + 1CB[8]</td>
<td>4.96</td>
<td>1.23</td>
<td>37.9</td>
</tr>
<tr>
<td>PBI-Ion-Lac + 3CB[8]</td>
<td>5.14</td>
<td>1.28</td>
<td>51.7</td>
</tr>
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</table>
**Fig. S16** Fluorescence spectra of **PBI-Ion-Lac** ($5 \times 10^{-6}$ M, $\lambda_{ex} = 500$ 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.

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