

Supplementary Information

**Silver Assisted Stereo-Directed Assembly of Branched Peptide Nucleic
Acids into Four-Point Nanostars**

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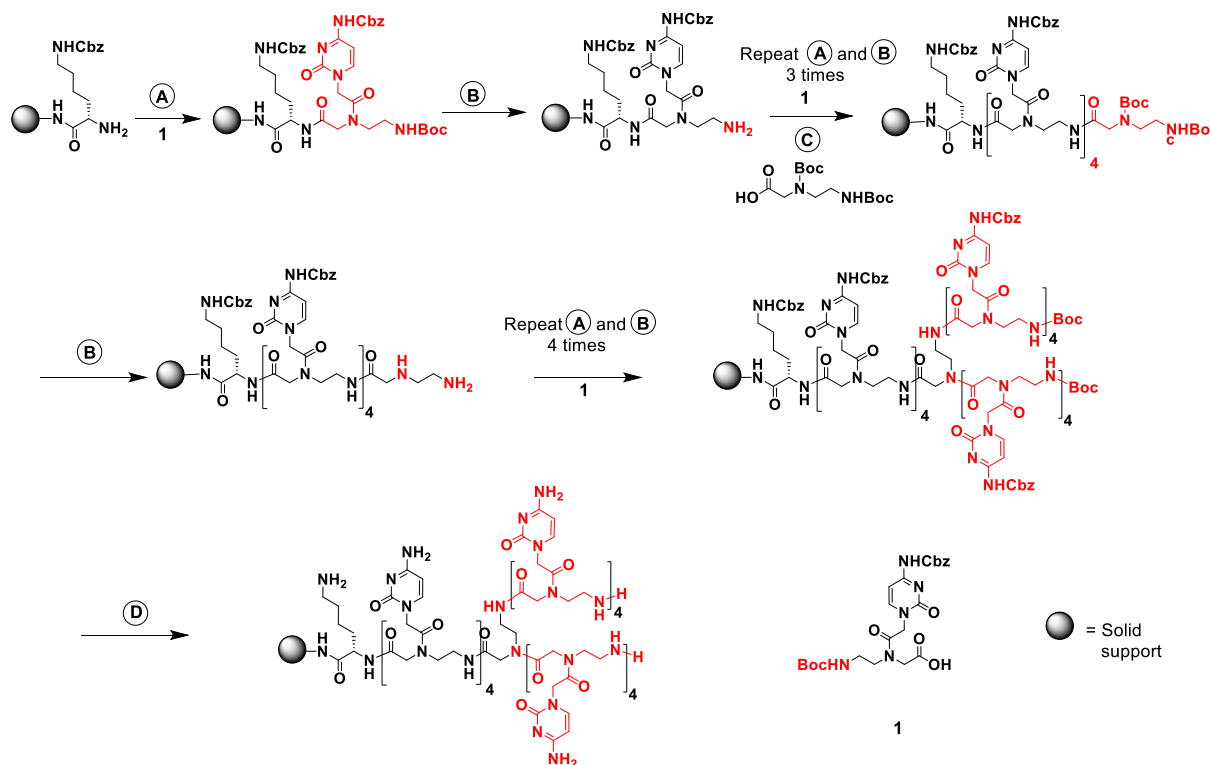
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Scheme S1. Solid phase synthesis of *br*-PNA 3



(A) Coupling: PNA-C monomer **1**, HOBt, HBTU, and DIEA. (B) 1. Boc deprotection, 50% TFA; 2. Neutralization, 5 % DIEA. (C) Coupling: *aeg* monomer, HOBt, HBTU, and DIEA. (D) TFA, TFMSA, and thioanisole.

Table S1. MALDI and HPLC characterization of PNAs

PNA	Molecular Formula	Calc Mass	Obsd Mass	Retention Time (min)
<i>br</i> (4 <i>S</i>)-PNA 1 (4 <i>S</i>)- <i>Amp</i> -(PNA C ₄) ₃	C ₁₃₁ H ₁₇₉ N ₆₅ O ₃₈	3272.29	3295.77 [M+Na] ⁺	12.60
<i>br</i> (4 <i>R</i>)-PNA 2 (4 <i>R</i>)- <i>Amp</i> -(PNA C ₄) ₃	C ₁₃₁ H ₁₇₉ N ₆₅ O ₃₈	3272.29	3273.18 [M+H] ⁺	12.75
<i>br</i> -PNA 3 <i>aeg</i> -(PNA C ₄) ₃	C ₁₃₀ H ₁₇₉ N ₆₅ O ₃₈	3260.28	3262.01 [M+H] ⁺	11.4

