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SUPPORTING INFORMATION

Synthesis, Self-Assembly, Base-Pairing of Nucleobase End-Functionalized

Block Copolymers in Aqueous Solution

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Figure S1. ¹H NMR spectrum of DTTCP in CDCl₃.



Figure S2. ¹H NMR spectrum of 9-(2-hydroxyethyl)adenine in DMSO-d₆.



Figure S3. ¹H NMR spectrum of 1-(2-hydroxyethyl)thymine in DMSO-*d*₆.



Figure S4. ¹H NMR spectrum of **A**-DTTCP (**3**) in DMSO-*d*₆.



Figure S5. ¹H NMR spectrum of **T**-DTTCP (**4**) in DMSO-*d*₆.



Figure S6. GPC (DMAc) traces of (a) P1, (b) P2, (c) P3 and (d) P4.



Figure S7. ¹H NMR spectrum of P1 without thymine in aqueous solution at different concentrations.

The self-assembly behavior of **P1** - **P4** were studied using pyrene as the fluorescence probe.¹⁻³ Determined from the fluorescence spectra (**Figure S8, S9**), the intensity of I₁ (wavelength λ = 373 nm) and I₃ (wavelength λ = 383) varied with the molar concentration of the aggregation solvent. As shown in **Figure S8b, S8d**, there were abrupt change points in the curve which could determine the critical micelle concentration (CMC) of **P1** and **P2** as 6.5 × 10⁻³ mM and 7.0 × 10⁻³ mM. Similarly, as shown in **Figure S9b, S9d**, the CMC of **P3** and **P4** were determined to be 6.0 × 10⁻³ mM and 6.5 × 10⁻³ mM, respectively.



Figure S8. (a, c) Fluorescence spectra and (b, d) the intensity of I_1/I_3 of P1 and P2 at different concentrations.



Figure S9. (a, c) Fluorescence spectra and (b, d) the intensity of I_1/I_3 of P3 and P4 at different concentrations.



Figure S10. TEM images of micelle at different concentrations of (a, b, c) thymine-containing amphiphilic block copolymers **P3** and (d) average size statistics of micelle measured by DLS.

The successful preparation of thymine derivatives- **P3** and **P4** were confirmed by ¹H NMR. As shown in **Figure S11**, they exhibited the characteristic peaks for the thymine-containing amphiphilic block copolymers. The presence of signal d corresponding to thymine's structure demonstrated that they were thymine-containing amphiphilic block copolymers.



Figure S11. ¹H NMR spectrum of (a) T-POEGMA-b-PBMA (P3) and (b) T- PBMA -b- POEGMA (P4) in DMSO-d₆.

¹H NMR spectra of P3 and P4 that bind adenine in aqueous solution at different concentrations are shown in Figure S12a and S12c. In these groups of experiments, the concentration of adenine was known and more than the concentration of thymine. The proton on thymine that was at the end of copolymer chains was assigned as d. In Figure S12a, with the increase of concentration, the protons on thymine (d) had shifted downfield, indicating the interaction between thymine and adenine was through H-bonding. The change of chemical shift of the proton on thymine (d) was more apparent in Figure S12b. While in Figure S12c and S12d, the proton on thymine (d) remained almost unchanged, indicating that there was no H-bonding interaction between the thymine-containing micelles and adenine. This was due to the original polymer's structural design, in P4, hydrophobic chains (PBMA) were inside the micelle as core as well as thymine which was on the end of hydrophobic chains (PBMA) that was also inside the micelle. For adenine to have an interaction with thymine, it would need to break the resistance of micelles, the process would be very difficult. So there was no apparent H-bonding interaction in this kind of micelles formed by P4.



Figure S12. (a, c) ¹H NMR spectrum and (b, d) the change of chemical shift of P3 and P4 that bind adenine in aqueous solution at different concentrations.

The variable temperature experiments were carried out. From **Figure S13a**, with the increasing of temperature, there was an apparent upfield shift. The chemical shift of the proton on thymine (d) at 75 °C, was very apparent compared with that at 25 °C. Higher temperature destroyed the hydrogen bonding between **A-T** and **A** was released from the thymine-containing micelles. **Figure S13b** could be more intuitive and clear to see the trend of chemical shifts. Form **Figure S13c** and **S13d**, the experimental phenomenon is the same as that of the previous experiment. With increasing temperature, there was an apparent upfield shift, indicating the hydrogen bonding between **A-T** was destroyed.



Figure S13. (a. c) ¹H NMR spectrum and (b, d) the change of chemical shift of **P3** at the concentration of 1.06×10^{-2} M and 0.35×10^{-2} M that bind adenine in aqueous solution at different temperatures.

In **Figure S14**, the NH₂ protons on the adenine attached to the block copolymers were not be detected which were labile. The protons on adenine (d, e) had shifted downfield (8.00 to 8.10 ppm, 8.07 to 8.16 ppm). The small molecule thymine protons shifted downfield (7.20 to 7.23 ppm).



Figure S14. ¹H NMR spectrum of P1 that bind thymine in aqueous solution at different concentrations.

¹H NMR spectra of **P1** micelle solutions before and after base pairing have been shown in **Figure S15**. The difference between them was after base pairing that was one more thymine peaks and the adenine protons shifted downfield (8.00 to 8.06 ppm, 8.07 to 8.10).



Figure S15. ¹H NMR spectrum of P1 micelle solution before and after base pairing.



Figure S16. ¹H NMR spectrum of P1 micelle solution without thymine at different temperature.



Figure S17. TEM images of micelle at different concentrations of (a,b,c) non-functionalized amphiphilic block copolymers and (d) average size statistics of micelle measured by DLS.

References

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