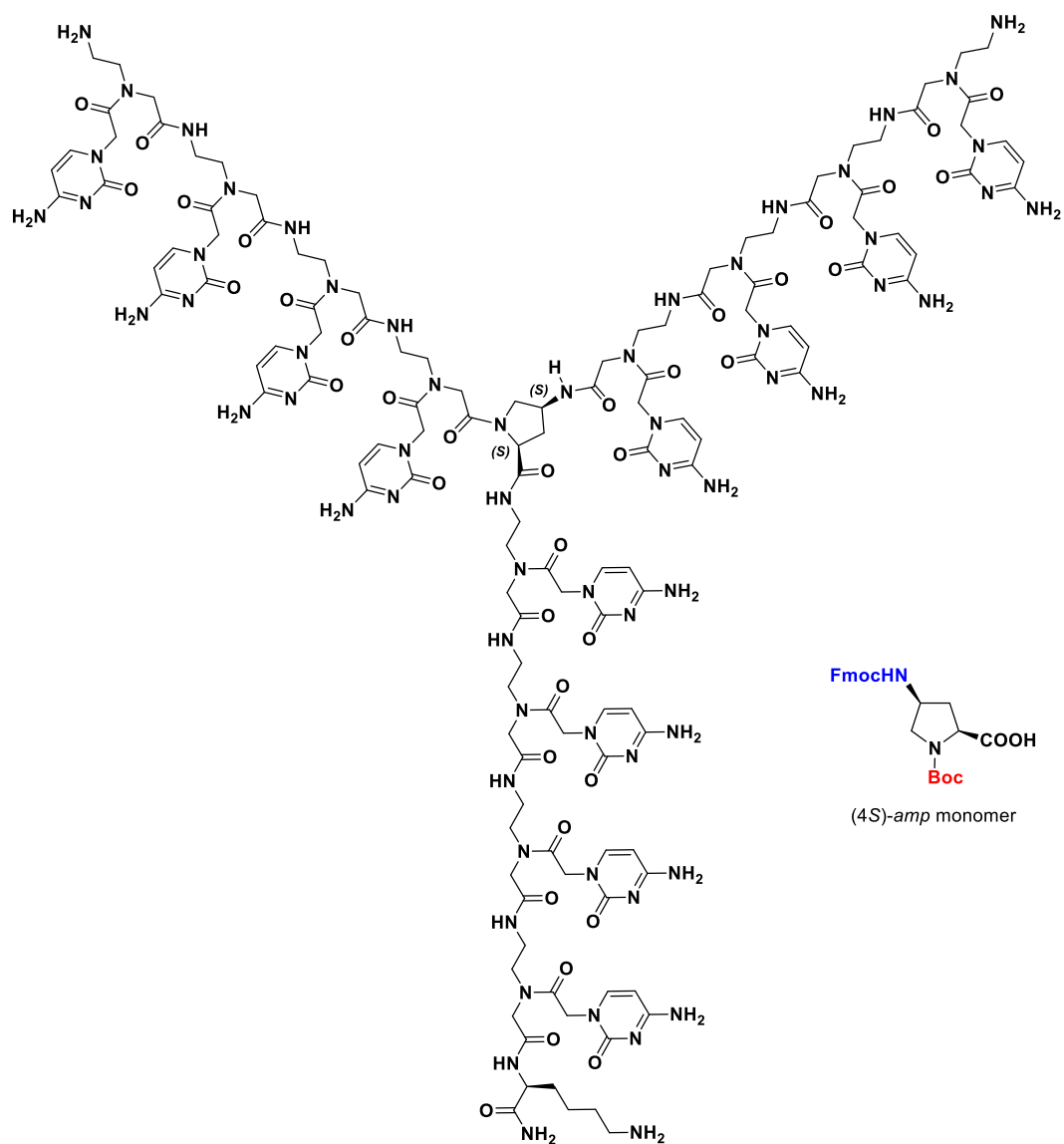


Figure S1. Structure of *br*(4*S*)-PNA 1 and (4*S*)-*Amp* monomer

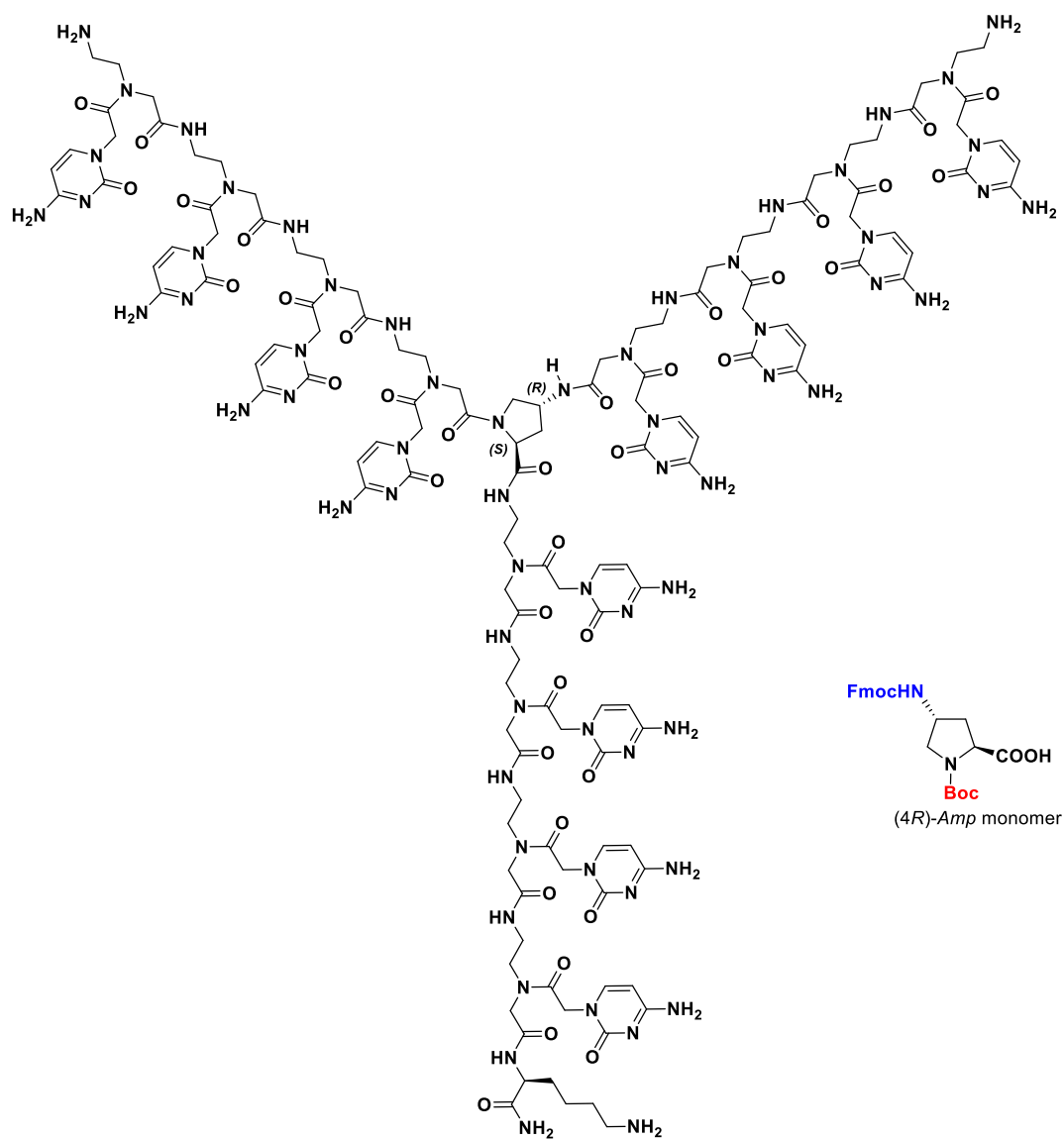


Figure S2. Structure of *br(4R)*-PNA **2** and (4*R*)-Amp monomer

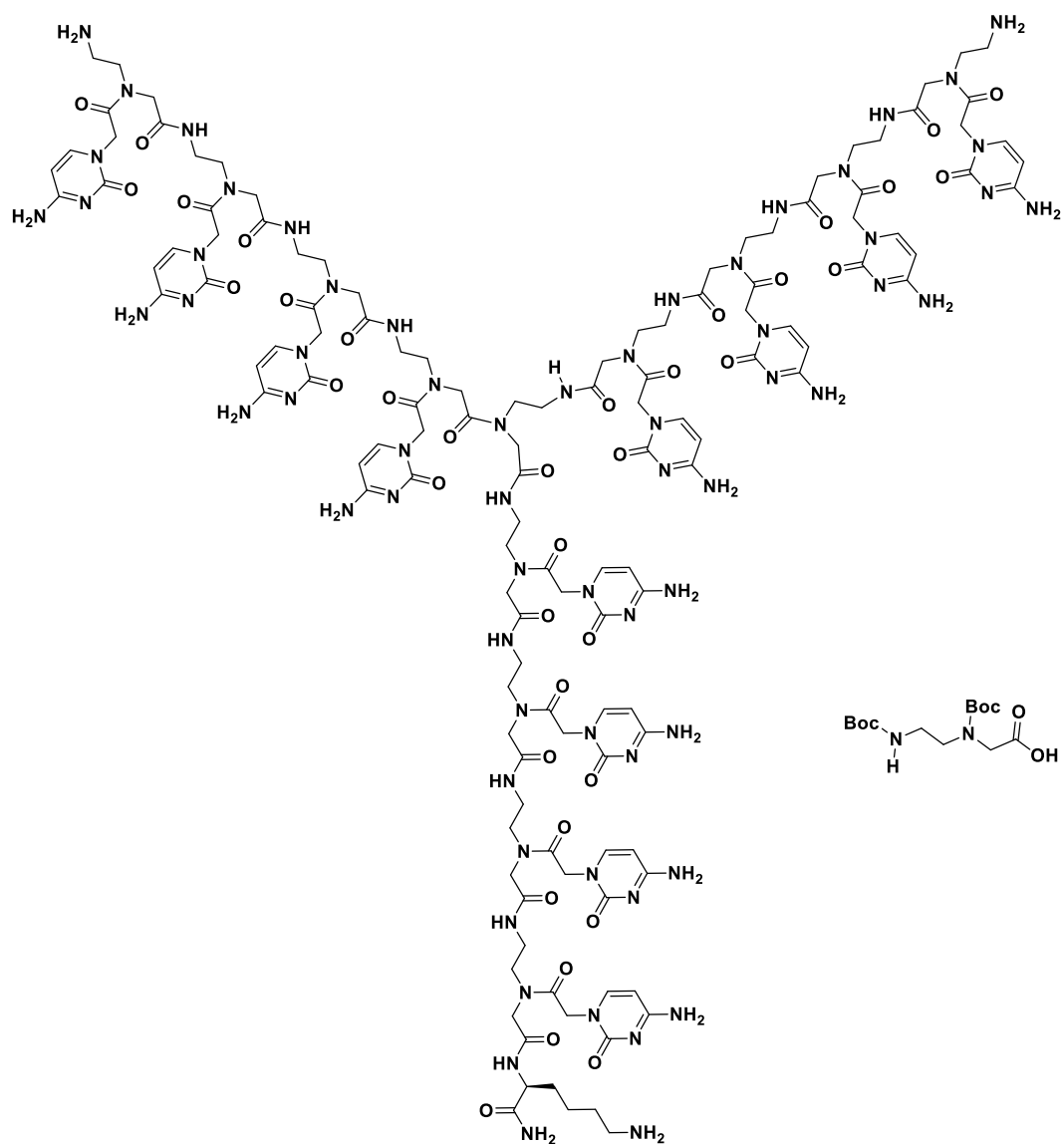


Figure S3. Structure of *br*-PNA **3** and *aeg* monomer

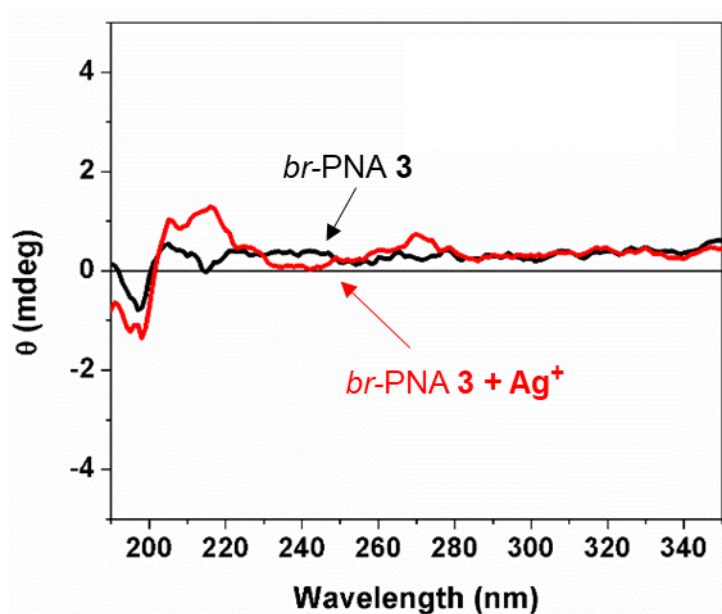


Figure S4. CD spectra of branched *br*-PNA **3** before (black trace) and after the addition of silver nitrate (red trace) in water. The concentration ratio of $[C]:[Ag^+]$ was maintained at 1:1.

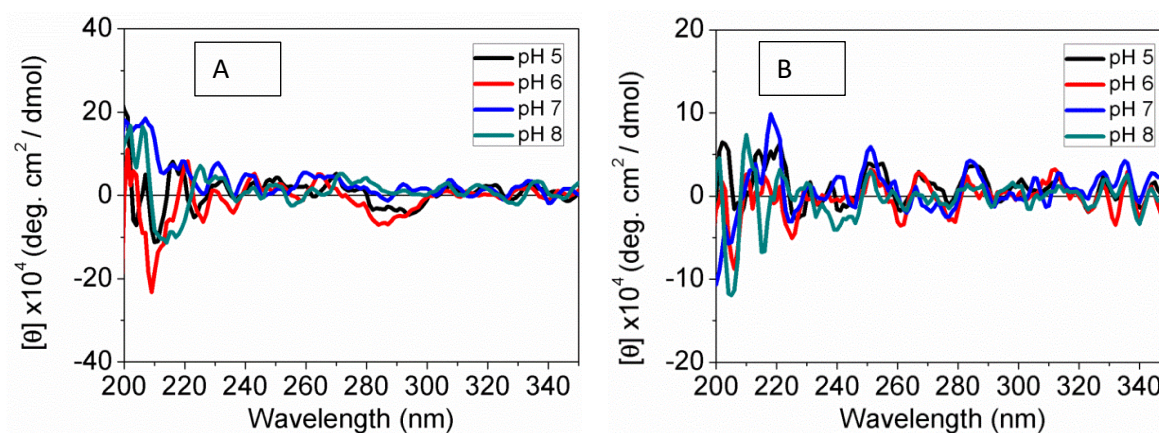


Figure S5: Circular dichroism spectra of branched PNAs as a function of pH. (A) *br*(4S)-PNA **1** and (B) *br*(4R)-PNA **2** in 10 mM phosphate buffered saline at pH 5-8.

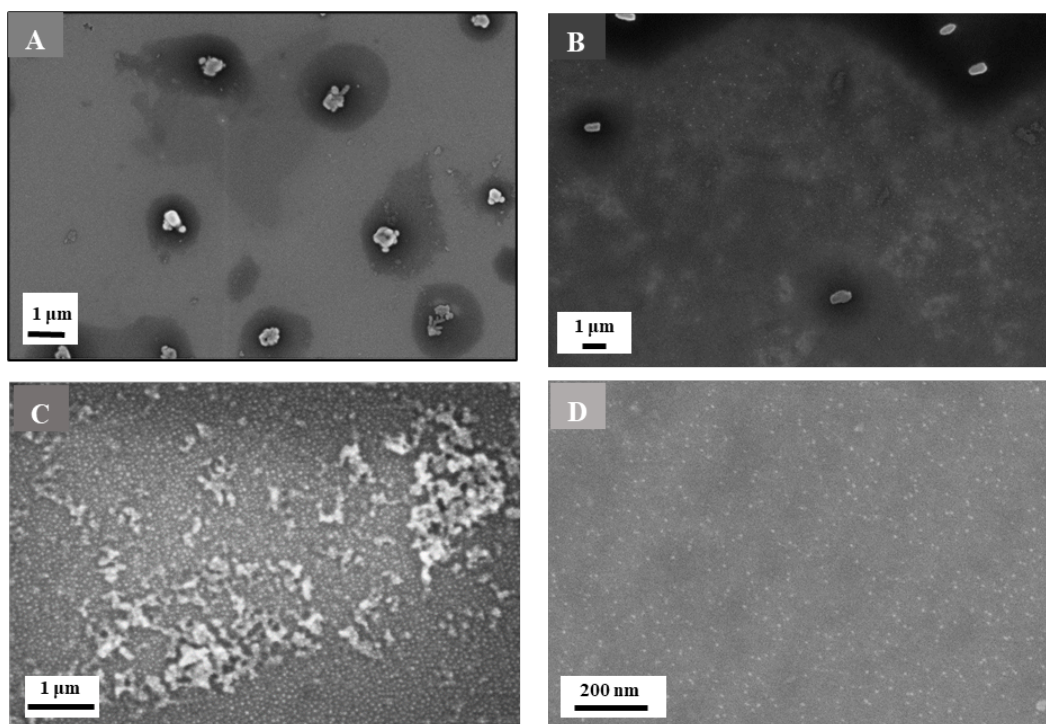


Figure S6. FESEM images of branched PNAs before addition of AgNO_3 in water. A) *br(4S)*-PNA 1, B) *br(4S)*-PNA 2, C) *br*-PNA 3. $[\text{C}] = 2 \text{ mM}$. (D) FESEM image of only AgNO_3 solution (2 mM) in water.

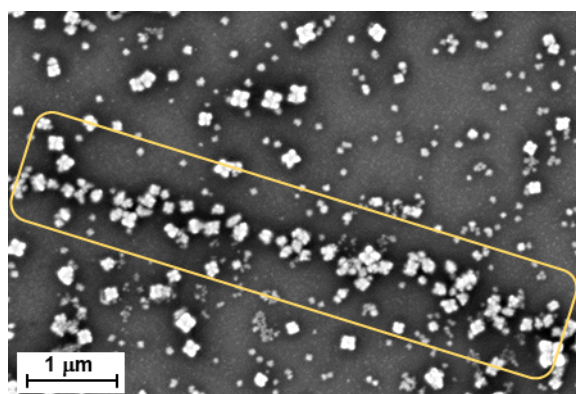


Figure S7. Aggregation of nanostars of *br(4S)*-PNA 1 with silver ions in water at $[\text{C}]: [\text{Ag}^+]$ of 2.5 mM: 2.0 mM. Incubation period was 12 h.

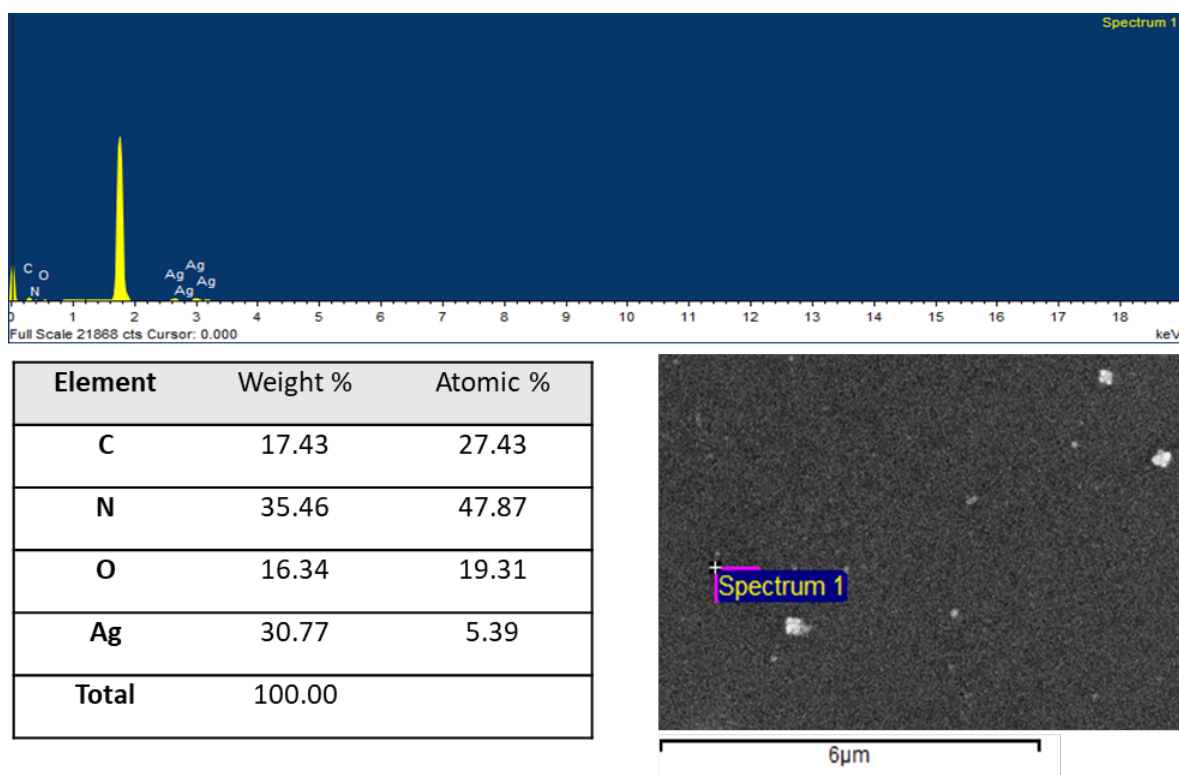
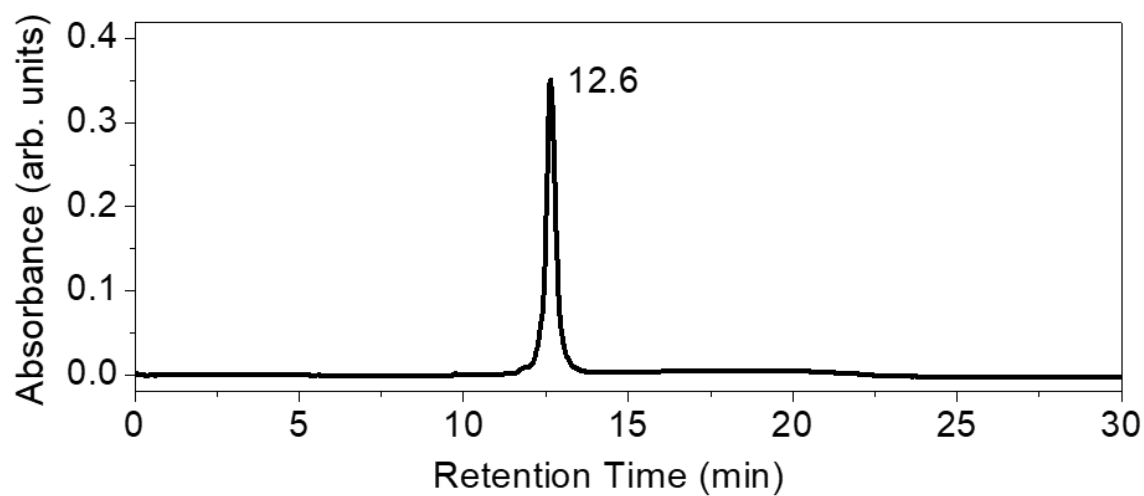
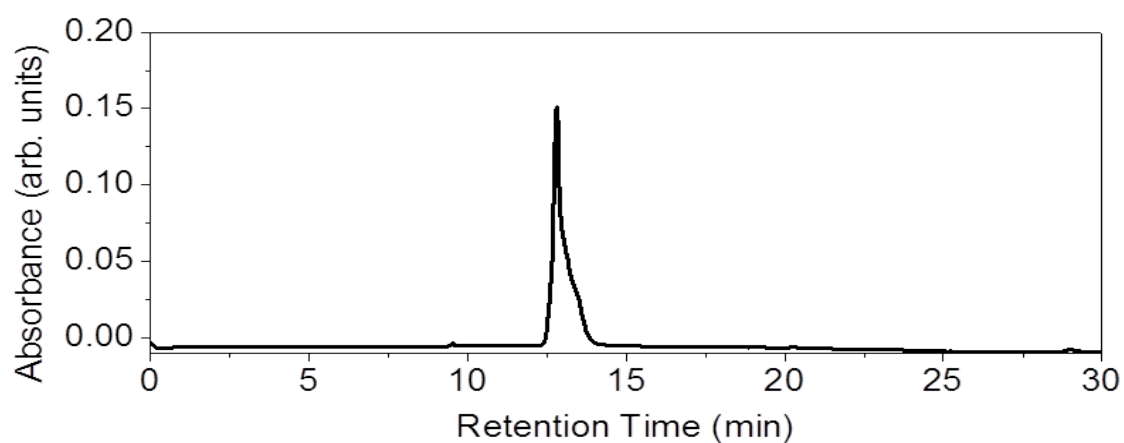


Figure S8. EDX spectra showing the elemental composition of nanostar-like morphology formed by *br(4S)*-PNA **1** with silver ions in water at [C]: [Ag⁺] of 2.0 mM: 2.0 mM.

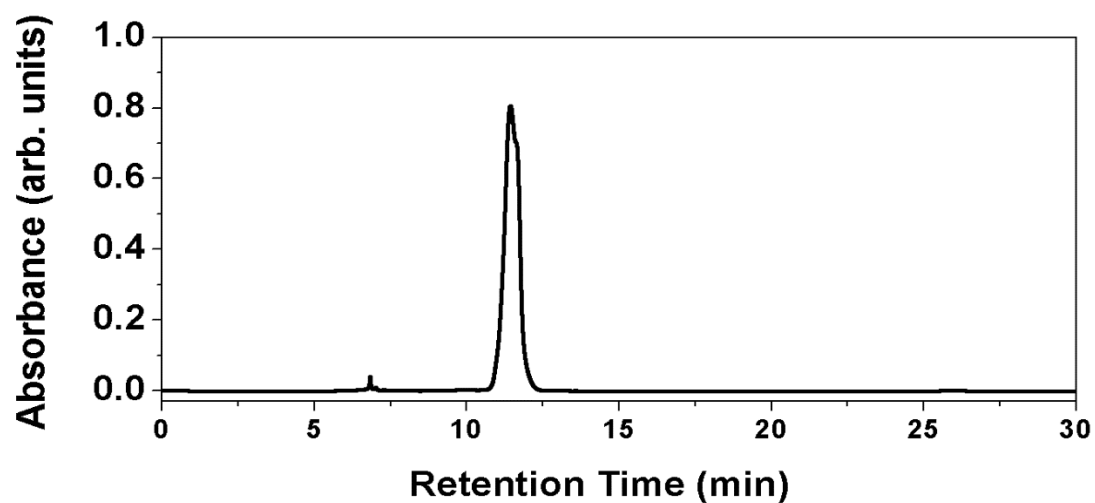
HPLC profile of *br*(4*S*)-PNA 1



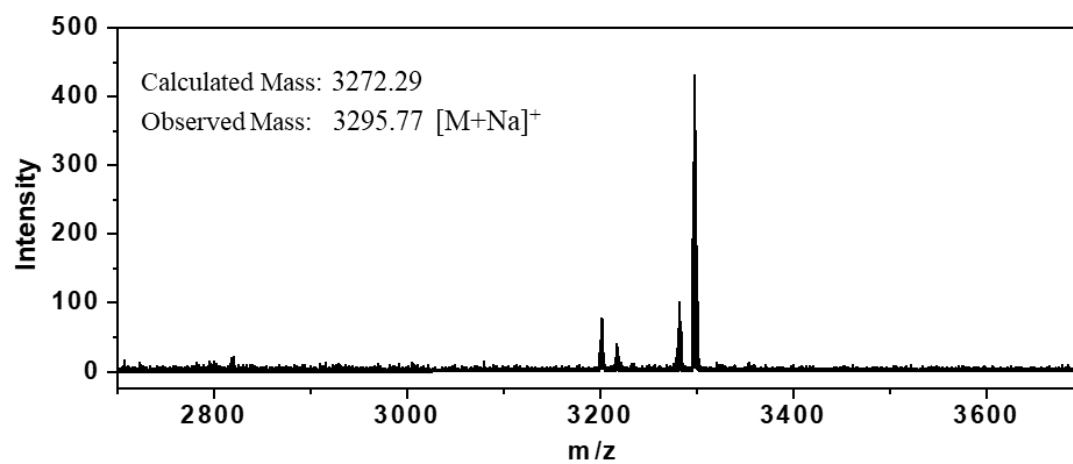
HPLC chromatogram of *br*(4*R*)-PNA 2



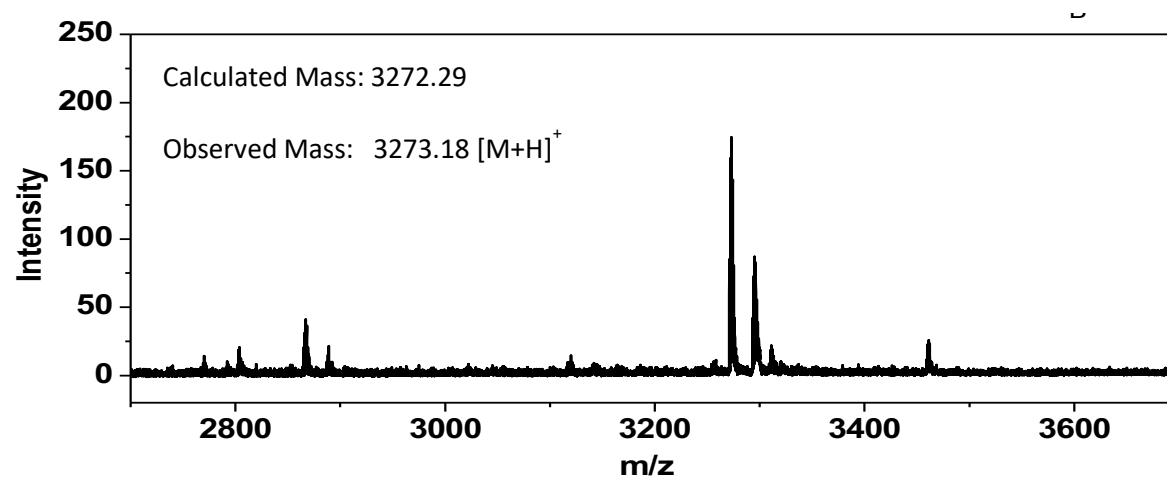
HPLC chromatogram of *br*-PNA 3



MALDI-TOF spectrum of *br*(4*S*)-PNA 1



MALDI-TOF Spectrum of *br*(4*R*)-PNA 2



MALDI-TOF spectrum of *br*-PNA 3

